

Transition Metal Dichalcogenides: Part I

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August 31, 2026

This draft is not aimed for distribution.

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Preface

Examples and Solved Problems

Well-known and Important Theories

Old, Fundamental Theories

Special Effects: Useful, Selected Articles

Experiments: Main Articles

Applications and Potential Applications: Main Articles

Amazing facts

(I'll reveal it later)

Puzzles for motivation

(I'll reveal it later)

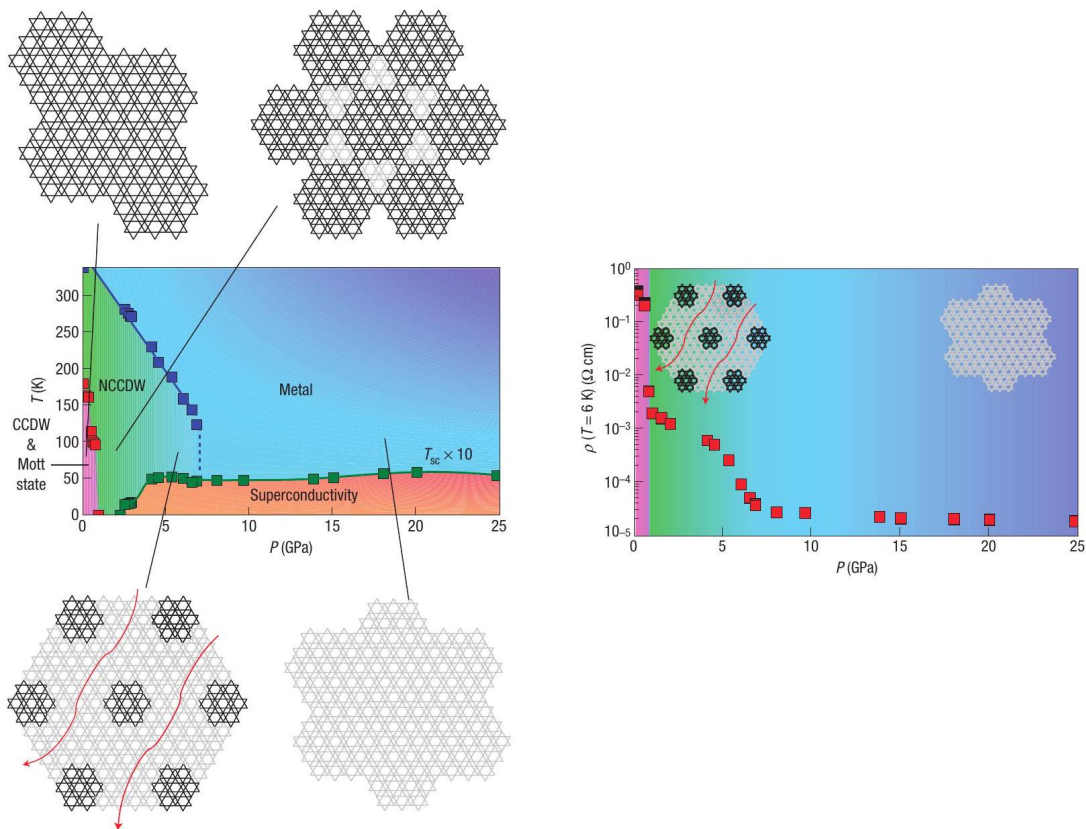
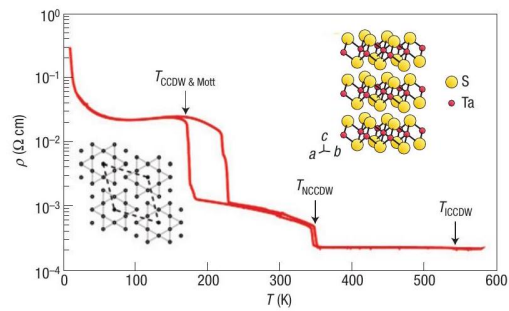
Part I

TMDCs in a Nutshell

1 Main Formulas and Ideas

1.1 Essence of Some Important Articles

1.1.1 Essence of “From Mott state to SC in 1T-TaS₂” by Sipos, Kusmartseva et al.



1.1.2 Essence of “Non-equilibrium quantum domain reconfiguration dynamics” by Vodeb et al.

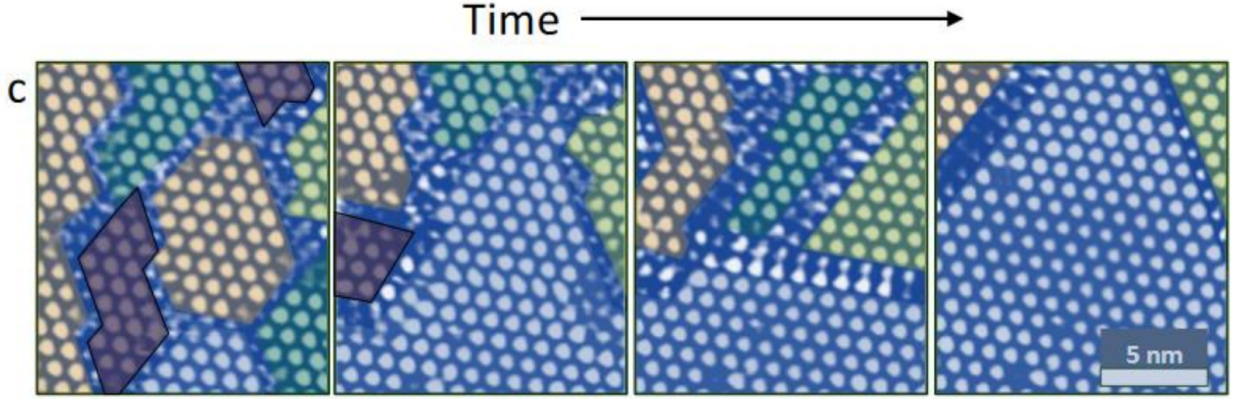


Figure 1.1: c) A series of STM measurements at regular time intervals showing domain reconfiguration. Domains are colored to signify a displacement relative to the main commensurate lattice (light blue). (STM parameters: -0.8 V, 50 pA).

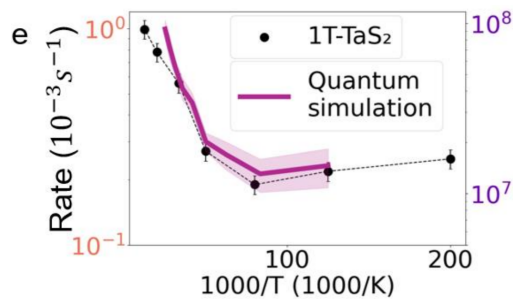
$$H_M = - \sum_{\langle ij \rangle} t_{ij} c_i^\dagger c_j + \sum_{\langle ij \rangle} V(i, j) q_i q_j - \mu \sum_i q_i,$$

$$H_{PQA}/k_B T = \left(- \sum_i \sigma_i^x / 2 + r[s(t)] \left(\sum_{\langle ij \rangle} V(i, j) q_i q_j - \mu \sum_i q_i \right) \right) / T_{eff}[s(t)]$$



Figure 1.2: c) An example of a relaxation sequence with parameters $t_a = 5\mu s$, $r = 9$ and $T_{eff} = 1.33$.

“Configurational coordinate” $f := \Delta N/N$, here N is the total number of polarons per frame
 “Reconfiguration rate” $R(T) = \frac{1}{\Delta t} \int_0^{t_{exp}} f(t) dt$



1.1.3 Essence of “Configurational Electronic States in Layered Transition Metal Dichalcogenides” by Vodeb et al.

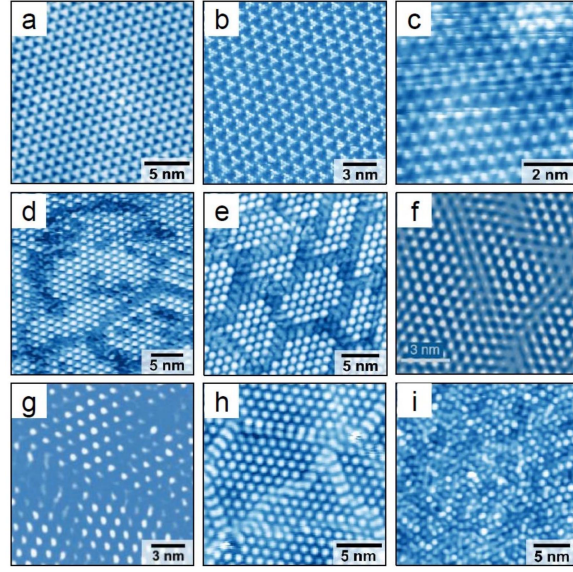


Fig. 5 Scanning tunneling microscope images for selected compounds showing the effect of doping, arranged in three successive groups of polaron crystals, domain states and a glassy state. The first three cases **a** – **c** represent polaronic crystals in 1T-TaS ($f_m = 1/13$), 1T-TaSe₂ ($f_m = 1/13$) and 1TTiSe₂ ($f_m = 1/4$) respectively. The latter cases **d** – **h** represent domain states of 1T-Ta_{0.99}Fe_{0.01}S₂ ($f \approx 1/12.6$), photodoped 1T-TaS₂ (fluence $F \simeq 1 \text{ mJ/cm}^2$, $f \approx 1/12.6$), 1T-Cu_{0.08}TiSe₂ ($f \approx 1/4.2$), 1T-Ti_{0.07}Ta_{0.93}Se₂ ($f \approx 1/12.6$) and 1T-TaSeS ($f \approx 12.6$) respectively. The last case **i** represents a glassy state in photodoped 1T-TaS₂ (fluence $F > 3.5 \text{ mJ/cm}^2$, $f \approx 1/11$).

The CLG model:

$$\mathcal{H} = \sum_{i < j} V(i, j) n_i n_j \quad (1)$$

where n_i is the occupational number of a polaron at site i with values either 0 or 1 and $V(i, j) = \frac{V_0 \exp(-\frac{r_{ij}}{r_s})}{r_{ij}}$ the Yukawa potential that describes the screening, where $V_0 = e^2/(\epsilon_0 a)$ in CGS units, $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$, where $\mathbf{r}_i$ is the dimensionless position of the i -th polaron and r_s is the dimensionless screening radius.

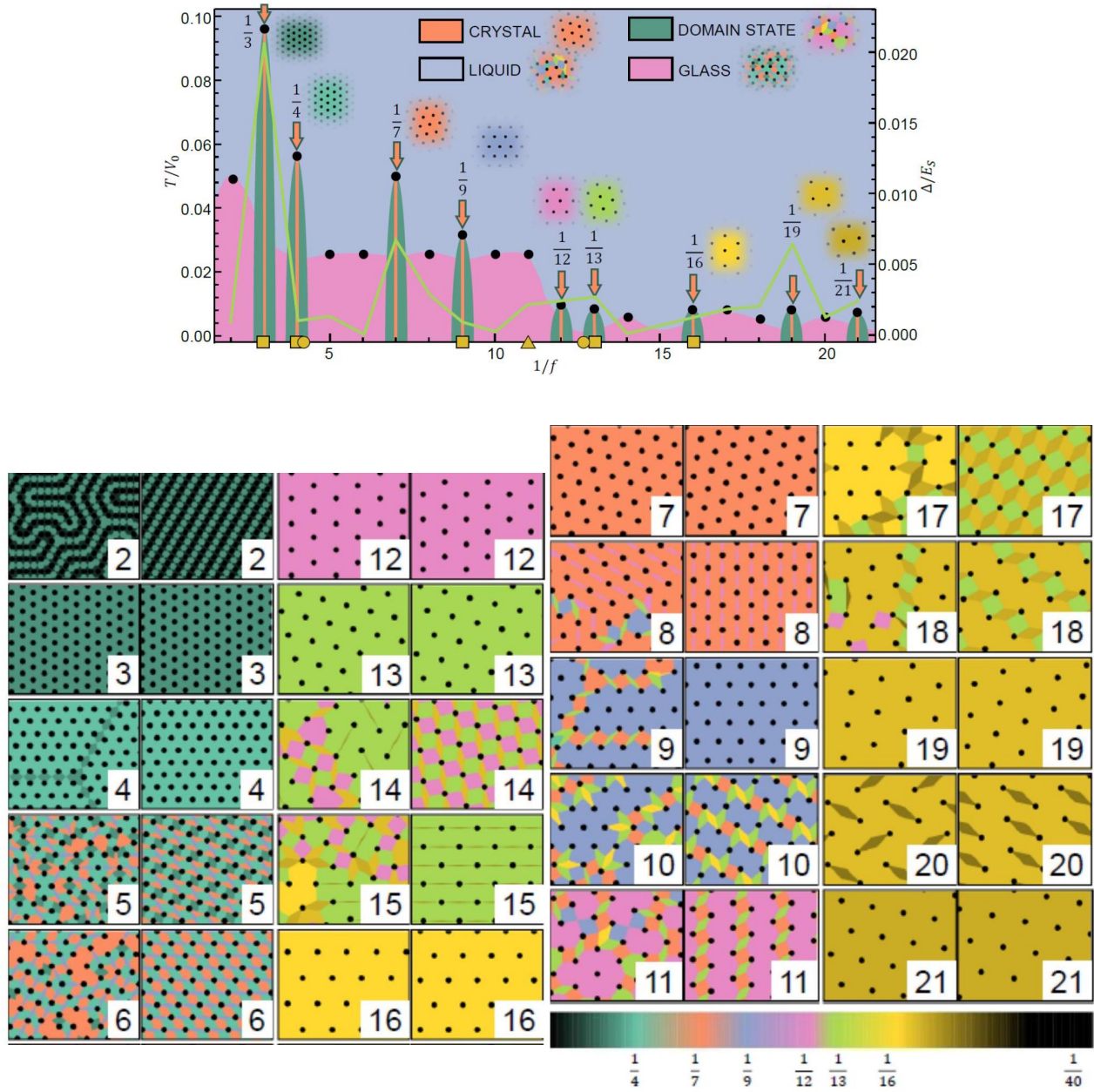
For 1 T – TaS₂, the magnitude of $V_0 = 2.810^{-4} \text{ eV}$, it comes from the Coulomb interaction and is defined as $\frac{e^2}{\epsilon_0 a}$ in CGS units, where e is the charge of a polaron and ϵ_0 is the static dielectric constant. We use values $a = 3.4 \text{ \AA}$ and $\epsilon_0 = 1.510^{45}$.

We can use some analytics. We introduce coordinates of electrons $(r_i, \theta_i) = x_i(a, 0) + y_i(a/2, a\sqrt{3}/2)$, then the magic filling is

$$1/f_m = x_i^2 + y_i^2 + x_i y_i \quad (2)$$

The ratio of polarons in the system divided by the number of lattice sites is defined as the filling f

Magic fillings: $f_m = 1/3, 1/4, 1/7, 1/9, 1/12, 1/13, 1/16, 1/19, 1/21, \dots$

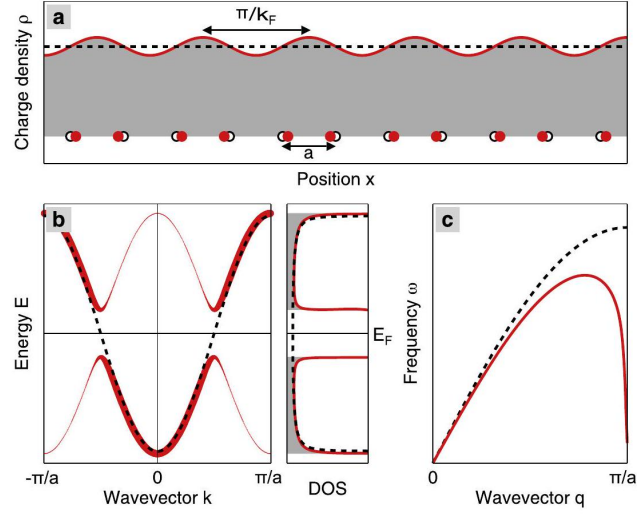


1.1.4 Essence of “On the origin of CDW in layered TMDCs” by Rossnagel

Review of CDW theory

$$\rho(\mathbf{r}) = \rho_0(\mathbf{r}) [1 + \rho_1 \cos(\mathbf{q}_0 \mathbf{r} + \phi)] \quad (1)$$

$$u_n = u_0 \sin(n |\mathbf{q}_0| a + \phi) \quad (2)$$



$$H_{\text{PI}} = \sum_{\mathbf{k}} \epsilon_{\mathbf{k}} a_{\mathbf{k}}^{\dagger} a_{\mathbf{k}} + \sum_{\mathbf{q}} \hbar \omega_{\mathbf{q}} b_{\mathbf{q}}^{\dagger} b_{\mathbf{q}} + \frac{1}{\sqrt{N}} \sum_{\mathbf{k}, \mathbf{q}} g_{\mathbf{q}} a_{\mathbf{k}+\mathbf{q}}^{\dagger} a_{\mathbf{k}} (b_{-\mathbf{q}}^{\dagger} + b_{\mathbf{q}}) \quad (3)$$

$$\delta E_{\text{band}} = -|v_{\mathbf{q}}|^2 \chi_0(\mathbf{q}), \quad \chi_0(\mathbf{q}) = \frac{1}{L} \sum_{\mathbf{k}} \frac{f_{\mathbf{k}+\mathbf{q}} - f_{\mathbf{k}}}{\epsilon_{\mathbf{k}} - \epsilon_{\mathbf{k}+\mathbf{q}}} > 0 \quad (6,7)$$

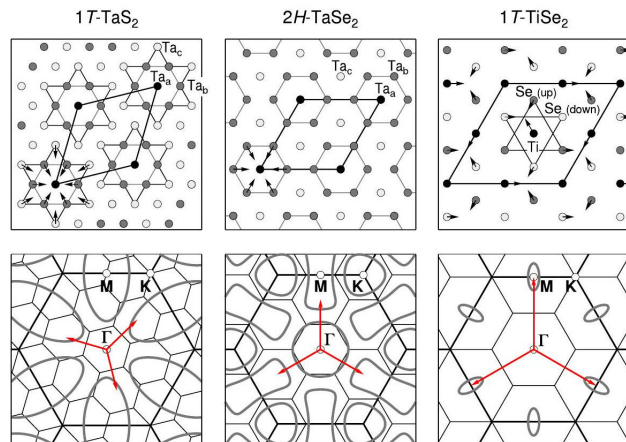
$$\frac{4g_{\mathbf{q}}^2}{\hbar \omega_{\mathbf{q}}} - 2U_{\mathbf{q}} + V_{\mathbf{q}} \geq \frac{1}{\chi_0(\mathbf{q})} \quad (9)$$

$$\chi_0(2\mathbf{k}_F, T) = \frac{1}{2} N(0) \ln \left(\frac{2.28 E_F}{k_B T} \right) \quad (12)$$

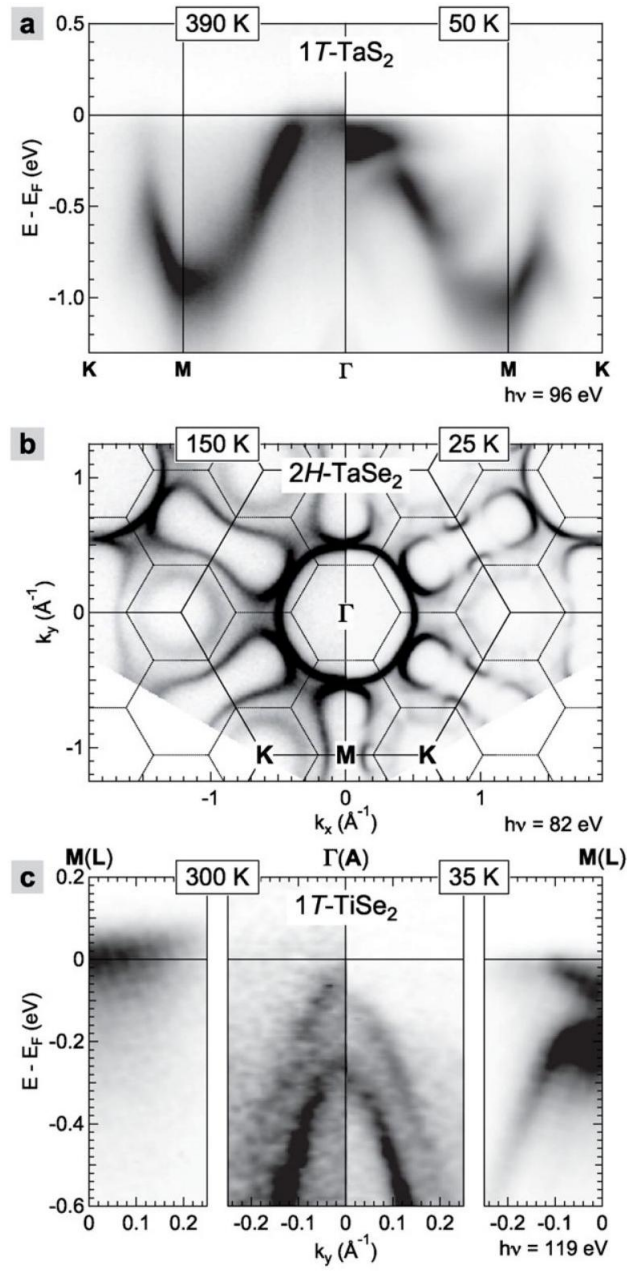
$$\tilde{\omega}_{\mathbf{q}}^2 = \omega_{\mathbf{q}}^2 \left(1 - \frac{4g_{\mathbf{q}}^2}{\hbar \omega_{\mathbf{q}}} \chi_0(\mathbf{q}) \right), \quad (13)$$

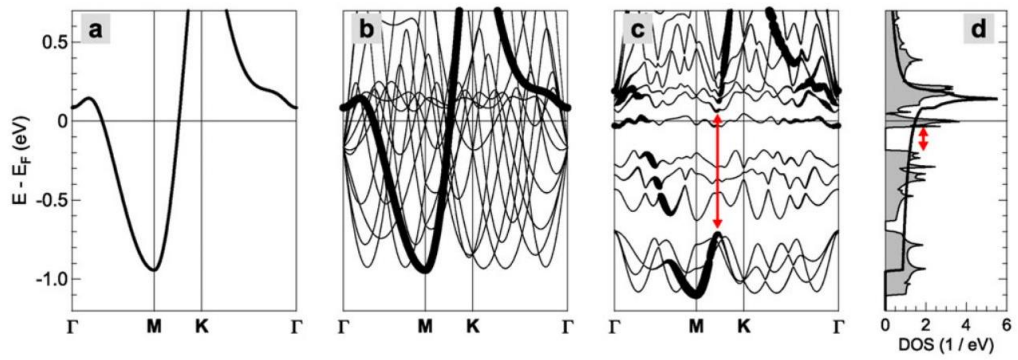
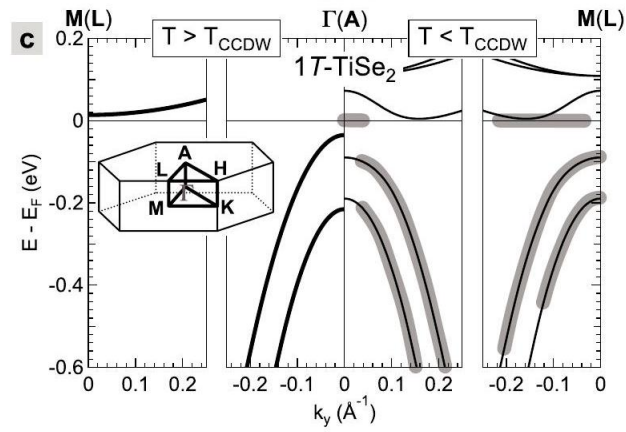
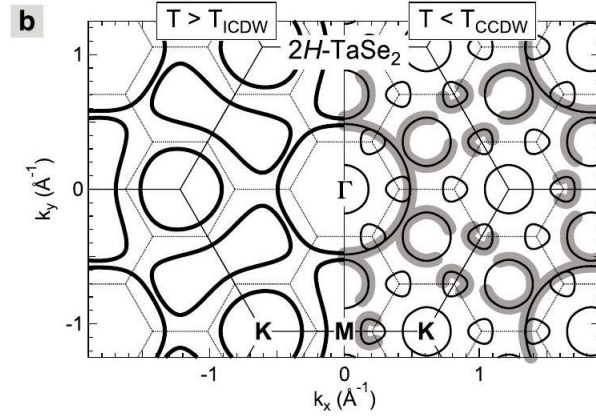
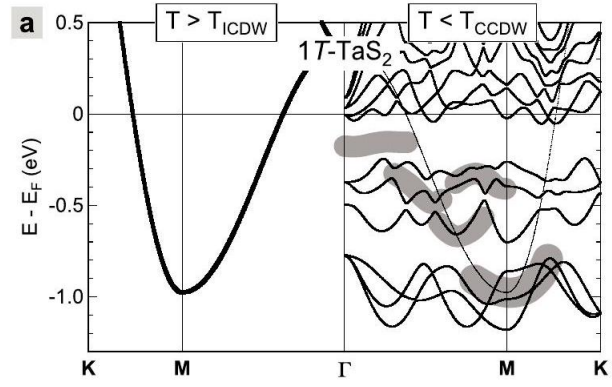
$$k_B T_0 = 2.28 E_F \exp \left(-\frac{1}{\lambda} \right), \quad \lambda = \frac{2g_{\mathbf{q}_0}^2 N(0)}{\hbar \omega_{\mathbf{q}_0}} \quad (15, 16)$$

3. CDW/ PLDs in the layer compounds 1 T-TaS₂, 2 H-TaSe₂ and 1 T-TiSe₂



4. Band structures and spectral weight distributions of reconstructed 1T-TaS₂, 2H-TaSe₂ and 1T-TiSe₂





Summary of experimental data

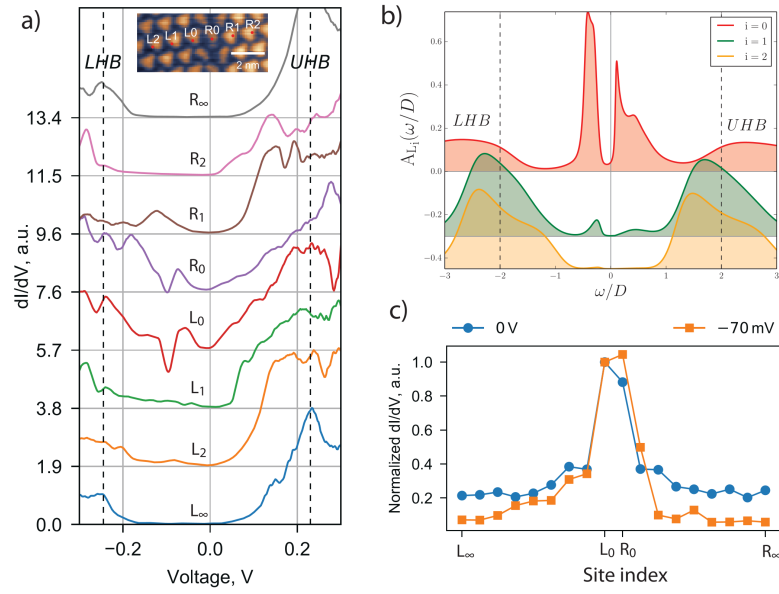
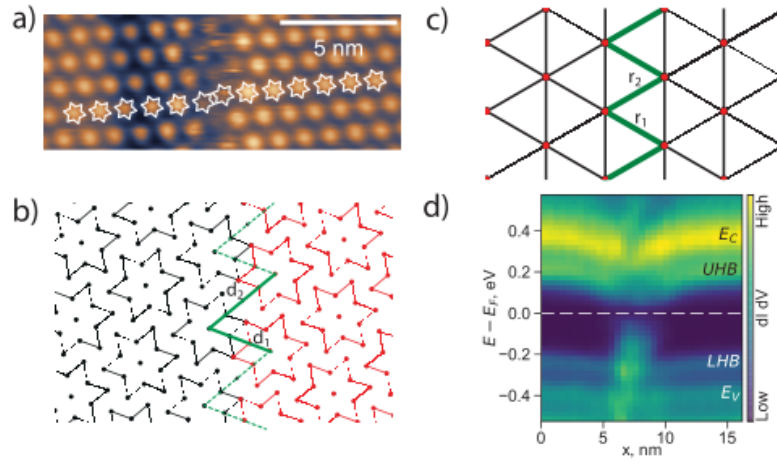
	1 T-TaS ₂	2H-TaSe ₂	1T-TiSe ₂
Transition temperatures			
T_{ICDW} (K)	543 ^a	122 ^b	-
T_{CCDW} (K)	183-221 ^a	90 ^b	202 ^c
Lattice distortion			
Superstructure	$\sqrt{13} \times \sqrt{13}^{\text{d}}$	$3 \times 3^{\text{b}}$	$2 \times 2 \times 2^{\text{c}}$
Displacement u_{max}/a	7% ^e	1.5% ^f	2.4% ^c
Energy gap			
$2\Delta(0)$ (meV)	100 – 400 ^g	24 – 160 ^h	60 – 120 ⁱ
Kohn anomaly ^j			
$\hbar\tilde{\omega}_{\mathbf{q}_0}$ (meV)	4.8 ^k	7.0 ^b	5.4 ^l
$1 - \tilde{\omega}_{\mathbf{q}_0}/\tilde{\omega}_{\mathbf{q}_{\text{max}}}$	73% ^k	22% ^b	42% ^l
$ \mathbf{q}_0 - \mathbf{q}_{\text{max}} \left(\text{\AA}^{-1} \right)$	0.32 ^k	0.26 ^b	0.44 ^l
LDA band structure			
E_{F} (eV)	$\sim 1.3^{\text{m}}$	$\sim 0.6^{\text{n}}$	$\sim 0.2^{\text{n}}$
$N(0)$ (states/eV u.c.)	1.4 – 1.7 ^o	5.2 ^o	0.9 – 1.5 ^p
Specific heat			
$N(0)^*$ (states/eV u.c.)	0.2 – 0.6(1.8) ^q	1.9 – 2.2 ^r	0.08 ^s
Θ_{D} (K)	249 ^q	201 ^r	251 ^s
Electrical resistivity			
ρ (m Ω cm) ^t	$\sim 0.2^{\text{u}}$	$\sim 0.1^{\text{v}}$	$\sim 1^{\text{w}}$
$\rho_{\perp}/\rho_{\parallel}$	$\sim 500^{\text{x}}$	$\sim 25^{\text{v}}$	$\sim 2.5^{\text{w}}$
Lattice constants ^y			
a (\AA)	3.365	3.435	3.536
c (\AA)	5.883	2×6.359	6.004

	1 T-TaS ₂	2H-TaSe ₂	1T-TiSe ₂
Electronic susceptibility			
$\chi_0(\mathbf{q}_0)/\chi_0(0) - 1$	58% ^a	35% ^b	<3% ^c
$1/\chi_0(\mathbf{q}_0)$ (eV/ state) ^d	0.7-0.9	~ 0.6	1.3-2.2
Electron-phonon coupling			
T_{SC} (K)	5 ^e	0.15 ^f	4.15 ^g
$\lambda_{\text{McMillan}}$ ^h	0.85	0.49	0.80
$4g_{\mathbf{q}_0}^2/\hbar\omega_{\mathbf{q}_0}$ (eV/ state) ⁱ	1.0 – 1.2 ^j	1.3 – 1.5 ^k	1.6 ^l
Band versus lattice energy			
$-\Delta E_{\text{band}}$ (meV) ⁱ	160 ^m	20 – 26 ⁿ	20 – 27 ^o
$-\Delta E_{\text{band}} / \langle u \rangle^2 \left(\text{eV} \text{\AA}^{-2} \right)^{\text{p}}$	3.4 ^q	11.3-15.3	3.7-5.0
$\frac{1}{2} M \omega_{\mathbf{q}_0}^2 \left(\text{eV} \text{\AA}^{-2} \right)^{\text{r}}$	10.0	6.5	2.7

1.1.5 Essence of “Mottness collapse in the DW of 1T-TaS₂” by Skolimowski et al.

$$H = \sum_{\langle i,j \rangle, \sigma} t_{ij} c_{i\sigma}^{\dagger} c_{j\sigma} + \sum_{i\sigma} \epsilon_i n_{i\sigma} + \sum_i U_i n_{i\uparrow} n_{i\downarrow}, \quad (1.1)$$

In the DW the Mott state collapses if at least one of r_1, r_2 is large enough, due to an increase in the kinetic energy of the DW subsystem.



1.1.6 Essence of “Emergent quantum phenomena in 2D 1T-TaS₂” by Chen et al.

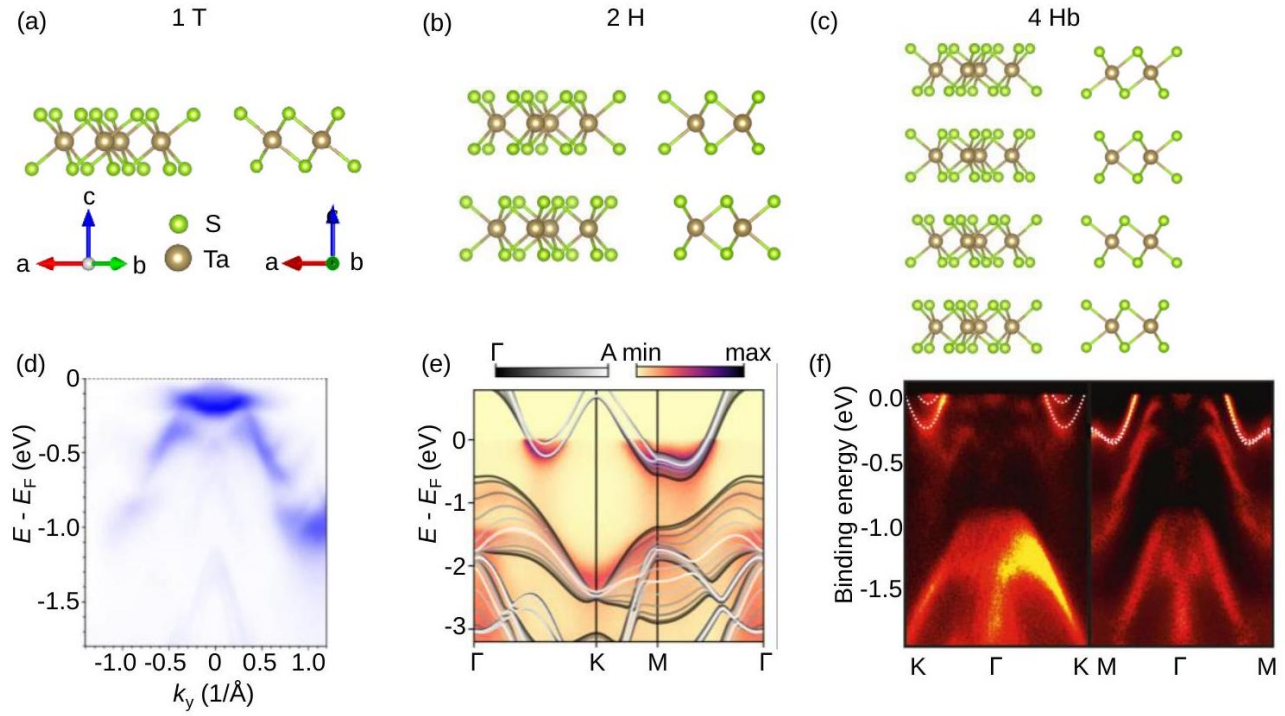


Figure 1 (a-c) Atomic structures of 1T-, 2H- and 4H-TaS₂. (d-f) A comparison of ARPES

spectra of bulk T-phase, H-phase and 4 Hb- TaS₂. (Figures adapted from refs. [18-20])

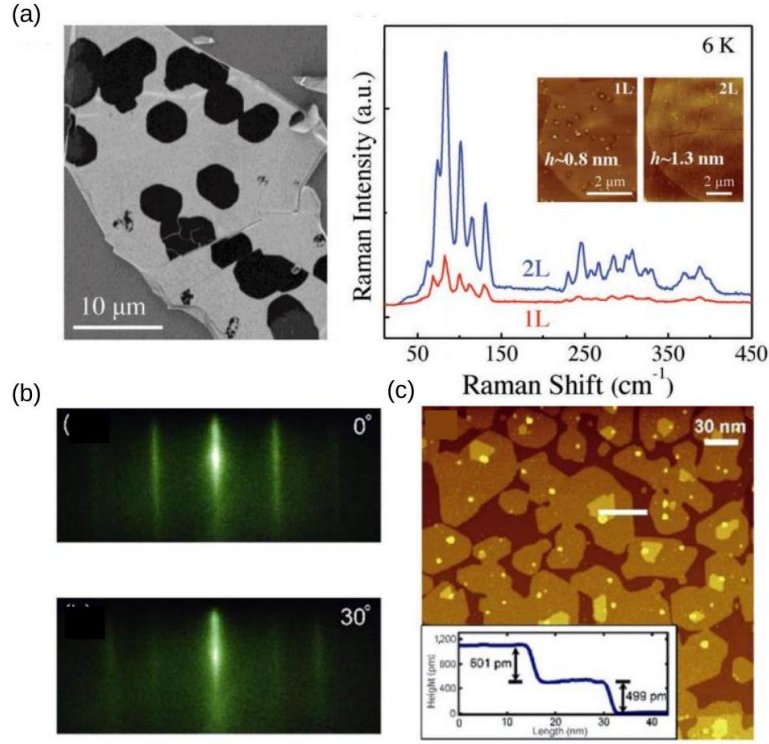


Figure 2 (a) SEM image of 1T-TaS₂ grown on *h*-BN. (b) Raman spectra taken from monolayer and bilayer 1T-TaS₂ samples. Insets are corresponding AFM images. (c) RHEED patterns of the monolayer TaS₂ thin film along two incident azimuth angles of 0° and 30°. (d) An STM topographic image shows a coexistence of monolayer and bilayer TaS₂. (Figures adapted from refs. [22, 24])

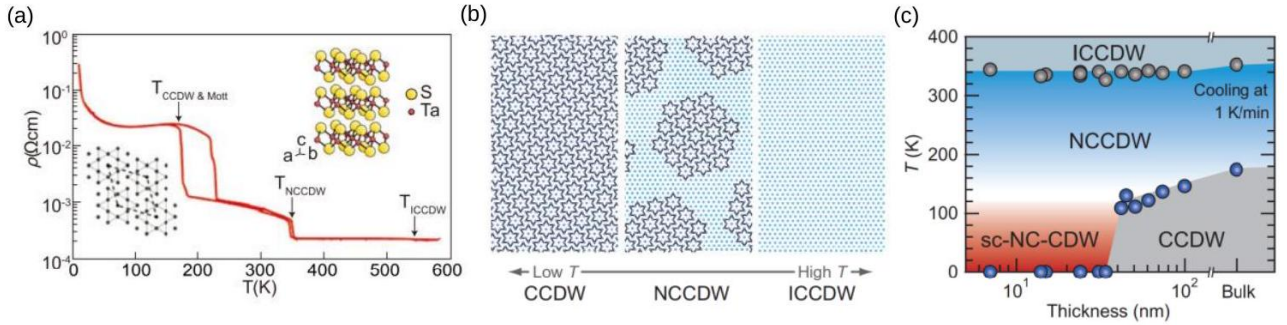


Figure 3 (a) Phase transitions of 1 T – TaS₂ with temperature measured by transport. (b) Schematic pictures of a Ta atom network in the CCDW (left), hexagonal NCCDW (middle), and ICCDW (right) phases. (c) Temperature-thickness phase diagram of 1T-TaS₂ nanothick crystals. (Figures adapted from refs. [10, 42])

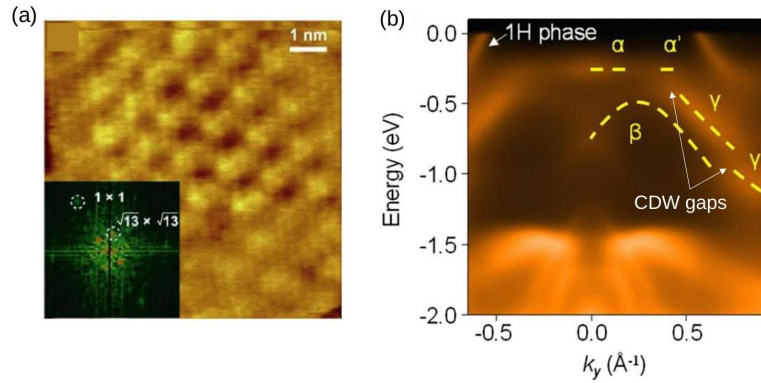
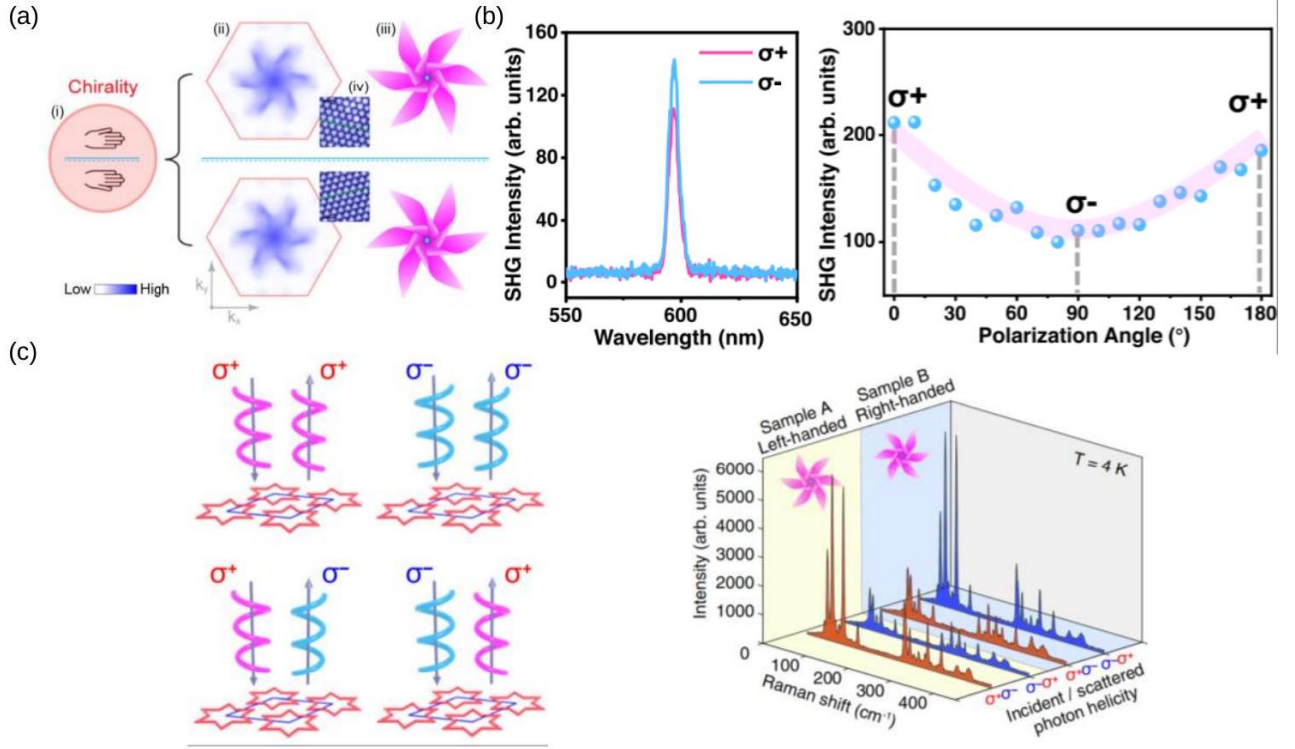


Figure 5 (a) Atomically resolved STM image of the 1T-TaS₂. The inset is the fast Fourier transform result. (b) ARPES maps taken along $\bar{\Gamma}\bar{M}$ with 45 eV p polarized light at 10 K. CDW gaps are marked with arrows. (Figures adapted from refs. [22, 30])

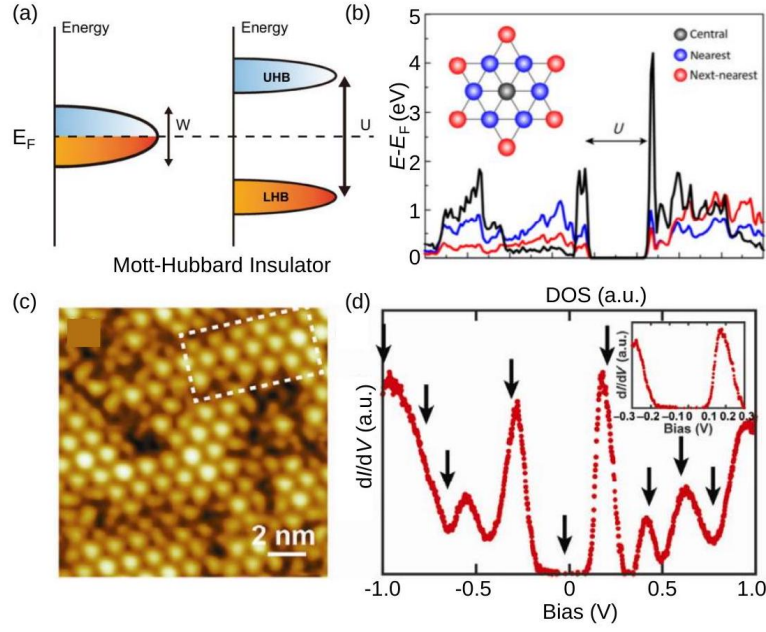


Figure 6 (a) Schematic diagram of the Mott-Hubbard Insulator. (b) PDOS of the three types of nonequivalent Ta atoms in an SOD for monolayer 1T-TaS₂. (c) The topographic image of monolayer TaS₂ with randomly distributed defects. (d) The large range dI/dV spectrum obtained on the center of an SOD. (Figures adapted from refs. [10, 23])

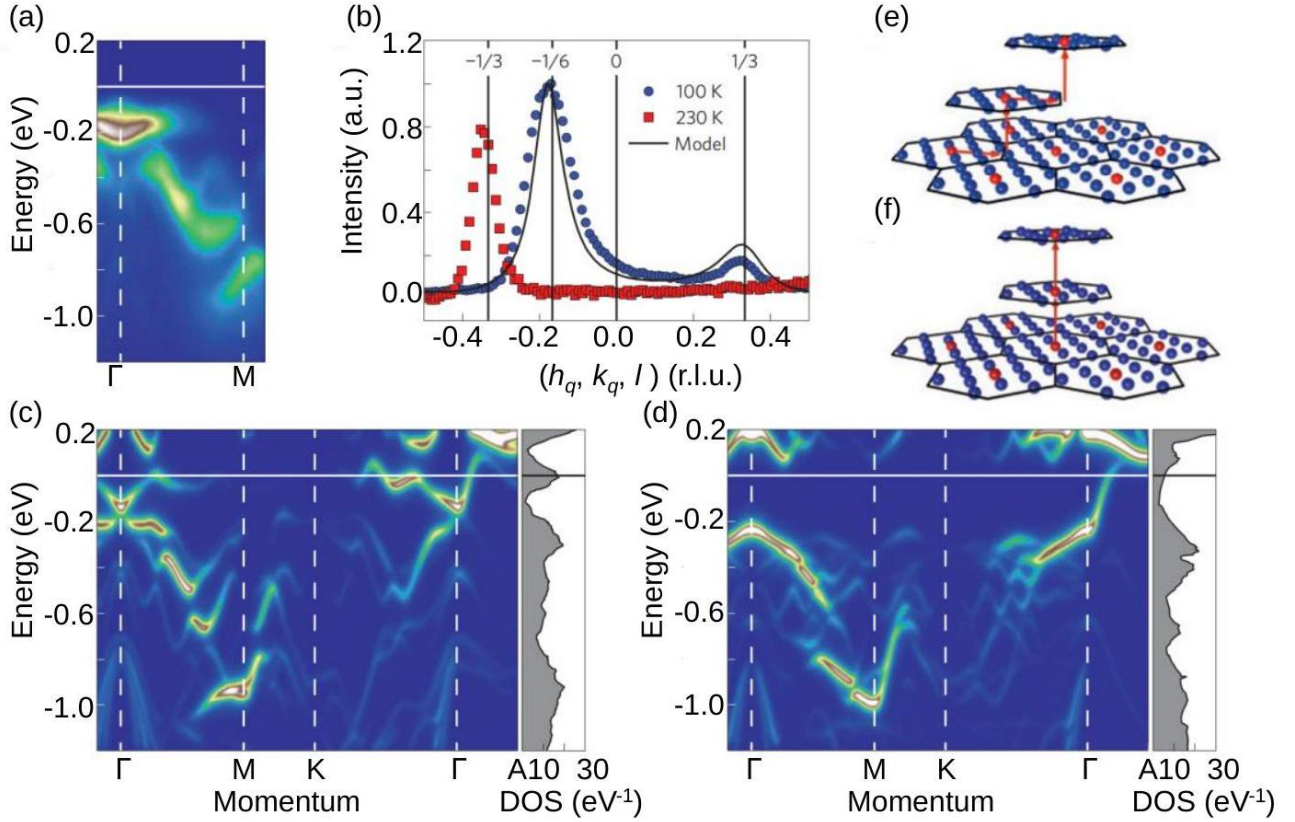


Figure 7 (a) ARPES data of 1 T – TaS₂ measured at 1 K. (b) XRD intensity of 1T- TaS₂

measured along the l -direction. (c-d) Calculated band structure for $T_S = 2\mathbf{a} + \mathbf{c}$ and $T_S = \mathbf{1c}$, respectively. $\mathbf{a}$, $\mathbf{c}$ are the lattice vectors of the undistorted structure. (e-f) Visualization of the

stacking with $T_S = 2\mathbf{a} + \mathbf{c}$ and $T_S = 1\mathbf{c}$, respectively. Red arrows indicate the stacking vectors that connect the central Ta-sites (shown in red) in successive layers. (Figures adapted from ref. [36])

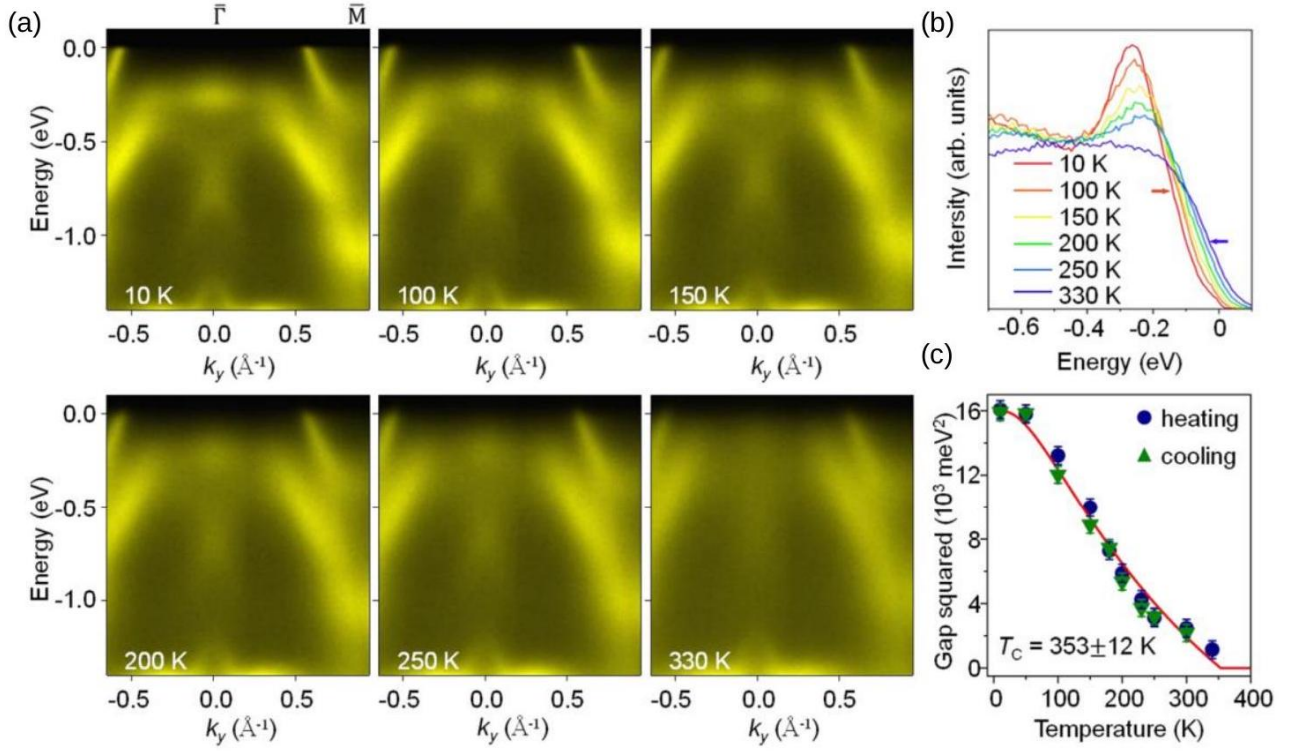


Figure 8 (a) Temperature dependence of ARPES spectra of the band structure and the energy gaps. (b) EDCs at the zone center at selected temperatures. (c) The extracted temperature dependence of the square of the energy gap. (Figures adapted from ref. [30])

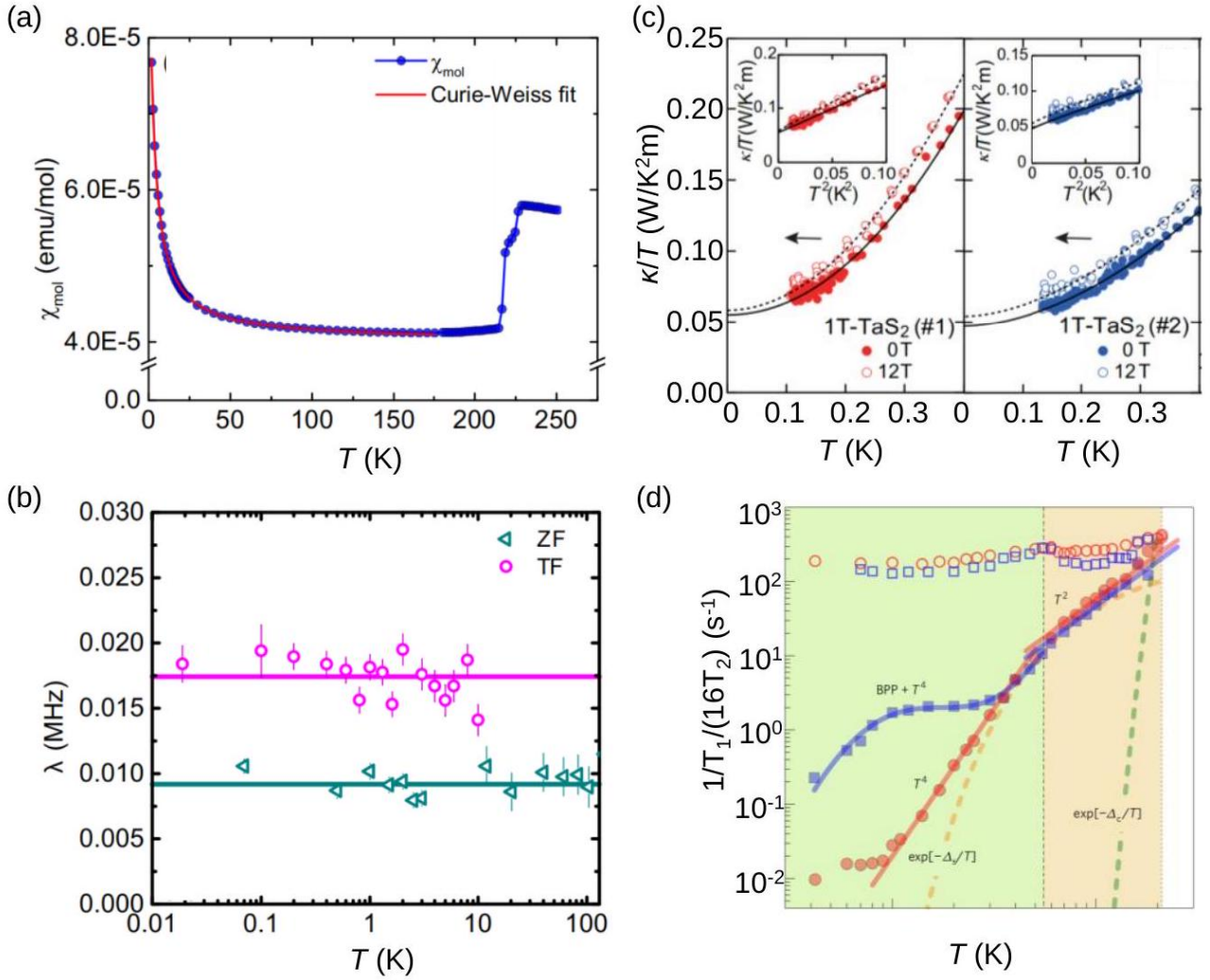


Figure 9 (a) Magnetic molar susceptibility vs temperature, obtained from SQUID magnetization measurements at constant magnetic fields of 1 and 3 T. (b) Temperature dependence of the muon spin damping rate λ . (c) Temperature dependences of κ/T for 1T-TaS₂ in zero magnetic field and at $\mu_0 H = 12$ T applied along c axis. (d) The temperature dependences of the Ta spin-lattice relaxation rate $1/T_1$ and of the Ta spin-spin relaxation rate $1/T_2$ for the Ta α and β sites. (Figures adapted from refs. [83-85])

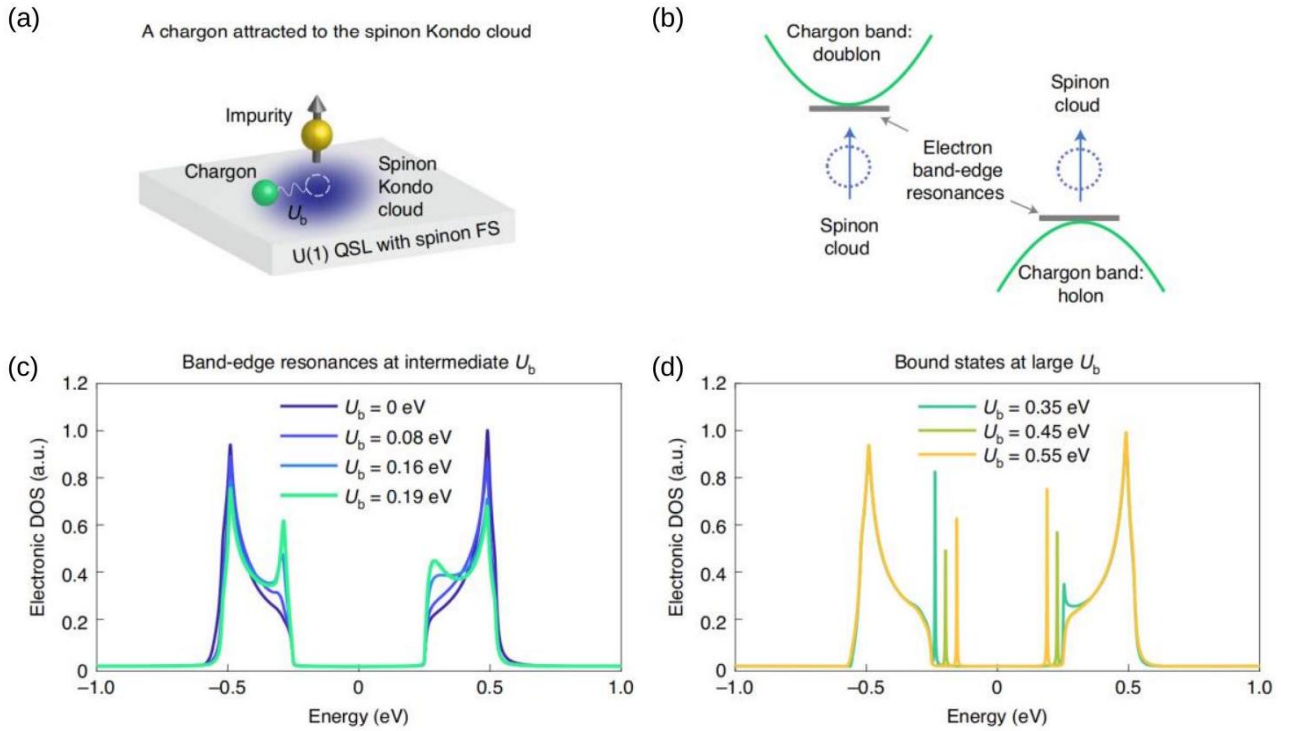
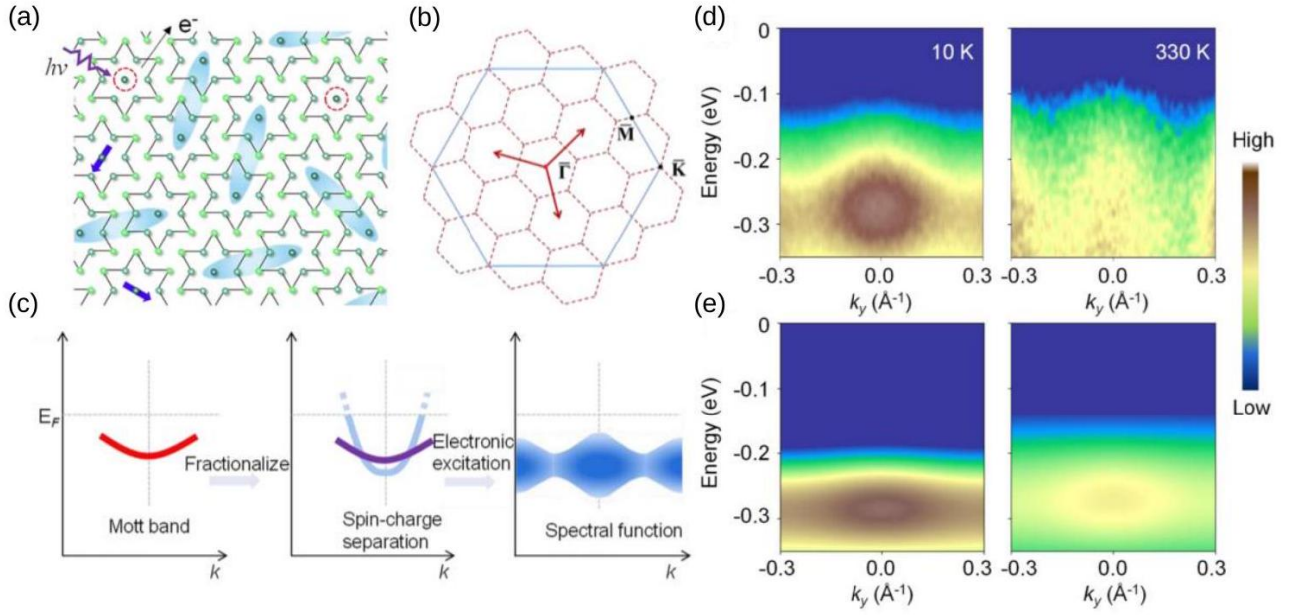


Figure 11 (a) Sketch of chargin binds to the spinon Kondo cloud. (b) Schematic diagram of formation of spinon-chargon band-edge resonance states. (c) With increasing binding interaction U_b , resonance peaks emerge at the Hubbard band edges. (d) With larger U_b , the

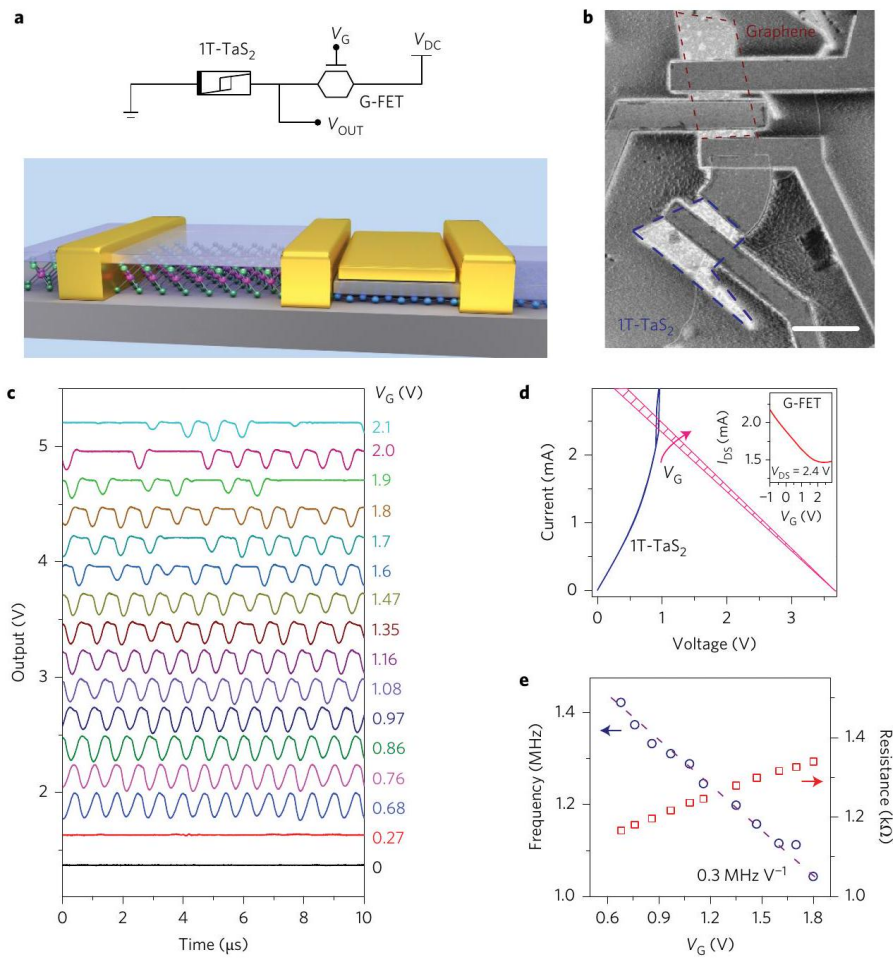
spinon-charge resonance states move inside the Mott gap and exhibit narrow peaks. (Figures adapted from ref. [91])

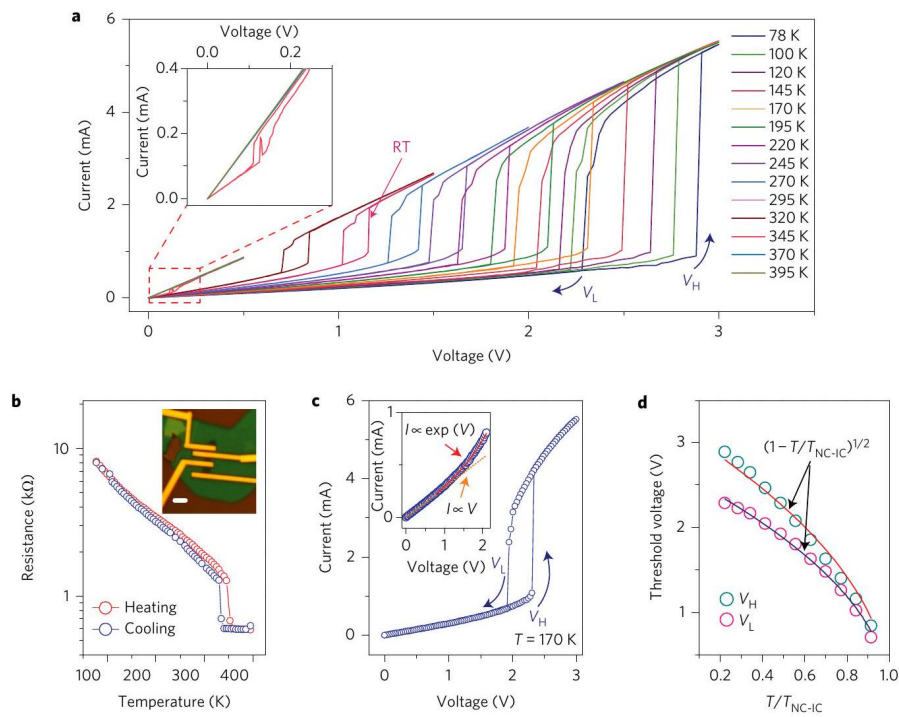
1.2 Essence of Most Important Articles about Experiments

(I'll read them later, it is a matter of a day)

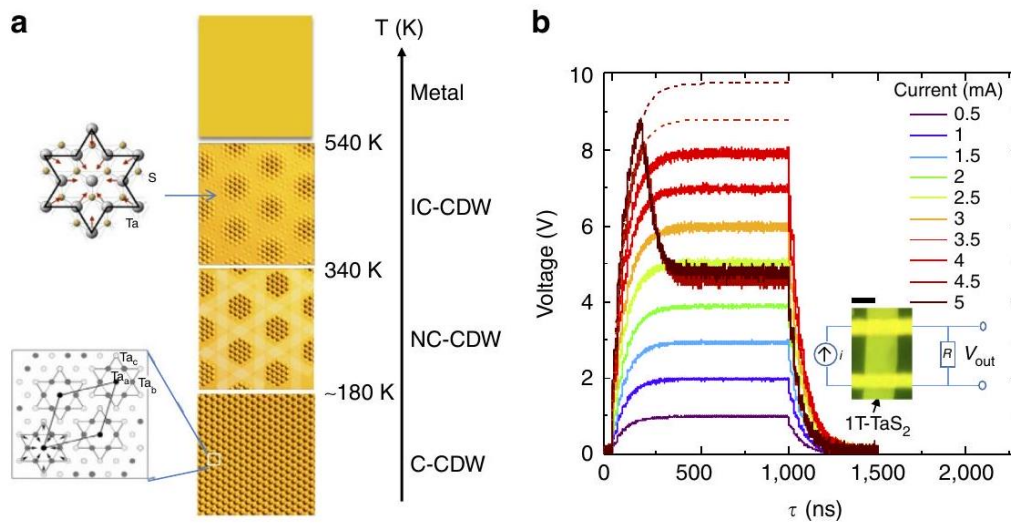
1.3 Essence of Most Important Articles about Applications

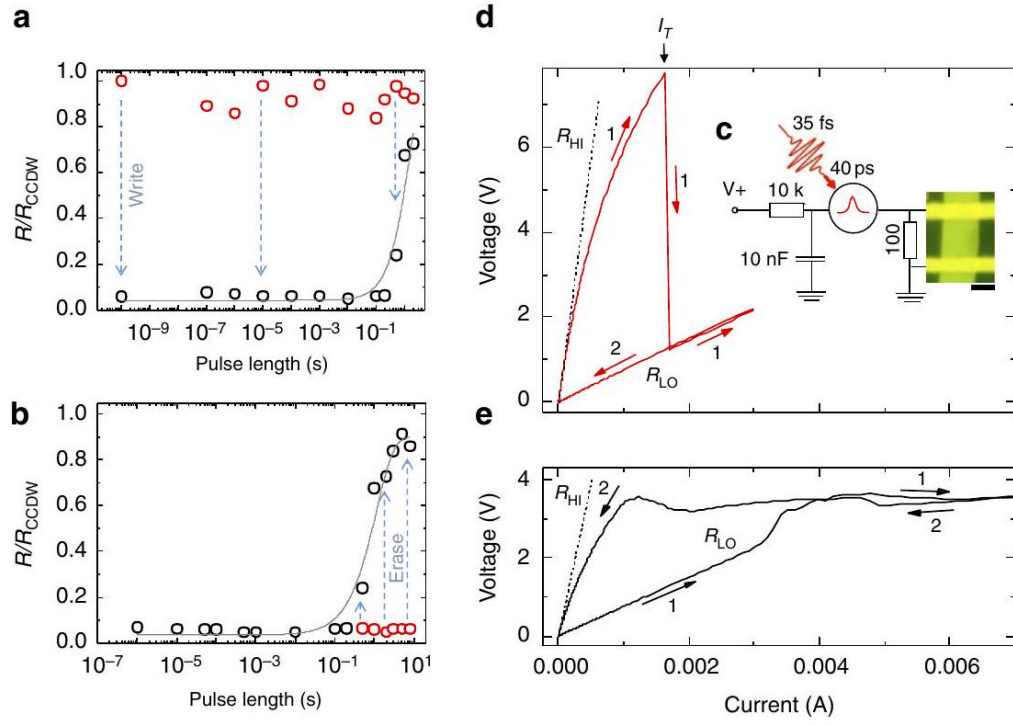
1.3.1 Essence of “A CDW oscillator based on an integrated TaS₂–boron nitride–graphene device” by Liu





1.3.2 Essence of “Fast electronic resistance switching involving hidden charge density wave states” by I. Vaskivskyi et al.





Part II

My Theory of TMDCs

2 Models of TMDCs

2.0.1 Construction of model for TMDCs

Which theory of polaron is applicable for TMDC and why?

Strong, weak polaron? Holstein, Frolich model? which to take? and which we definitely can't take??

2.0.2 Basic Properties of TMDCs: Derivation

Derivation of the formula for hopping timescale.

Consider a two-site tight-binding model with Hamiltonian

$$H = -t \left(c_1^\dagger c_2 + c_2^\dagger c_1 \right),$$

which, in the basis of states localized on the two sites, can be written as

$$H = \begin{pmatrix} 0 & -t \\ -t & 0 \end{pmatrix} = -t\sigma_x.$$

If the electron is initially localized on site 1,

$$|\psi(0)\rangle = |1\rangle,$$

its time evolution is

$$|\psi(\tau)\rangle = e^{-iH\tau/\hbar}|1\rangle = \cos\left(\frac{t\tau}{\hbar}\right)|1\rangle + i\sin\left(\frac{t\tau}{\hbar}\right)|2\rangle.$$

Therefore, the probability of finding the electron on site 2 is

$$P_2(\tau) = \sin^2\left(\frac{|t|\tau}{\hbar}\right).$$

A substantial change in the electron position occurs when the argument of the sine becomes of order unity,

$$\frac{|t|\tau}{\hbar} \sim 1,$$

which gives the characteristic hopping timescale

$$\tau_{\text{hop}} \sim \frac{\hbar}{|t|}.$$

More precisely, complete transfer from site 1 to site 2 occurs when

$$\frac{|t|\tau}{\hbar} = \frac{\pi}{2},$$

and therefore

$$\tau_{\text{transfer}} = \frac{\pi\hbar}{2|t|}.$$

Thus, a smaller hopping amplitude t corresponds to a longer characteristic timescale and therefore to slower electronic motion between the sites.

Derivation of hopping time of electron in tantalum disulfide.

For monolayer 1T-TaS₂ in the commensurate charge-density-wave phase, the low-energy electronic state associated with the Star-of-David clusters has an estimated bandwidth of approximately

$$W \simeq 28 \text{ meV}$$

[citation: Gao et al., “Orbital textures and evolution of correlated insulating state in monolayer 1T phase transition metal dichalcogenides”]. The centers of the Star-of-David clusters form an effective triangular lattice. For a nearest-neighbor tight-binding model on a triangular lattice, the dispersion can be written as

$$E(\mathbf{k}) = -2t \left[\cos(k_x a) + 2 \cos\left(\frac{k_x a}{2}\right) \cos\left(\frac{\sqrt{3}k_y a}{2}\right) \right].$$

The minimum and maximum energies of this band are $E_{\min} = -6t$ and $E_{\max} = 3t$, respectively, so that its bandwidth is

$$W = E_{\max} - E_{\min} = 9|t|.$$

Therefore, the effective hopping amplitude between neighboring Star-of-David clusters can be estimated as

$$|t| \simeq \frac{W}{9} \simeq \frac{28 \text{ meV}}{9} \simeq 3.1 \text{ meV}.$$

The characteristic coherent hopping timescale is determined by the inverse hopping energy,

$$\tau_{\text{hop}} \sim \frac{\hbar}{|t|}.$$

Using $\hbar \simeq 658 \text{ meV fs}$ gives

$$\tau_{\text{hop}} \simeq \frac{658 \text{ meV fs}}{3.1 \text{ meV}} \simeq 212 \text{ fs} \simeq 0.21 \text{ ps}.$$

Thus, the characteristic electronic hopping time between neighboring Star-of-David clusters in monolayer 1T-TaS₂ is of the order of

$$\boxed{\tau_{\text{hop}} \sim 0.2 \text{ ps}}.$$

This estimate refers to hopping between effective Star-of-David cluster orbitals rather than microscopic hopping between individual neighboring Ta atoms.

“`latex`”

Derivation of the triangular-lattice tight-binding dispersion.

Consider a nearest-neighbor tight-binding model on a two-dimensional triangular lattice,

$$H = -t \sum_{\langle i,j \rangle} (c_i^\dagger c_j + \text{h.c.}).$$

Each lattice site has six nearest neighbors, whose displacement vectors can be chosen as

$$\begin{aligned} \boldsymbol{\delta}_1 &= (a, 0), & \boldsymbol{\delta}_2 &= (-a, 0), \\ \boldsymbol{\delta}_3 &= \left(\frac{a}{2}, \frac{\sqrt{3}a}{2}\right), & \boldsymbol{\delta}_4 &= \left(-\frac{a}{2}, -\frac{\sqrt{3}a}{2}\right), \end{aligned}$$

$$\boldsymbol{\delta}_5 = \left(-\frac{a}{2}, \frac{\sqrt{3}a}{2} \right), \quad \boldsymbol{\delta}_6 = \left(\frac{a}{2}, -\frac{\sqrt{3}a}{2} \right).$$

For a Bloch state, the hopping contribution to the energy is

$$E(\mathbf{k}) = -t \sum_{\boldsymbol{\delta}} e^{i\mathbf{k} \cdot \boldsymbol{\delta}}.$$

Since the six neighbors form three pairs of opposite vectors, we can use

$$e^{i\mathbf{k} \cdot \boldsymbol{\delta}} + e^{-i\mathbf{k} \cdot \boldsymbol{\delta}} = 2 \cos(\mathbf{k} \cdot \boldsymbol{\delta}),$$

which gives

$$E(\mathbf{k}) = -2t \left[\cos(k_x a) + \cos\left(\frac{k_x a}{2} + \frac{\sqrt{3}k_y a}{2}\right) + \cos\left(-\frac{k_x a}{2} + \frac{\sqrt{3}k_y a}{2}\right) \right].$$

Using the trigonometric identity

$$\cos(A + B) + \cos(A - B) = 2 \cos A \cos B,$$

the dispersion becomes

$$E(\mathbf{k}) = -2t \left[\cos(k_x a) + 2 \cos\left(\frac{k_x a}{2}\right) \cos\left(\frac{\sqrt{3}k_y a}{2}\right) \right].$$

This is the nearest-neighbor tight-binding dispersion for an electron moving on a two-dimensional triangular lattice, which can be used as a simple effective description of hopping between neighboring Star-of-David clusters in the commensurate CDW phase of 1T-TaS₂.

Derivation of the tight-binding dispersion from the Hamiltonian.

Consider the nearest-neighbor tight-binding Hamiltonian

$$H = -t \sum_{\langle i,j \rangle} \left(c_i^\dagger c_j + \text{h.c.} \right).$$

For a single electron, a Bloch state can be written as

$$|\mathbf{k}\rangle = \frac{1}{\sqrt{N}} \sum_j e^{i\mathbf{k} \cdot \mathbf{R}_j} |j\rangle,$$

where $|j\rangle$ denotes a state localized at lattice site j . The action of the Hamiltonian on a localized state moves the electron to all nearest-neighbor sites,

$$H|j\rangle = -t \sum_{\boldsymbol{\delta}} |j + \boldsymbol{\delta}\rangle,$$

where $\boldsymbol{\delta}$ runs over the nearest-neighbor displacement vectors. Applying the Hamiltonian to the Bloch state gives

$$H|\mathbf{k}\rangle = -\frac{t}{\sqrt{N}} \sum_j e^{i\mathbf{k} \cdot \mathbf{R}_j} \sum_{\boldsymbol{\delta}} |j + \boldsymbol{\delta}\rangle.$$

We now introduce a new site index l defined by

$$\mathbf{R}_l = \mathbf{R}_j + \boldsymbol{\delta}, \quad \mathbf{R}_j = \mathbf{R}_l - \boldsymbol{\delta}.$$

Consequently,

$$e^{i\mathbf{k}\cdot\mathbf{R}_j} = e^{i\mathbf{k}\cdot\mathbf{R}_l} e^{-i\mathbf{k}\cdot\boldsymbol{\delta}},$$

and therefore

$$H|\mathbf{k}\rangle = -\frac{t}{\sqrt{N}} \sum_{\boldsymbol{\delta}} \sum_l e^{i\mathbf{k}\cdot\mathbf{R}_l} e^{-i\mathbf{k}\cdot\boldsymbol{\delta}} |l\rangle.$$

Since the factor $e^{-i\mathbf{k}\cdot\boldsymbol{\delta}}$ is independent of l , it can be taken outside the sum,

$$H|\mathbf{k}\rangle = -t \sum_{\boldsymbol{\delta}} e^{-i\mathbf{k}\cdot\boldsymbol{\delta}} \left[\frac{1}{\sqrt{N}} \sum_l e^{i\mathbf{k}\cdot\mathbf{R}_l} |l\rangle \right].$$

The expression in brackets is precisely the original Bloch state $|\mathbf{k}\rangle$, so

$$H|\mathbf{k}\rangle = \left[-t \sum_{\boldsymbol{\delta}} e^{-i\mathbf{k}\cdot\boldsymbol{\delta}} \right] |\mathbf{k}\rangle.$$

Comparing this expression with the eigenvalue equation

$$H|\mathbf{k}\rangle = E(\mathbf{k})|\mathbf{k}\rangle,$$

we obtain the tight-binding dispersion

$$E(\mathbf{k}) = -t \sum_{\boldsymbol{\delta}} e^{-i\mathbf{k}\cdot\boldsymbol{\delta}}.$$

For a lattice in which every nearest-neighbor vector $\boldsymbol{\delta}$ is accompanied by the opposite vector $-\boldsymbol{\delta}$, the corresponding terms can be combined using

$$e^{-i\mathbf{k}\cdot\boldsymbol{\delta}} + e^{i\mathbf{k}\cdot\boldsymbol{\delta}} = 2 \cos(\mathbf{k} \cdot \boldsymbol{\delta}),$$

which leads directly to the cosine form of the tight-binding dispersion used for the triangular lattice. ““

2.0.3 General properties of TaS2

Why so the 1T and 1H phases give such a different physics?

(GPT:)

The difference between the physics of 1T-TaS*2 and 1H-TaS*2 originates from the different coordination of Ta by the surrounding S atoms. In 1T-TaS*2, Ta is approximately octahedrally coordinated, whereas in 1H-TaS*2 it has trigonal-prismatic coordination. Although the Ta atom has the same five 5d orbitals in both structures,

$$d * xy, \quad d * xz, \quad d * yz, \quad d * x^2 - y^2, \quad d_{z^2},$$

the potential created by the surrounding S atoms is different. Therefore, the crystal-field Hamiltonian

$$H_{\text{CF}} = \sum_m \epsilon_m d_m^\dagger d_m$$

gives different orbital energies ϵ_m . In the ideal octahedral limit of the $1T$ structure, the d orbitals approximately split into

$$t_{2g} = (d_{xy}, d_{xz}, d_{yz})$$

and

$$e_g = (d_{x^2-y^2}, d_{z^2}),$$

with

$$\epsilon_{t_{2g}} < \epsilon_{e_g}.$$

In the trigonal-prismatic environment of the $1H$ structure, the splitting is qualitatively different:

$$a'_1 = d_{z^2}, \quad e' = (d_{x^2-y^2}, d_{xy}), \quad e'' = (d_{xz}, d_{yz}).$$

These local orbital levels form bands when orbitals on different Ta sites hybridize. A simplified tight-binding Hamiltonian can be written as

$$H = \sum_{i,m,\sigma} \epsilon_m n_{im\sigma} + \sum_{\langle ij \rangle, m, n, \sigma} t_{mn}^{ij} d_{im\sigma}^\dagger d_{jn\sigma}.$$

After Fourier transformation, this becomes

$$H_{mn}(\mathbf{k}) = \epsilon_{mn}^{\text{CF}} + t_{mn}(\mathbf{k}),$$

and diagonalization gives the band energies

$$H(\mathbf{k})u_{\nu\mathbf{k}} = E_\nu(\mathbf{k})u_{\nu\mathbf{k}}.$$

Thus, changing the Ta-S geometry changes both the crystal-field energies ϵ_m and the hopping amplitudes t_{mn} , which changes the orbital composition, dispersion and bandwidth of the bands:

$$\text{geometry} \rightarrow \epsilon_m, ; t_{mn} \rightarrow E_\nu(\mathbf{k}) \rightarrow N(E).$$

Here the density of states is

$$N(E) = \sum_{\nu, \mathbf{k}} \delta(E - E_\nu(\mathbf{k})).$$

For TaS₂, the nominal Ta⁴⁺ configuration is approximately $5d^1$, so the Ta- $5d$ -derived bands close to the Fermi level are particularly important. In $1T$ -TaS₂, the resulting electronic structure is susceptible to a strong CDW reconstruction. In the commensurate CDW phase, 13 Ta atoms form a Star-of-David cluster, and the original Ta- d bands are reconstructed into cluster-derived bands. In particular, a narrow approximately half-filled band appears near the Fermi energy. Since its bandwidth W is small, electron-electron interactions become comparatively important when

$$\frac{U}{W} \gtrsim 1.$$

This provides the basis for the Mott-Hubbard physics, local-moment physics, magnetic frustration and possible quantum-spin-liquid behavior discussed for $1T$ -TaS₂. The $1H$ phase has a different crystal-field splitting and different hopping amplitudes and does not undergo the same Star-of-David reconstruction. Therefore, it does not produce the same narrow half-filled Star-of-David-derived band. The overall connection is consequently

different Ta-S geometry $\rightarrow$ different orbital energies and hopping $\rightarrow$ different bands near $E_F \rightarrow$ different

2.1 Open problems about TMDCs

2.1.1 Open Problems in 1T-TaS₂

What is the microscopic origin of the insulating state in the commensurate CDW phase?

The low-temperature commensurate charge-density-wave phase of 1T-TaS₂ is insulating, but the relative roles of Mott physics, interlayer hybridization, stacking, and band formation remain debated. An important question is under which conditions the insulating gap should be understood as a correlation-driven Mott gap and under which conditions it can arise predominantly from three-dimensional band structure.

How important are electron–electron correlations in 1T-TaS₂?

The narrow band associated with the David-star clusters naturally enhances correlation effects, but the effective values of the Hubbard interaction U , bandwidth W , and their dependence on stacking and dimensionality are not completely established. A central problem is to determine when U/W is sufficiently large to produce genuinely Mott-like behavior.

How does interlayer stacking determine the electronic state?

Different relative arrangements of David-star clusters in neighboring layers can strongly modify interlayer hopping and the electronic band structure. A major unresolved problem is to establish the actual stacking configurations present in real samples and quantitatively connect them to metallic, band-insulating, or correlation-driven electronic states.

What is the real three-dimensional structure of the commensurate CDW phase?

Although individual TaS₂ layers have a well-defined David-star reconstruction, the ordering of these clusters along the c axis is considerably more complicated. Determining whether the low-temperature structure contains ordered stacking, stacking disorder, domains, or mixtures of different configurations is essential for understanding the electronic structure.

How does the electronic structure evolve from bulk to monolayer 1T-TaS₂?

Reducing the thickness suppresses interlayer hopping and substantially changes screening and electronic correlations. A central question is whether the system crosses over from a three-dimensional band-dominated insulator in bulk samples to a genuinely two-dimensional Mott state in the monolayer limit.

What is the origin of the insulating state in monolayer 1T-TaS₂?

Experiments on monolayer samples reveal a strongly insulating state and a very narrow electronic band associated with the David-star reconstruction. It remains important to determine quantitatively whether this state is a conventional Mott insulator, a more complicated correlated state, or a state strongly modified by the substrate and dielectric environment.

How strongly does the substrate modify monolayer 1T-TaS₂?

Experiments on monolayers necessarily involve a substrate or supporting material. Charge transfer, dielectric screening, strain, disorder, and hybridization with the substrate can modify the observed electronic spectrum. Separating intrinsic monolayer physics from extrinsic substrate effects therefore remains an important challenge.

What determines the bandwidth of the David-star flat band?

The narrow band close to the Fermi energy plays a central role in correlation-based descriptions of 1T-TaS₂. Its bandwidth depends on intralayer hopping, interlayer coupling, structural distortions, and possibly correlations themselves. Establishing the microscopic contributions to this bandwidth is necessary for constructing reliable effective models.

What are the correct effective interaction parameters for 1T-TaS₂?

Different theoretical calculations can produce substantially different estimates of the effective Coulomb interaction. Determining realistic values of U , intersite interactions V , hopping amplitudes t , and screened interactions for different thicknesses and environments remains an important methodological problem.

Are nonlocal Coulomb interactions essential?

Many simplified descriptions use a single-band Hubbard model with only an on-site interaction U . However, the David-star orbital extends over several Ta atoms, making nonlocal Coulomb interactions potentially important. Determining whether extended Hubbard models are required for a quantitative description remains an open question.

Is single-site DMFT sufficient for describing 1T-TaS₂?

Single-site DMFT captures local dynamical correlations but neglects spatial correlations. Because the relevant electronic states are associated with clusters arranged on a triangular lattice, an important problem is to determine whether cluster DMFT, extended DMFT, or other nonlocal methods are necessary.

Does 1T-TaS₂ realize a quantum spin liquid?

If the commensurate phase is a Mott insulator with one localized electron per David-star cluster, the clusters effectively form a triangular lattice of spin-1/2 degrees of freedom. The absence of conventional long-range magnetic order motivates a possible quantum-spin-liquid interpretation, but its experimental status remains unresolved.

What happens to the expected local magnetic moments?

A simple Mott picture predicts localized spin-1/2 moments associated with the David-star clusters. However, experiments have not established conventional magnetic order corresponding to these moments. Understanding whether the spins form a quantum spin liquid, singlets, stacking-dependent states, or another correlated phase remains a major problem.

What drives the formation of the charge-density wave?

The CDW in 1T-TaS₂ cannot be understood simply as a textbook Peierls instability based on perfect Fermi-surface nesting. The relative roles of momentum-dependent electron-phonon coupling, electronic susceptibility, orbital structure, lattice energetics, and electronic correlations remain subjects of investigation.

How does the incommensurate CDW transform into the nearly commensurate CDW?

The transition involves the emergence of locally commensurate regions separated by domain walls. A microscopic description should explain why this particular domain structure becomes

energetically favorable and how its characteristic length scale depends on temperature and microscopic interactions.

How does the nearly commensurate phase transform into the commensurate phase?

The disappearance and rearrangement of the domain-wall network during cooling involve large-scale reconstruction of the CDW texture. Understanding the kinetics, energetics, nucleation processes, and possible role of defects in this transition remains an important problem.

What determines the structure and dynamics of CDW domain walls?

Domain walls in the nearly commensurate phase are not simply geometric boundaries; they possess their own atomic and electronic structure. Determining their formation energy, width, electronic states, interactions, and mobility is necessary for understanding the macroscopic behavior of the material.

Are domain walls metallic?

Electronic states associated with CDW domain walls have been proposed as possible conducting channels. However, whether individual domain walls are intrinsically metallic and how their conductivity depends on their atomic structure, correlations, and surrounding CDW domains remains an important question.

What determines the reconfiguration of the domain-wall network?

External perturbations can reorganize the domain pattern into configurations different from the equilibrium state. A major problem is to identify the microscopic rules governing domain-wall motion, creation, annihilation, and topological rearrangement.

What stabilizes the photoinduced hidden state?

Ultrafast optical excitation can transform 1T-TaS₂ into a long-lived metastable hidden state. The microscopic mechanism responsible for its remarkable stability and its relation to CDW domain topology, lattice distortions, stacking, and electronic correlations remain central open questions.

What is the electronic structure of the hidden state?

The hidden state has transport and structural properties different from those of the equilibrium commensurate phase. Determining whether its increased conductivity originates from domain walls, modified stacking, changes in Mottness, altered band structure, or a combination of these effects remains an active problem.

How are metastable states encoded in the CDW configuration?

1T-TaS₂ can support multiple long-lived electronic states after optical or electrical excitation. An important question is whether these states correspond to distinct domain-wall topologies, different stacking configurations, different defect densities, or other collective degrees of freedom.

Why are some nonequilibrium configurations long-lived?

A nonequilibrium state would normally relax toward thermal equilibrium. In 1T-TaS₂, however, certain photoinduced configurations can survive for very long times. Understanding the energy barriers and topological or structural constraints that prevent relaxation is an important theoretical challenge.

How does stacking change during nonequilibrium switching?

Most descriptions of photoinduced switching emphasize intralayer CDW reconfiguration, but interlayer stacking can strongly influence the electronic structure. Determining whether switching between metastable states also involves collective changes in stacking is an important unresolved problem.

What controls the transition from the Mott/CDW state toward superconductivity?

Pressure, chemical substitution, and other perturbations can suppress the commensurate insulating state and produce superconductivity. Understanding whether superconductivity emerges from the destruction of Motttness, from CDW domain structures, from changes in stacking, or from another mechanism remains an important question.

What is the superconducting pairing mechanism in 1T-TaS₂?

Although superconductivity appears when the low-temperature insulating/CDW phase is suppressed, the microscopic pairing interaction and its relationship to CDW fluctuations and electronic correlations remain incompletely understood.

Do CDW domain walls play a role in superconductivity?

Superconductivity often appears in regimes where the perfectly commensurate CDW is replaced by an inhomogeneous or nearly commensurate state. This raises the question of whether superconductivity develops preferentially in domain walls, metallic regions between commensurate domains, or throughout the reconstructed electronic system.

How should the competition between CDW order, Motttness, and superconductivity be modeled?

These phenomena involve lattice distortions, electron–phonon coupling, strong electronic interactions, and three-dimensional stacking simultaneously. Constructing a microscopic model capable of describing all of them within a unified framework remains a major theoretical challenge.

How do phonons participate in equilibrium and nonequilibrium phase transitions?

The David-star reconstruction involves substantial lattice displacement, making lattice dynamics essential to the physics. Identifying which phonon modes control CDW formation, melting, recovery, and photoinduced switching remains an important problem.

Can the complete nonequilibrium dynamics be simulated microscopically?

Experiments can follow photoinduced changes on femtosecond-to-millisecond timescales, while theoretical calculations generally treat only restricted electronic or lattice degrees of freedom. Developing simulations that simultaneously capture electronic correlations, lattice dynamics, domain formation, and interlayer stacking remains a major challenge.

What causes the differences between nominally similar 1T-TaS₂ samples?

Experimental results depend strongly on sample thickness, disorder, strain, substrate, preparation method, thermal history, and stacking configuration. Understanding which discrepancies between experiments represent genuine new physics and which originate from sample-dependent effects remains essential.

Can a unified microscopic model of 1T-TaS₂ be constructed?

Different aspects of 1T-TaS₂ are often described using different models: electron–phonon models for CDW formation, Hubbard models for Mottness, tight-binding or DFT descriptions for stacking, and phenomenological models for domain walls. A major long-term problem is to develop a unified framework that connects these phenomena quantitatively.

2.1.2 Open Problems in TMDCs which can be solved using polaronic theories**What determines exciton and trion dynamics in TMDCs?**

Excitons dominate the optical response of monolayer TMDCs because of their large binding energies. However, the mechanisms controlling exciton formation, thermalization, diffusion, recombination, and conversion into charged excitons are still not completely understood. An important problem is to determine how these processes depend on temperature, carrier density, dielectric environment, disorder, and excitation conditions.

How do excitons interact with phonons?

Exciton–phonon coupling strongly influences linewidths, relaxation, transport, and photoluminescence in TMDCs. An important open question is how different phonon modes contribute to exciton scattering and how this coupling changes with temperature, strain, substrate, and dimensionality.

What is the microscopic origin of dark excitonic states?

TMDCs contain spin-forbidden and momentum-forbidden excitons that can have energies comparable to or below those of optically bright excitons. Their precise energetic ordering and their role in relaxation and photoluminescence remain important questions, particularly in materials such as WS₂ and WSe₂.

How can the valley degree of freedom be controlled?

The K and K' valleys provide an additional electronic degree of freedom that can potentially be used for information processing. Major questions concern how valley polarization and valley coherence are generated, how long they survive, what determines intervalley scattering, and how they can be manipulated electrically, optically, magnetically, or mechanically.

What limits valley coherence and valley lifetime?

Although valley-selective optical excitation is well established, experimentally observed valley polarization often decays rapidly. Understanding the relative importance of electron–hole exchange, phonons, disorder, defects, and many-body scattering remains an important problem.

How important are many-body interactions in realistic TMDC devices?

Carrier–carrier and carrier–exciton interactions can substantially modify the electronic and optical spectra. A central question is how screening, doping, temperature, and dielectric environment modify quasiparticle energies, exciton binding energies, and collective phenomena.

What new many-body phases appear at high carrier densities?

Strong interactions may produce phenomena such as exciton gases, electron–hole liquids, exciton condensation, correlated insulating phases, or superconductivity. Determining which phases can actually be stabilized in experimentally accessible TMDC systems remains an active problem.

What is the microscopic role of defects?

Vacancies, substitutions, adsorbates, grain boundaries, and other defects can create localized electronic states and strongly affect optical and transport properties. It remains challenging to establish quantitative relations between particular atomic defects and experimentally observed electronic or optical signatures.

Can defects be deliberately engineered?

Instead of treating defects only as undesirable disorder, an important direction is to use controlled defects to engineer single-photon emitters, localized excitons, magnetic moments, catalytic sites, or modified transport properties.

What determines charge transport in realistic TMDC samples?

The intrinsic mobility predicted for ideal crystals is often substantially higher than experimentally measured mobility. The relative importance of phonons, charged impurities, vacancies, substrate disorder, contact resistance, dielectric screening, and grain boundaries is still being investigated.

How can metal–TMDC contacts be understood and optimized?

Contact resistance and Schottky barriers remain major limitations for TMDC electronic devices. Important questions concern Fermi-level pinning, interface states, metal-induced gap states, tunneling barriers, and how the atomic structure of the contact determines charge injection.

How does strain modify the electronic and optical properties?

TMDCs can sustain relatively large mechanical deformations, making strain engineering particularly promising. A major problem is to understand quantitatively how nonuniform strain changes band gaps, excitons, valley properties, phonons, and carrier localization.

Can strain create controlled exciton potentials?

Spatially varying strain can generate effective potentials for excitons and funnel them toward particular regions. Understanding the limits of this effect and whether strain-defined excitonic circuits or localized quantum emitters can be reliably produced remains an open direction.

How do substrates influence intrinsic TMDC properties?

The measured properties of a monolayer depend strongly on its environment. Substrates modify dielectric screening, introduce disorder and strain, affect phonons, and can transfer charge to the TMDC. Separating intrinsic properties from substrate-induced effects remains a fundamental experimental and theoretical problem.

How does dielectric screening modify quasiparticles and excitons?

Because TMDCs are atomically thin, Coulomb interactions are unusually sensitive to the surrounding dielectric environment. A major question is how environmental screening modifies quasiparticle gaps, exciton binding energies, exciton radii, and many-body interactions.

What happens at TMDC heterostructure interfaces?

Van der Waals heterostructures allow different two-dimensional materials to be combined without conventional lattice matching. However, charge transfer, band alignment, interface reconstruction, screening, and hybridization at these interfaces are not yet completely understood.

What controls interlayer excitons?

In type-II TMDC heterostructures, electrons and holes can reside in different layers and form long-lived interlayer excitons. Important problems include understanding their lifetime, diffusion, interactions, thermalization, recombination, and possible condensation.

How does twist angle modify TMDC physics?

Rotating two TMDC layers relative to one another creates moiré superlattices and strongly modifies electronic and excitonic states. Determining the relation between twist angle, lattice relaxation, moiré potential, electronic bandwidth, and interactions remains a major research problem.

What correlated phases occur in moiré TMDCs?

Narrow moiré bands can enhance electron–electron interactions and produce correlated insulating states, magnetism, generalized Wigner crystals, and potentially superconductivity. Establishing microscopic models for these phases and determining their phase diagrams are major theoretical challenges.

How should moiré TMDC systems be modeled microscopically?

Continuum models, tight-binding descriptions, Hubbard-type models, and first-principles calculations are all used for moiré systems. Connecting these descriptions and determining reliable interaction and hopping parameters directly from realistic materials remain difficult problems.

What is the role of lattice relaxation in twisted structures?

Atoms in twisted bilayers do not remain in the positions predicted by simply superimposing two rigid lattices. Structural relaxation can substantially modify the moiré potential and electronic structure, making the coupled treatment of atomic reconstruction and electronic correlations an important problem.

Can TMDCs host robust quantum spin or valley states?

Strong spin–orbit coupling and spin–valley locking make TMDCs promising platforms for quantum information. An important question is whether sufficiently long-lived and controllable spin, valley, or excitonic quantum states can be realized under realistic experimental conditions.

What determines spin relaxation in TMDCs?

Spin lifetimes depend on spin–orbit coupling, intervalley scattering, phonons, disorder, carrier density, and external fields. A quantitative microscopic description capable of explaining experiments across different TMDC materials is still incomplete.

How do magnetic interactions emerge in TMDC-based systems?

Magnetism can arise through defects, magnetic dopants, proximity to magnetic materials, or intrinsic correlated states in moiré systems. Understanding the microscopic mechanisms and determining whether robust two-dimensional magnetic phases can be engineered remain important research directions.

How does proximity to other materials modify TMDC states?

Placing a TMDC next to a superconductor, ferromagnet, topological material, or another strongly spin–orbit-coupled system can induce new interactions through proximity effects. Understanding the strength, spatial dependence, and microscopic origin of these induced interactions remains an active problem.

Can superconductivity be controlled in TMDCs?

Several TMDCs exhibit superconductivity intrinsically or after electrostatic doping. Important questions concern the pairing mechanism, the influence of spin–orbit coupling, dimensionality, disorder, and competing phases, and whether superconductivity can be systematically engineered in atomically thin structures.

What unconventional superconducting states can occur in TMDCs?

Broken inversion symmetry and strong spin–orbit coupling can produce unusual superconducting states, including Ising superconductivity. Determining the possible pairing symmetries and the conditions for topological or other unconventional superconducting phases remains an important theoretical problem.

How do electronic correlations interact with charge-density waves?

Several TMDCs exhibit charge-density-wave phases in which lattice distortions, electron–phonon coupling, and electron–electron interactions are simultaneously important. Separating these contributions and determining their relative importance remains a central problem, particularly in strongly correlated TMDCs.

What drives charge-density-wave formation in different TMDCs?

Fermi-surface nesting alone generally does not provide a universal explanation of CDW formation. Understanding the roles of momentum-dependent electron–phonon coupling, lattice instabilities, orbital physics, and electronic correlations remains an important materials-specific problem.

How do nonequilibrium phases emerge after optical excitation?

Ultrafast laser excitation can drive TMDCs into transient or metastable states that cannot be described simply by an increased electronic temperature. Understanding how electrons, excitons, phonons, and structural degrees of freedom cooperate during these transformations is an important open problem.

Can metastable states be controlled reproducibly?

Some TMDCs exhibit long-lived states created by optical, electrical, or mechanical perturbations. Determining the microscopic origin of their stability, switching mechanisms, relaxation pathways, and possible use as information-storage states remains an active research direction.

How should strongly nonequilibrium TMDCs be described theoretically?

Conventional equilibrium band-structure methods are insufficient for many ultrafast experiments. Developing realistic nonequilibrium theories combining electronic correlations, excitons, electron–phonon coupling, and time-dependent structural dynamics remains a major challenge.

How accurately can first-principles methods predict TMDC properties?

Standard density-functional theory often fails to quantitatively describe quasiparticle gaps, excitons, and strongly correlated states. Understanding when DFT, hybrid functionals, GW, Bethe–Salpeter calculations, DFT+ U , and DMFT are appropriate remains an important methodological question.

How can theory connect realistic materials to effective models?

First-principles calculations provide detailed electronic structures, whereas many-body calculations often require simplified Hamiltonians. Constructing reliable low-energy models and determining hopping parameters, Coulomb interactions, spin–orbit couplings, and electron–phonon interactions without uncontrolled approximations remain central theoretical problems.

Which phenomena are intrinsic and which are sample-dependent?

Different experiments on nominally identical TMDC materials sometimes produce substantially different electronic, optical, and transport properties. Determining whether these differences arise from intrinsic physics or from strain, defects, substrate effects, contamination, stacking, thickness, and preparation conditions remains a fundamental issue.

How do properties evolve from monolayers to bulk crystals?

Many electronic and optical properties change dramatically with the number of layers. A complete microscopic understanding of the crossover from the two-dimensional limit to three-dimensional bulk behavior, including changes in screening, band structure, excitons, phonons, and correlations, remains incomplete.

Part III

Examples and Solved Problems

Part IV

Well-known and Important Theories

3 2D transition metal dichalcogenides by Manzeli, Ovchinnikov, Pasquier, Yazyev, Kis

Abstract

Graphene is very popular because of its many fascinating properties, but its lack of an electronic bandgap has stimulated the search for 2D materials with semiconducting character.

Transition metal dichalcogenides (TMDCs), which are semiconductors of the type MX_2 , where M is a transition metal atom (such as Mo or W) and X is a chalcogen atom (such as S, Se or Te), provide a promising alternative.

Because of its robustness, MoS_2 is the most studied material in this family. (and what is known about it? what is the difference compared to TaS_2 ?)

TMDCs exhibit a unique combination of atomic-scale thickness, direct bandgap, strong spin-orbit coupling and favourable electronic and mechanical properties.

This makes them interesting for fundamental studies and for applications in high-end electronics, spintronics, optoelectronics, energy harvesting, flexible electronics, DNA sequencing and personalized medicine. (I don't know yet, how they can be applied there, but I'll maybe check it later)

In this Review, the methods used to synthesize TMDCs are examined and their properties are discussed, with particular attention to their charge density wave, superconductive and topological phases.

The use of TMDCs in nanoelectronic devices is also explored, along with strategies to improve charge carrier mobility, high frequency operation and the use of strain engineering to tailor their properties.

Two-dimensional transition metal dichalcogenides (TMDCs) are an emerging class of materials with properties that make them highly attractive for fundamental studies of novel physical phenomena and for applications ranging from nanoelectronics and nanophotonics to sensing and actuation at the nanoscale.

The past years have seen a strong resurgence of interest in 2D TMDCs, sparked by the demonstration of the first transistor¹ and by the discovery of strong photoluminescence in MoS_2 monolayers^{2,3}. (check these papers later, they are very cited)

TMDCs have a very long and fruitful history. Their structure was first determined by Linus Pauling in 1923 (REF. 4). (???)

By the late 1960s, around 60 TMDCs were known, at least 40 of them with a layered structure⁵. (???)

The first reports on the use of adhesive tapes for producing ultrathin MoS_2 layers, by Robert Frindt, date back to 1963 (REF. 6), and the production of monolayer MoS_2 suspensions was first achieved in 1986 (REF. 7).

In parallel with the development of research on carbon nanotubes and fullerenes in the 1990s, Reshef Tenne and others led strong efforts in the area of inorganic fullerenes and nanotubes, which commenced with the discovery of WS_2 nanotubes and nested particles⁸, followed by the synthesis of MoS_2 nanotubes and nanoparticles⁹.

The rapid growth of graphene-related research that started in 2004 stimulated the development of techniques (which techniques?) well-suited for working with layered materials, opening the way to new studies of TMDCs and, in particular, of their ultrathin films.

Several recent reviews cover the optical properties of TMDCs and their heterostructures, as well as their use in various photonics and optoelectronics applications^{10–12}.

In this Review, the focus is mainly on recent results related to the electronic properties of TMDCs.

We start by introducing the structural phases and electronic band structure of TMDCs, examining in particular their charge density wave, superconducting and topological phases.

We then examine the methods that can be used to synthesize these materials.

The use of TMDCs in devices and the strategies that can be implemented to enhance mobility are discussed next, along with their high-frequency performance and the use of strain engineering to tune the materials properties.

3.0.1 Structure

TMDCs exist in several structural phases resulting from different coordination spheres (co-ordination spheres?) of the transition metal atoms.

The two common structural phases are characterized by either trigonal prismatic (2H) or octahedral (1T) coordination of metal atoms (FIG. 1a).

These structural phases can also be viewed in terms of different stacking orders of the three atomic planes (chal-cogen-metal-chalcogen) forming the individual layers of these materials.

The 2 H phases correspond to an ABA stacking in which chalcogen atoms in different atomic planes occupy the same position A and are located on top of each other in the direction perpendicular to the layer.

By contrast, the 1T phases are characterized by an ABC stacking order (ABC stacking order???) .

Depending on the particular combination of transition metal (group IV, V, VI, VII, IX or X) and chalcogen (S, Se or Te) elements, the thermodynamically stable phase is either the 2 H or 1T phase, but the other can often be obtained as a metastable phase.

The current knowledge on the existence of the two phases, in either stable or metastable form, and on other properties of TMDCs is summarized in the 'periodic table' shown in FIG. 1b.

For example, for five of six possible chemically distinct bulk TMDCs formed by group VI transition metals (metal=Mo or W; chalcogen=S, Se or Te) the 2 H phase is thermodynamically stable and the 1T phase can be obtained as a metastable phase.

An exception is represented by WTe₂, for which the stable bulk phase at room temperature is the orthorhombic 1 T_d phase.

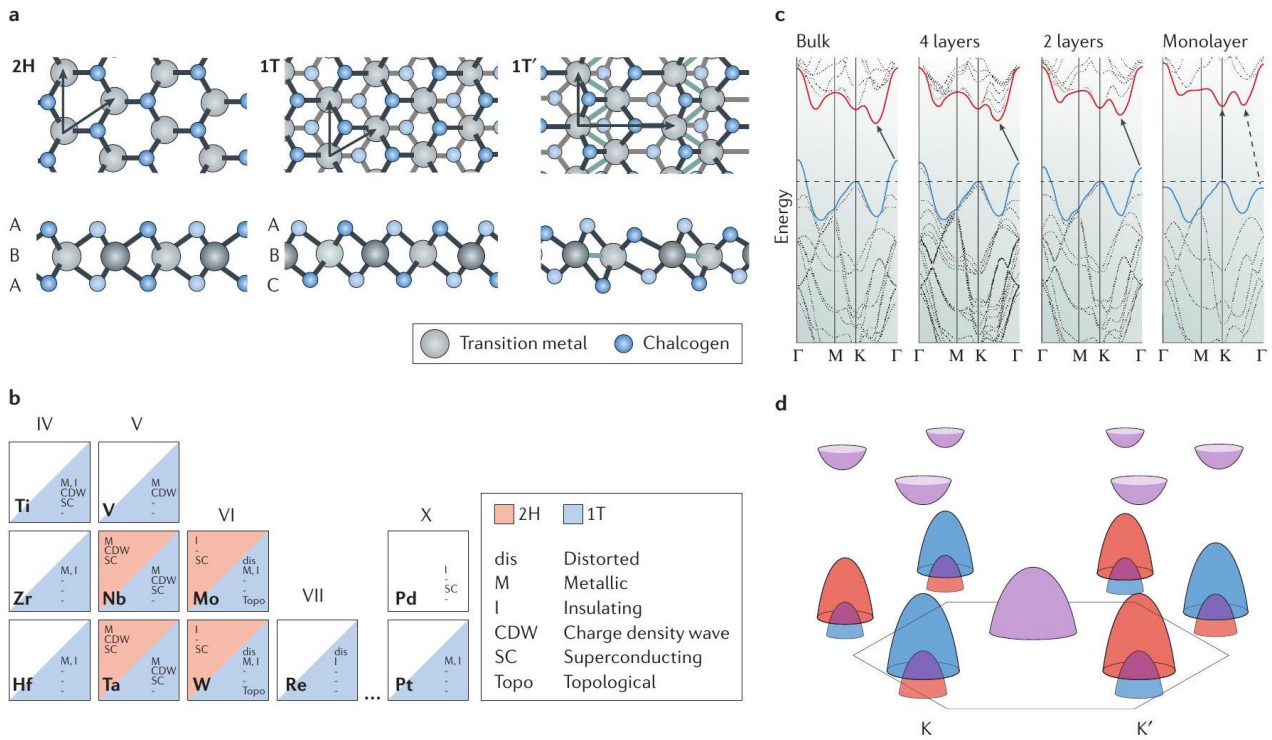


Figure 1 | Structure and electronic properties of TMCDs.

a | Atomic structure of single layers of transition metal dichalcogenides (TMDCs) in their trigonal prismatic (2H), distorted octahedral (1 T) and dimerized (1 T') phases. Lattice vectors and the stacking of atomic planes are indicated.

b | 'Periodic table' of known layered TMDCs, organized based on the transition metal element involved, summarizing their existing structural phases (2H, 1 T or other, as in the case of Pd-based TMDCs) and indicating the presence of distorted structural phases and observed electronic phases.

c | Evolution of the band structure of 2H – MoS₂ calculated for samples of decreasing thickness.

d | Schematic representation of the band structure of monolayer 2H – MoS₂, showing the spin splitting of the bands at the K and K' points on the corners of the Brillouin zone. Orange and blue colours indicate up and down spin polarization. Panel c is adapted with permission from REF. 2, American Chemical Society. Panel d is adapted with permission from REF. 17, American Physical Society.

The structure of TMDCs is further defined by the stacking configuration of the individual layers in the case of multilayer and bulk samples, and by possible distortions that lower the periodicity. These distortions, if pronounced, can result in the formation of metal-metal bonds - as it happens, for example, in the dimerization of the 1T phase of group VI TMDCs, which results in the 11' phase, or in the tetramerization of rhenium dichalcogenides such as 1 T – ReS₂ - or in weaker lattice distortions accompanying charge density wave phases, which display rich physics and complex phase diagrams, as discussed below.

3.0.2 Electronic band structure

The diversity of chemical compositions and structural phases of TMDCs results in a broad range of electronic properties, both from the point of view of the band structure character (metallic or insulating) and of the emergence of correlated and topological phases.

We discuss here the basic features of the band structure of TMDCs formed by group VI transition metals Mo and W combined with S and Se (an overview of the electronic properties of TMDCs is presented in FIG. 1b).

In their thermodynamically stable 2 H phase, MoS_2 , MoSe_2 , WS_2 and WSe_2 are semiconductors. This property drew attention to these TMDCs as 2D materials for electronic devices ¹.

The evolution of the band structure of 2H – MoS_2 as calculated from first principles ² (density functional theory) upon reducing its thickness from bulk to monolayer is shown in FIG. 1c.

The positions of the valence and conduction band edges change with decreasing thickness, and the indirect bandgap semiconductor bulk material turns into a direct bandgap semiconductor monolayer ^{2,3}. (what is the indirect and direct band gap?)

The calculated values for the bandgap of bulk and monolayer 2H – MoS_2 are 0.88 and 1.71 eV, respectively ¹³. The experimental value for the bandgap of monolayer 2H – MoS_2 is 2.16 eV (REF. 13).

Importantly, the valence band maximum and the conduction band minimum are located at the two inequivalent high-symmetry points K and K', which correspond to the corners of the hexagonal Brillouin zone. This property is common to monolayer 2H – MoS_2 (and other group VI monolayer 2 H -TMDCs) and to graphene, and enables the observation of valley-dependent physical phenomena and potential valleytronics applications.

Another important peculiarity of monolayer 2 H TMDCs is that they lack inversion symmetry, which results in a spin splitting of the electronic bands driven by the spin-orbit interaction. Because points K and K' do not correspond to the time-reversal invariant momenta, the spin degeneracy of the conduction and valence band extrema at these points is lifted. This effect is particularly strong in the valence band, in which spin splitting values range from 0.15 eV in monolayer 2H – MoS_2 to 0.46 eV in 2H – WSe_2 (REF. 14). This trend is understood by considering that the spin-orbit interaction is a relativistic effect, and hence is stronger for heavier elements. Even though the spin splitting of the conduction band is about an order of magnitude weaker ¹⁵, it is not negligible. Because of time-reversal symmetry, the spin splitting of bands at K and K' is opposite; the resulting band structure of monolayer 2H – MoS_2 relevant to realistic charge-carrier concentrations is schematically represented in FIG. 1d. This property is referred to as spin-valley coupling ¹⁶ and implies that the valley polarization of charge carriers is automatically translated into their spin polarization. This intrinsic property of TMDCs may be used to design spintronic devices that do not involve magnetic materials ^{17,18}.

Charge density wave phases.

At low temperature, a 1D metal with non-interacting electrons is unstable against a small periodic distortion of the underlying lattice, which is accompanied by the opening of a bandgap at the Fermi energy, resulting in insulating behaviour. The period of the distortion, which arises from the interaction between electrons and phonons, is given by $Q = 2k_F$, where k_F is the Fermi momentum ^{19,20}. Such a distortion leads to a modulation of the electronic charge density, the so-called charge density wave (CDW). Chan and Heine ²¹ demonstrated that a modulation of the charge density without a coupling to phonons cannot exist, therefore establishing the equivalence between CDWs and the concept of periodic lattice distortions. A 2D or 3D metal

with a nested Fermi surface (that is, a Fermi surface with large parallel sections separated by a nesting vector Q_N) has a hidden 1D character and can also undergo a CDW distortion with periodicity Q_N at low temperature, owing to a logarithmic singularity in the electronic response function (or bare susceptibility)^{19,21,22}.

The discovery of CDW phases in the group V layered dichalcogenides, in both the 2H and 1T phases of TaS₂ and TaSe₂, and in 2H – NbSe₂, led to renewed interest in this theory^{23,24}.

The phenomenology of the CDW in dichalcogenides is rich and diverse and strongly depends on the chemical composition and crystalline phase of the material.

For example, 2H – NbSe₂ undergoes a triple- Q transition at $T_{CDW} = 33$ K.

This CDW is nearly commensurate (that is, the CDW wavelength is nearly an integer multiple of the lattice constant) and results in the formation of a superlattice with roughly 3×3 periodicity; the wave vectors are $Q_i = b_i/3(1 - \delta)$, where $\delta \ll 1$ represents the decommensuration, and b_i are the three reciprocal vectors of a triangular lattice²⁵.

Unlike in other CDW materials, the periodicity is almost independent of temperature and does not show any first-order transition to a commensurate phase, sometimes referred to as lock-in transition. The displacement of the atoms is very small (of the order of $0.05\text{\AA}$) and the effect of the CDW on the physical properties is moderate, with only a small increase of the resistivity²⁶. If the temperature is further lowered, the material becomes superconducting²⁷.

By contrast, 1T- TaS₂ exhibits a sequence of incommensurate ($T \approx 600$ K), nearly commensurate ($T \approx 350$ K) and commensurate ($T \approx 180$ K, with a $\sqrt{13} \times \sqrt{13}$ periodicity) transitions with a significant displacement of Ta atoms (up to $0.24\text{\AA}$) that strongly effects the electronic properties (FIG. 2a). The transition from the normal state to the incommensurate phase is second order and is accompanied by a small jump in the resistivity. By contrast, the nearly commensurate and commensurate transitions are strongly first order and are associated with a large increase in resistivity^{26,23}. Furthermore, the commensurate phase exhibits an interesting Mott insulating character arising from the narrowing of the conduction band induced by the distortion^{28,29}.

Following these results on bulk TMDCs, CDW phases in monolayer TMDCs were investigated, with particular attention to the CDW ordering vector and transition temperature³⁰. First-principles calculations suggested that 2H – NbSe₂ in its monolayer form has a CDW phase with a different periodicity compared to that of the bulk (4×1 , as opposed to $3 \times 3 \times 1$) and a larger gain of electronic energy, hence a higher transition temperature³¹. Experimentally, a considerable enhancement of the transition temperature from $T_{CDW} = 33$ K in the bulk to $T_{CDW} = 145$ K in the monolayer was reported³². However, other authors have not found such an enhancement and reported a 3×3 periodicity for the monolayer³³. By contrast, for the isostructural 2H – TaSe₂, first-principles calculations suggested the same periodicity for the bulk and the monolayer (3×3)³⁴. Several studies addressed the CDW phase in thin films of 1T- TaS₂ with thicknesses down to one monolayer^{35–37}, but the evolution of the commensurate and nearly commensurate phases upon reducing the dimensionality is still under debate. Experimental studies of 1T-TiSe₂ with reduced thickness revealed a CDW with the same ordering vector as in the bulk (resulting in a 2×2 superlattice), with a slight enhancement of the critical temperature^{38,39}. The absence of a hole pocket in the Fermi surface at the Γ point indicates that the pristine material is a small bandgap semiconductor rather than a semimetal with a small band overlap (this question has long been debated for bulk samples, with several experiments supporting either view).

The CDW in 1T-TiSe₂ is therefore a semi-conductor-to-semiconductor transition, with a slight increase of the bandgap induced by the distortion. The electronic structure of 1T-TiSe₂ is strongly reminiscent of the excitonic insulator proposed by Kohn, Jérôme and Rice^{40,41},

but never unambiguously observed in real systems. The question of whether the CDW in TiSe_2 should be regarded as a manifestation of an exciton condensate, or simply as driven by electron-phonon interactions, is still a matter of debate ^{38,39}.

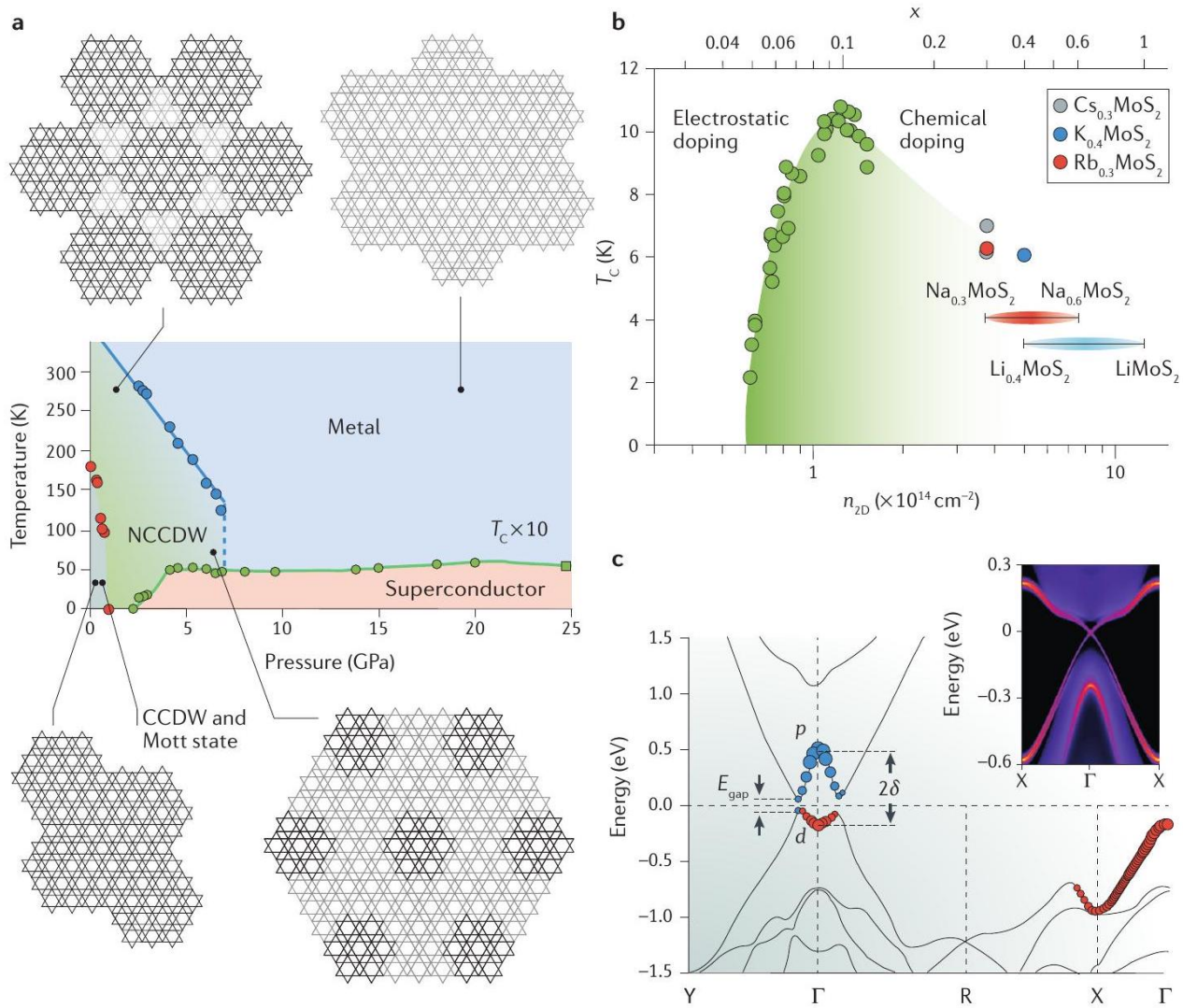


Figure 2 | Correlated and topological phases of TMDCs.

a | Temperature-pressure phase diagram of 1T – TaS₂ showing various charge density wave (CDW) phases. The deformation patterns corresponding to the different phases are shown.

b | Phase diagram of superconductivity in electrostatically and chemically doped 2H – MoS₂.

c | Band structure of monolayer 1 T' – MoS₂ showing the band inversion characteristic of the quantum spin Hall phase. The inset shows the dispersion of the topological edge states. 2δ , inverted gap energy; CCDW, commensurate CDW; E_{gap} , fundamental gap energy; n_{2D} , electron carrier density; NCCDW, nearly commensurate CDW; T_C , superconductive transition temperature.

Panel **a** is adapted with permission from REF. 29, Macmillan Publishers Limited. Panel **b** is adapted with permission from REF. 56, AAAS. Panel **c** is adapted with permission from REF. 62, AAAS.

Although the theory underlying CDW driven by Fermi surface nesting is well established, the question of whether this theory actually applies to TMDCs (or any real system) is debated.

The difficulty of identifying a nesting vector by inspecting the Fermi surface and the strong modifications of the electronic structure induced by the distortions have led some to argue that the Fermi surface nesting hardly has a role in TMCDs, and that the distortions are mainly due to strongly anisotropic electron-phonon matrix elements with enhanced values at the CDW wave vector ^{30–34}.

(so authors do not answer this question about applicability at all?)

Superconductivity

Interestingly, all bulk TMDCs displaying a CDW state in their phase diagram also exhibit superconductivity, with the exception of 2H – NbS₂, which is only superconducting ⁴². The two phases can either compete or coexist. However, superconductivity is much more robust than the CDW phase, as it does not depend on the nesting of the Fermi surface. In TMDCs, the superconducting state can be either intrinsic or induced by chemical doping, electrostatic doping or applied pressure. In the 2 H phase of NbSe₂, TaS₂ and TaSe₂, superconductivity coexists with the CDW phase at low temperatures ^{27,43–45}.

In TMDCs with the 1T phase, such as semimetallic 1T-TiSe₂ (REFS 46,47) and 1 T – TaS₂ (REFS 29,48), the superconducting state emerges as the CDW order melts, either under applied pressure or upon chemical doping by means of copper intercalation. A competition between a low-temperature distorted phase and a superconducting phase was also observed in the newly found material IrTe₂. The exact nature of the distorted phase has not been clearly identified yet; its suppression upon chemical doping leads to superconductivity with a critical temperature of up to 3 K (REF. 49).

The superconducting behaviour of bulk TMDCs persists in the 2D limit. Recently, the first experimental evidence for truly 2D intrinsic superconductivity in TMDCs was reported for monolayer 2H – NbSe₂ (REF. 33).

The 2D superconducting state is of the Kosterlitz-Thouless type ⁵⁰, as evidenced by the voltage-current characteristic measured close to the critical temperature ^{51,52}.

Although the critical temperature ($T_C = 3$ K) is even lower than that of the bulk material ($T_C = 7$ K), the in-plane critical field B_{C2} (the minimum magnetic field required to destroy the superconducting state) is an order of magnitude larger than that of the bulk and, more importantly, about seven times larger than the paramagnetic Pauli limit ⁵¹. (what is this Pauli limit? and why is it so?)

The enhancement of the in-plane critical field is not a new phenomenon in itself, but the underlying mechanism is unusual and is understood as arising from the combination of reduced dimensionality and strong spin-orbit coupling ⁵³. In a monolayer 2 H phase TMDC, the spin splitting of the K and K' valleys can be seen as an effective out-of-plane Zeeman field. Because of the spin-valley coupling, such spin splitting is compatible with Cooper pairing, and therefore the superconducting state in monolayer TMDCs is characterized by an Isinglike polarization of spins in the out-of-plane direction. This makes the superconducting state more robust against in-plane magnetic fields. In addition to the theoretical interest, it was pointed out that Ising superconductors could be useful for observing topological superconductivity and as an alternative route to engineer Majorana fermions in solid-state systems ^{53–55}.

Superconductivity can also be induced in gated thin films of 2H – MoS₂ (FIG. 2b), in which electrostatic charge doping accumulates charge carriers in the outer layer, simulating a monolayer doped sample ^{52,56,57}. Superconductivity induced by gating has also been realized in thin films of 2H – WS₂ and 2H – MoSe₂ (REFS 58,59).

Topological phases

TMDCs have also attracted considerable interest as materials that could host novel topological electronic phases^{60,61}. According to theoretical predictions, monolayer group VI TMDCs in their 1T' phase exhibit a band structure with inverted chalcogen p and transition metal d bands⁶² (FIG. 2c). In addition, the presence of a relatively strong spin-orbit interaction results in the opening of bandgaps of a few tens of millielectronvolts in 1T' sulfides and selenides of molybdenum and tungsten. This gives rise to the quantum spin Hall phase, or, equivalently, to the 2D Z_2 topologically insulating phase, characterized by the presence of helical edge states immune to backscattering. These theoretical predictions are still awaiting experimental confirmation, but TMDC-based quantum spin Hall insulators would enable technological applications of this topological electronic phase.

These 2D materials are certainly more suitable for practical applications than other quantum spin Hall insulators known to date: that is, HgTe/CdTe^{63,64} and InAs/GaSb⁶⁵ quantum wells and bilayer Bi^{49,66,67}. Bulk distorted 1T-phase tellurides of molybdenum and tungsten are semimetals, which gives rise to very large non-saturating magnetoresistance in WTe₂ (REFS 68,69). The non-centrosymmetric polymorphs of these materials were predicted to host a Weyl semimetal phase^{70–72}, which was, to some degree, experimentally confirmed^{73,74}.

3.0.3 Synthesis

MoS₂ and WS₂ are probably the only TMDCs that occur in nature in the form a layered crystal. The first highperformance transistors made of monolayers of MoS₂ were obtained from crystals of the naturally occurring mineral molybdenite¹. Bulk crystals of other TMDCs are grown using the chemical vapour transport method⁵, which enabled the first studies of the optical and electrical properties of MoS₂, MoSe₂ and WSe₂ crystals in the 1960 s⁵. In this growth method, the precursors (Mo and Se in the case of MoSe₂)⁷⁵ are mixed in stoichiometric proportions with the addition of a transport agent (I₂, Br₂ or ICl₃) and put into an evacuated ampoule inside a multi-zone furnace with a varying temperature gradient. The material is transported to the colder part of the ampoule, where crystal growth takes place. A detailed review of crystal growth and characterization can be found in REF. 76.

High-quality natural or synthetic crystals can be used as a source of thin flakes. Similarly to graphene, which can be obtained by mechanical peel-off with sticky tape from graphite, single crystals of TMDCs can serve as a source of monolayers^{1,77,78}, which can then provide a platform for a range of fundamental studies and device demonstrations. Because micromechanical exfoliation requires only bulk crystals, a decent optical microscope and adhesive tape, it is a very popular method for rapid prototyping of devices based on TMDCs and other layered materials, and has greatly contributed to the rapid expansion of research in this area. However, this method is not scalable; moreover, the relatively small areas of uniform material and the haphazard nature of material deposition can be limiting factors for more extensive studies. Liquid-phase exfoliation based on organic solvents^{79,80} is a scalable alternative to mechanical exfoliation and allows the production of solutions containing flakes with controllable thickness. The first experiments on liquid-phase exfoliation through Li intercalation date back to the 1970 s⁸¹, with a report on solutions containing single-layer MoS₂ from the 1980 s⁷. Recent methods for the exfoliation of TMDCs in liquid using Li intercalation are being intensively explored^{82,83}. The drawbacks of exfoliation through Li intercalation include reported phase transitions from the semiconducting 2H to the metallic 1T phase^{82,84,85} and the limited size of the flakes, which results in overlaps between the flakes and in a large in-plane resistance of the films⁸².

One of the first scalable methods developed for the direct growth of TMDCs was molecular

beam epitaxy (MBE).

The principle of operation is schematically illustrated in FIG. 3a through the example of the growth of GaSe on MoS₂. Detailed information on this growth method can be found in REF. 86. An ultrahigh vacuum chamber (with pressure typically below 10^{-10} mbar) contains several sources - in this case Ga and Se - to form molecular beams. Deposition is performed on a preheated substrate while the thickness and substrate crystallinity are monitored in situ by reflection high-energy electron diffraction and low-energy electron diffraction. The group of Atsushi Koma published numerous reports on the MBE growth of TMDCs in the 1980s and 1990s, demonstrating the successful growth of MoSe₂ and GaSe on a number of substrates, including other layered materials ^{87–90}. MBE-based growth of 2D materials largely differs from traditional 3D epitaxy.

Because TMDCs do not contain dangling bonds, they can in principle be grown on other layered materials and passivated surfaces (for example H -passivated Si) without the need to satisfy lattice matching conditions.

The weak van der Waals interaction can be exploited to achieve epitaxial growth, in which the lattice structure of the substrate can be used to align the orientation of the overlayer ⁹¹ - an essential requirement for growing high-quality films. Epitaxial growth can occur either if the substrate and the overlayer are lattice-matched, such as for MoSe₂ on GaAs, or if a commensuration condition can be satisfied, such as for MoS₂ on sapphire ⁹¹. If these conditions are not met, the resulting films will be polycrystalline and contain many dislocations, such as for MBE-grown MoSe₂ on an amorphous SiO₂ substrate ⁹². Such defects and grain boundaries can result in variable-range hopping through localized states in MBE-grown MoSe₂ and MoTe₂ on sapphire substrates ⁹³. MBE performed in ultrahigh vacuum growth chambers combined with scanning tunnelling microscopy or angle-resolved photoelectron spectroscopy provided access to the intrinsic properties of materials such as MoSe₂ (REFS 94,95) and NbSe₂ (REF. 33). Furthermore, various types of vertical heterostructures of 2D materials could be realized, for example, SnSe₂/WSe₂ (REF. 96), MoSe₂/Bi₂Se₃ (REF. 97) and MoSe₂/ graphite ⁹⁸. Thus, MBE is a useful tool for fundamental studies of 2D materials and their combinations, although the electrical properties of as-grown films require further improvement.

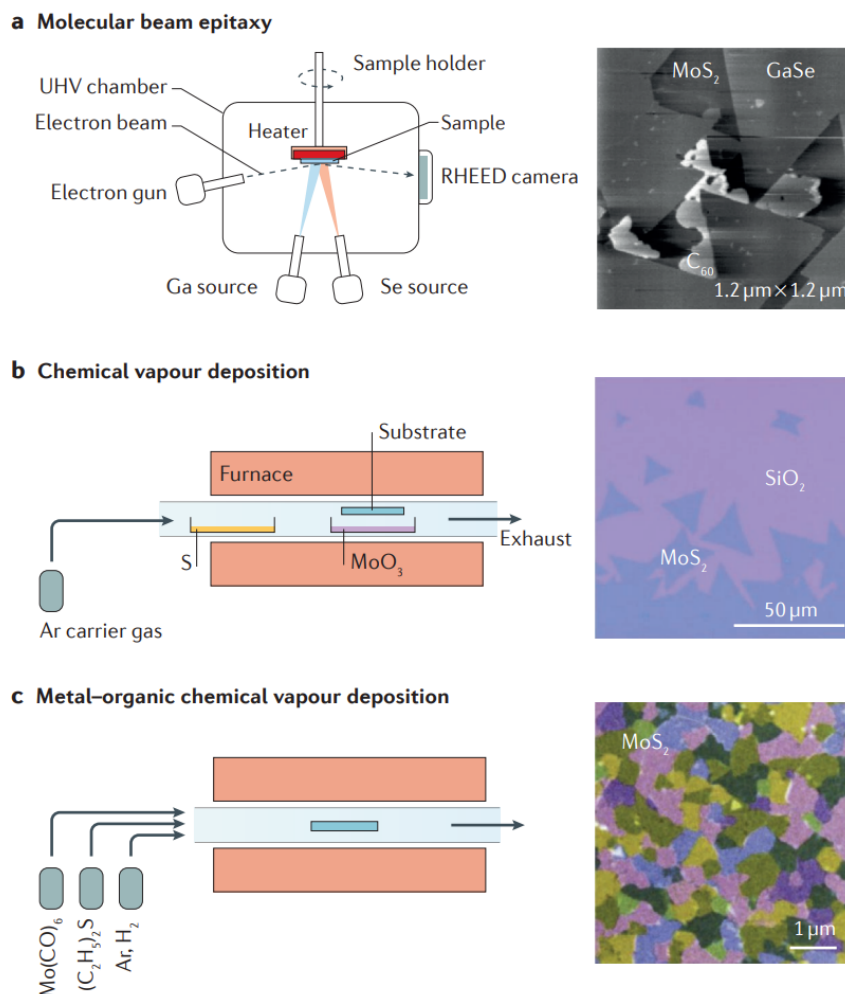


Figure 3 | Growth methods for the synthesis of ultrathin TMDCs. **a** | In molecular beam epitaxy, high-purity elemental source materials are co-evaporated in ultrahigh vacuum. The right panel is an atomic force microscope image of monolayer GaSe grown on MoS₂. **b** | Chemical vapour deposition is based on the direct chemical reaction between different precursor materials. An optical image of triangular single-crystalline domains of MoS₂ grown on SiO₂ is shown on the right. **c** | Metal-organic chemical vapour deposition is based on the decomposition of metal-organic precursors and their subsequent chemical reaction. On the right, a false-colour dark-field transmission electron microscopy image shows a continuous monolayer of MoS₂ with different grain orientations. RHEED, reflection high-energy electron diffraction; TMDC, transition metal dichalcogenide. Panel **a** is adapted with permission from REF. 90, Elsevier. Panel **b** is adapted with permission from REF. 220, American Chemical Society. Panel **c** is adapted with permission from REF. 110, Macmillan Publishers Limited.

The most practical method for the synthesis of high-quality TMDCs is chemical vapour deposition (CVD, FIG. 3b). This method does not require ultrahigh vacuum chambers and is thus cheap and relatively easy to integrate into existing industrial processes. The first reports of MoS₂ synthesis were based on the sulfurization of Mo pre-deposited on the substrate⁹⁹, upon dip coating of substrates in a (NH₄)₂ MoS₄ solution followed by annealing in gas flow^{10,101}, or upon the growth of multilayers from MoO₃ and S precursors¹⁰². However, in these early reports there was no control over the material thickness; only in 2013 the growth of monolayer domains of MoS₂ on SiO₂ was reported in two simultaneous publications^{103,104}. The working principle of CVD is shown in FIG. 3b; in the example shown, MoO₃ and S react at elevated temperature, leading to the growth of MoS₂ on the substrate. The as-grown domains on SiO₂

have good optical and electrical properties, displaying room temperature field-effect mobilities on the order of $5 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ (REFS 103,104), but have random lattice orientation with respect to each other and thus form grain boundaries of different types. These grain boundaries are predicted to have a plethora of electronic properties, for example, 60° grain boundaries could have metallic nature¹⁰⁵. The investigation of the electrical transport properties of large-area devices fabricated from similar materials showed that the presence of grain boundaries decreases the mobility of large area films¹⁰⁶. The need to control the orientation of domains motivated further developments; for example, atomically smooth c-plane sapphire was used to promote the epitaxial CVD growth of monolayer MoS_2 (REF. 91). In contrast to the growth on SiO_2 substrates, systematic alignment was observed, owing to the commensurate lattices of MoS_2 and sapphire. A two-probe field-effect mobility of $\sim 25 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ was preserved on a length scale of $80 \mu\text{m}$, through ~ 16 grain boundaries. Thus, the engineering of the alignment of separate flakes can lead to a better control of the electrical properties of large area films.

A growth method related to CVD is metal-organic CVD (MOCVD), which is based on the use of gas-phase precursors^{107–110}, and was first used for TMDC synthesis in the 1990 s¹⁰⁷. Gas precursors are supplied to the main chamber with controlled flux (FIG. 3c). Recently, waferscale synthesis of MoS_2 and WS_2 on various substrates was demonstrated, and the resulting samples displayed good electrical properties. For example, the MoS_2 sample had an electron mobility of $\sim 30 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ (REF. 110). The discussed CVD results mainly regard MoS_2 growth. In addition to MoS_2 , other TMDCs, such as MoSe_2 (REFS 111-113), WS_2 (REFS 107, 10, 114-120), WSe_2 (REFS 109, 121-123), ReS_2 (REFS 124-126), ReSe_2 (REF. 127), MoTe_2 (REFS 128,129) or WTe_2 (REF. 129), can be grown both by CVD and MOCVD. However, the electrical properties of the large-area films of these materials are not yet well characterized and require further investigation.

Different types of TMDC heterostructures can also be grown using CVD. In particular, atomically sharp interfaces between monolayers of MoS_2 and MoSe_2 (REF. 130), WSe_2 and MoSe_2 (REF. 131), MoS_2 and WS_2 (REF. 132), MoSe_2 and WSe_2 (REF. 131), WS_2 and WSe_2 (REF. 130), and

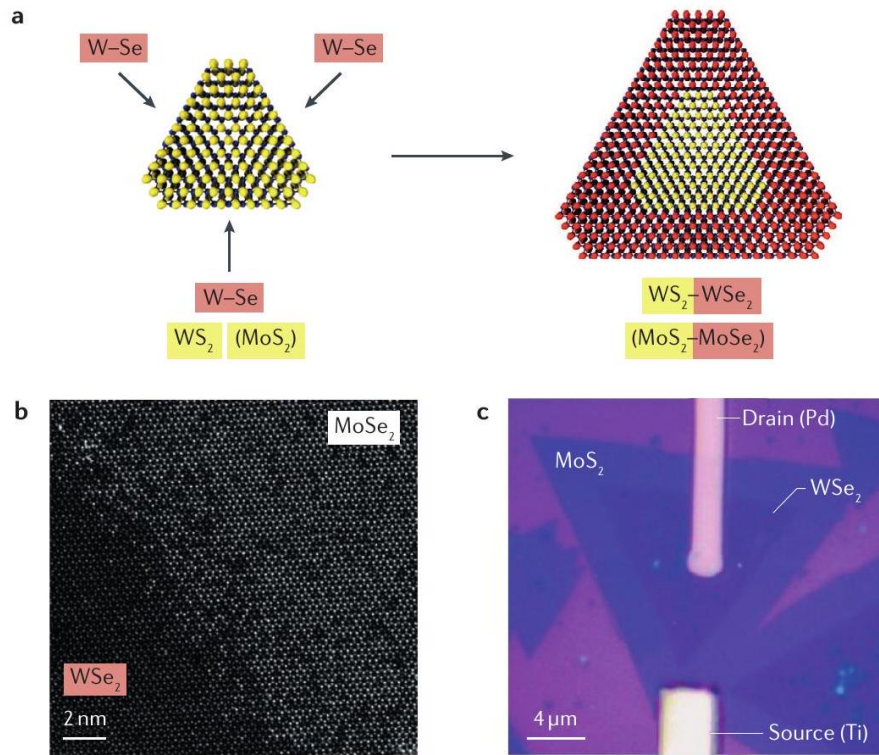


Figure 4 | Examples of synthesis of 2D TMDC lateral heterostructures.

a | Schematic drawing showing the growth of lateral heterostructures based on 2D transition metal dichalcogenide (TMDC) materials. b | High-angle annular dark-field scanning transmission electron microscopy image of the lateral heterostructure formed between MoSe_2 and WSe_2 . c | Optical image of a p-n junction based on a $\text{MoS}_2/\text{WSe}_2$ lateral heterostructure. Panel a is adapted with permission from REF. 130, Macmillan Publishers Limited. Panel b is adapted with permission from REF. 131, Macmillan Publishers Limited. Panel c is adapted with permission from REF. 133, AAAS.}

WSe_2 and MoS_2 (REF. 133) have been realized by CVD. The benefits of this approach over manual assembly through transfer techniques are that the interfaces are atomically sharp, as shown in FIG. 4a,b, and that there are no residues from the transfer process. Theoretical modelling predicts exotic behaviours for such heterostructures¹³⁴: for example, efficient charge separation¹³⁴ and valley filtering within one material¹⁷. Moreover, these artificial materials could be used as p-n diodes without resorting to in situ doping or transfer processes, as shown in the example in FIG. 4c, where a lateral boundary between WSe_2 and MoS_2 serves as a p-n junction¹³⁴ and can be used as a light-emitting diode.

3.0.4 Semiconductor devices

Mobility engineering. The suitability of 2D materials for applications based on quantum transport is determined by the mean free path of charge, spin or valley carriers, which for charge carriers is directly proportional to the charge carrier mobility. Although the theoretically predicted values for the charge carrier mobility are very promising for 2D TMDCs^{135–137}, the mobility is in practice limited by disorder and by the presence of scattering sources. These can be intrinsic charged point defects or defects in the surrounding dielectric or at the semiconductor/dielectric interface, which can trap charges and scatter mobile charge carriers. Intrinsic and remote optical phonons in the environment of the 2D semiconductor can further limit the mobility close to room temperature.

Theoretical calculations for monolayer MoS₂ predict a room-temperature electron mobility in the range of $10 - 1,000 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and low-temperature values exceeding $10^5 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, depending on factors such as the impurity density and the dielectric environment^{135,138,139}. The measured mobility for atomically thin MoS₂ is almost two orders of magnitude lower than that of its bulk counterpart^{1,78,140}. The degradation of the mobility when going from bulk to thin-film samples can be understood considering that atomically thin materials are more sensitive to environmental factors owing to their increased surface-to-volume ratio. Remote optical phonons and Coulomb scattering from the interfacial charge traps are proposed to be the dominant reasons behind the low carrier mobility in MoS₂ atomically thin layers.

The encapsulation of monolayer MoS₂ with a HfO₂ dielectric layer enabled the first demonstration of a transistor based on monolayer MoS₂ (REF. 1) and, in general, on a 2D TMDC semiconductor. Subsequent temperature-dependent mobility measurements¹⁴¹ on monolayer MoS₂ in a multiprobe geometry gave the first insights into mobility degradation in monolayer TMDCs. For devices with an exposed MoS₂ channel, mobility increases with increasing temperature until it reaches a peak value at $T \approx 200 \text{ K}$, after which it starts to degrade again, indicating that scattering from charged impurities is the dominant mechanism limiting the mobility at low temperatures. In this regime, increasing the temperature increases the thermal energy of the carriers and their thermal velocity, which in turn reduces the scattering cross section. Above $\sim 200 \text{ K}$, phonon scattering becomes the dominant scattering mechanism. As temperature increases,

the number of phonon modes available for scattering increases, resulting in reduced mobility. The deposition of a thin layer of a dielectric material with a high dielectric constant κ , such as HfO₂, on MoS₂ enhances the low-temperature mobility, owing to the effective screening of the static Coulomb scattering from charged impurities¹³⁹ (FIG. 5a). Adding a metallic top gate on the surface of the dielectric results in a further increase in the mobility; the measured electron mobility has an impurity-limited value of $120 - 180 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. The mobility starts decreasing above 20 K (FIG. 5a) and in the $100 - 300 \text{ K}$ range it can be fitted using the power-law dependence $\mu \approx T^{-\gamma}$, where γ has values in the range of $0.55 - 0.78$. This value is much smaller than the experimental values found for bulk crystals ($\gamma = 2.6$ (REF. 140)) or for bare monolayers ($\gamma = 1.4$ (REF. 141)), showing that the presence of the top gate can reduce the rate of mobility degradation with rising temperature, and can allow the observation of the metal-insulator transition and of band transport¹⁴¹. Temperature-dependent conductivity measurements further support this interpretation. Bare MoS₂ devices show transport features that can be fitted using a variable-range hopping model, which is typical of electrical transport through localized states in disordered low-dimensional systems. Here, the disorder can come from intrinsic defects, adsorbates or defects in the substrate. In the presence of a material with a high dielectric constant and top gate, the transport displays thermally activated behaviour with conductance proportional to $e^{-E_a/k_B T}$ (where E_a is the activation energy and k_B is the Boltzmann constant), which indicates the effective screening of charged impurities and results in a reduction of disorder.

Dielectric environment engineering promises an effective approach to mobility enhancement^{139,141}. However, it is important to understand the intrinsic electrical transport properties of 2D semiconductors in the absence of the dielectric layer, which can influence the charge impurity scattering or the remote optical phonon scattering. A promising avenue for the achievement of high mobilities consists in the elimination of external impurities, such as adsorbates from the atmosphere or impurities originating from the fabrication process. This can be done by in situ annealing in vacuum¹⁴², which enhances the conductivity of the MoS₂ channel, increases n-type doping levels and significantly reduces the contact resistance, resulting in low-temperature mobilities of $250 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and $375 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ in unencapsulated mono- and bilayer MoS₂, respectively. Combining this approach with the use of substrates with a high dielectric constant

results in the highest room-temperature mobility reported to date ($\sim 150 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for monolayer MoS_2 deposited on HfO_2)¹⁴³. Using polymer substrates with high optical phonon frequencies also resulted in improved mobility for MoSe_2 (REF. 144).

The encapsulation of MoS_2 in hexagonal boron nitride¹⁴⁵ (hBN; FIG. 5b), combined with the use of graphene as the contact between the metal and the MoS_2 layer¹⁴⁶, resulted in the highest low-temperature mobilities measured to date, owing to the reduced number of adsorbates and the low roughness of the hBN substrate. Magnetotransport measurements revealed low-temperature values of the Hall mobility reaching $34,000 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for six layers of MoS_2 and $1,000 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for monolayer MoS_2 (FIG. 5c). The values for the critical exponent y are in the range of 1.9-2.5, which is higher than that for HfO_2 (REF. 141). This could be attributed to the less efficient suppression of homopolar phonon modes by a relatively thin hBN film as compared to 30 nm of HfO_2 with metallic gates. Modelling of the various potential scattering sources suggests that long and short-range interfacial scattering are the limiting factors for the low-temperature impurity-dominated mobility¹⁴⁵. Because the impurity-dominated mobility increases with the layer thickness, it can be excluded that short-range intrinsic defects and bulk charged impurities have a role in determining its value. A similar improvement in the mobility as a result of encapsulation was reported for WS_2 (REFS 147-149).

These high mobility values enabled the observation of Shubnikov-de Haas (SdH) oscillations in the electrical conductivity at low temperatures and high magnetic fields. However, for the MoS_2 sample with graphene contacts encapsulated in hBN¹⁴⁵, the presence of high-mobility graphene implies that the SdH oscillations could contain contributions both from graphene and MoS_2 . The contribution of graphene to the SdH oscillations is suggested by the observation of plateau-like behaviour in the measured Hall resistance, which could be attributed to the onset of the quantum Hall states in graphene and by the discrepancy between the carrier densities estimated from Hall measurements and from SdH oscillations. Magnetoresistance measurements performed on p-type WSe_2 encapsulated in hBN¹⁵⁰ with metallic electrodes enabled the observation of SdH oscillations (FIG. 5d) and of the quantum Hall states in mono and bilayer WSe_2 . In this case, the absence of graphene excludes any contribution to the SdH oscillations other than that from the WSe_2 layers, and the carrier density extracted from the SdH oscillation frequencies agrees well with the Hall measurements assuming a twofold degeneracy of the Landau levels.

The reduction of extrinsic sources of scattering highly improves the low-temperature mobility. An avenue for further improvement would consist of implementing the strategies used for controlling the intrinsic limiting factors for the mobility, such as crystal defects. By combining methods that reduce intrinsic scattering with encapsulation techniques, which reduce extrinsic scattering, could lead to further improvements in both room- and low-temperature mobilities.

High-frequency operation. High mobilities are important for device operation based on quantum transport. However, reducing the channel length can result in improved transistor performance and operating frequency, reducing the importance of the mobility for devices with sub- 10 nm gate lengths. At such short length scales many 2D materials are expected to show ballistic transport. The main limiting factor for device performance in this case is direct tunnelling between the contacts, which can degrade the off-state currents and thus lower the on/off current ratio.

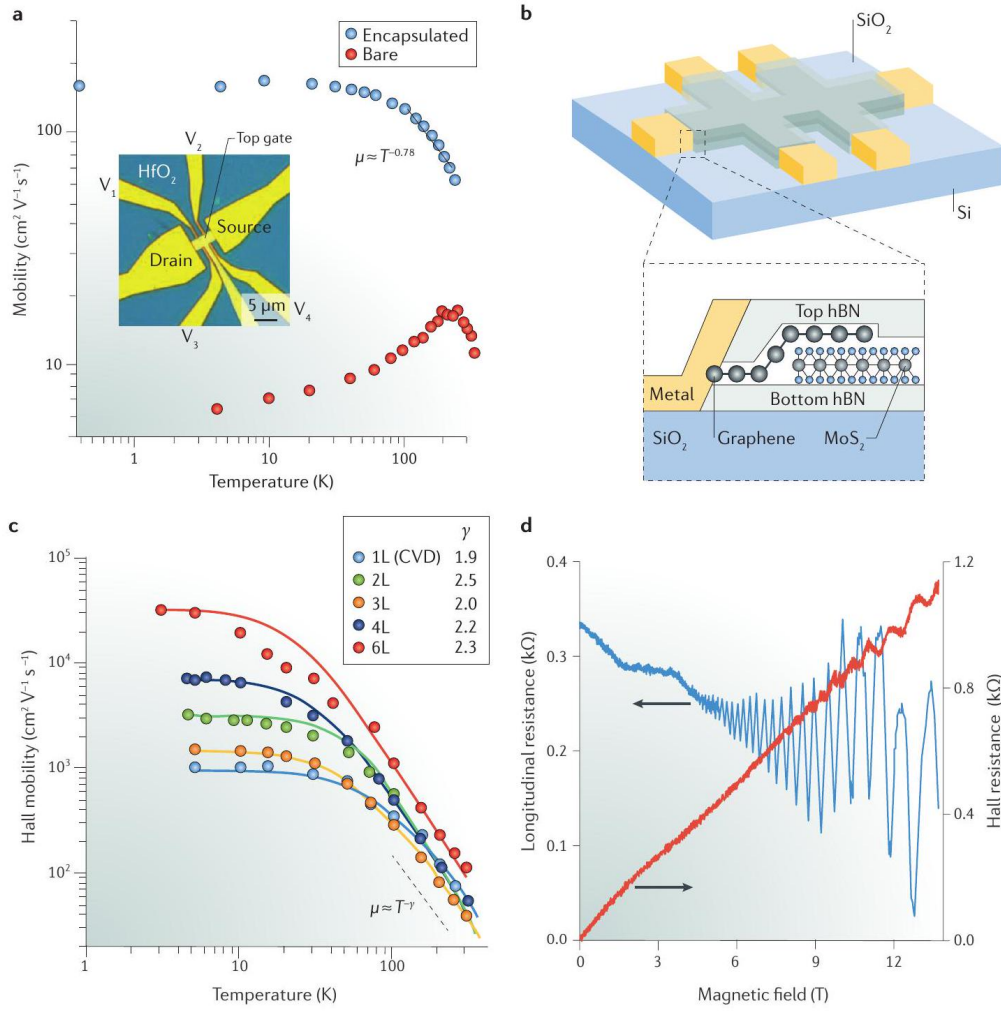


Figure 5 | Mobility in TMDC-based devices.

a | Temperature dependence of the mobility for a transistor based on monolayer MoS₂ with the exposed channel, and for the same transistor encapsulated in HfO₂ and with a top gate. This last device is shown in the inset.

b | Schematic depiction of a MoS₂ Hall bar device encapsulated in hexagonal boron nitride (hBN). The close-up view shows a cross section of the metal-graphene- MoS₂ contacts.

c | Temperature dependence of the Hall mobility, μ_h , for MoS₂ devices with various thicknesses encapsulated in hBN. The dashed line shows the power law $\mu_h \approx T^{-\gamma}$; the values of γ used for the fit for each device are shown. The low-temperature values of μ_h reach 34,000 cm² V⁻¹ s⁻¹ for 6 layers of MoS₂ and 1,020 cm² V⁻¹ s⁻¹ for monolayer MoS₂.

d | Shubnikov-de Haas oscillations in encapsulated monolayer WSe₂. The longitudinal (R_{xx}) and Hall (R_{xy}) resistances are measured as a function of the magnetic field at a temperature of 1.6 K and a hole density of 7.9×10^{12} cm⁻². Shubnikov-de Haas oscillations appear in R_{xx} starting at magnetic field ~ 4.5 T. The oscillations exhibit a density-to-frequency ratio of $2e/h$ (where e is the charge of the electron and h is the Planck constant), which is an indicator of twofold degenerate Landau levels. The Shubnikov-de Haas oscillations in R_{xx} are followed by the appearance of steps in R_{xy} , indicating the developing quantum Hall states. CVD, chemical vapour deposition; L , layer; n_{2D} , 2D carrier density; TMDC, transition metal dichalcogenide.

Panel **a** is adapted with permission from REF. 141, Macmillan Publishers Limited. Panels **b** and **c** are adapted with permission from REF. 145, Macmillan Publishers Limited. Panel **d** is adapted with permission from REF. 150, American Physical Society.

For devices based on graphene, owing to the high mobility and saturation velocity, the high-frequency performance exhibits low impedance, large transconductance ($g_m = dI_{ds}/dV_{gate}$) and high intrinsic cut-off frequency f_T (the frequency at which the current gain becomes unity). However, in addition to the current gain, which is relevant in demodulators for telecommunication, the power and voltage gain are important factors for high-frequency operation. For graphene, because of the absence of a bandgap, the maximum oscillation frequency f_{max} (the power gain cut-off frequency) is not as high as f_T . Also, the voltage gain ($A_v = g_m/g_{ds}$) is limited by the relatively high drain conductance g_{ds} , because the absence of a bandgap makes it difficult to achieve current saturation in graphene transistors ^{151,152}.

High-frequency 2D TMDC devices, owing to the presence of a sizable bandgap, are expected to exhibit voltage and power gain in addition to the current gain. Simulations of ballistic quantum transport predict that values of f_T above 100 GHz could be obtained in MoS₂ transistors with a channel length of 15 nm (REF. 153). Although still far from this number, the first radiofrequency MoS₂ devices ¹⁵⁴ integrated with coplanar waveguides showed operation in the gigahertz frequency range with a de-embedded cut-off frequency for current amplification (f_T) of 6 GHz, as well as a power gain cut-off (f_{max}) of 8.2 GHz and voltage amplification above 5 GHz, demonstrating the feasibility of realizing logic circuits based on TMDCs operating in the gigahertz range.

Reducing the channel length below 100 nm and improving the contacts by edge injection ¹⁵⁵ results in $f_T = 25\text{GHz}$, $f_{max} = 16\text{GHz}$ and voltage amplification up to 45 GHz. Further optimization of the contacts and device geometry could be achieved using self-aligned devices ¹⁵⁶. In addition, the promising radio-frequency behaviour of MoS₂ transistors enables the fabrication of electronic elements such as radio frequency amplifiers and digital inverters on rigid and flexible substrates ^{156,157}. Although the reported radio-frequency performance of flexible MoS₂ transistors ($f_T \approx 13.5\text{GHz}$, $f_{max} \approx 10.5\text{GHz}$) is comparable to that of flexible devices based on silicon nanomembranes ($f_T \approx 3.8\text{GHz}$, $f_{max} \approx 12\text{GHz}$)¹⁵⁸ and worse than that of flexible devices based on III-V semiconductors ($f_T \approx 105\text{GHz}$, $f_{max} \approx 22.9\text{GHz}$)¹⁵⁹, the realization of radio-frequency electronics on flexible substrates exploits the extraordinary mechanical properties of 2D materials, such as the high Young's modulus, high breaking strength and elastic behaviour. These properties make TMDCs an attractive alternative to commercial semiconductors for state-of-the-art flexible radio-frequency circuits. More detailed studies are needed to investigate the radio-frequency performance of flexible MoS₂ devices subject to deformation.

Strain engineering in TMDCs. The high strength of 2D TMDCs, which can endure strains of up to 10% before breaking ¹⁶⁰, makes them promising candidates for strain engineering, because it allows the application of strains high enough to induce considerable changes in the materials properties. Their three-fold symmetry is also advantageous, making it possible to vary the properties using lower strains as compared with those needed in graphene, which has six-fold symmetry ^{161,162}. Calculations suggest that tensile strain would reduce the bandgap of semiconducting TMDCs ^{163–165}, turning them into indirect semiconductors ^{163,164,166–172}, and that the bandgap would fully close at a level of biaxial tensile strain of $\sim 10\%$ ^{163,164}. In addition to the bandgap, strain is expected to modulate the charge carrier effective masses ^{166,173}, thermal conductivity ^{174,175}, dielectric properties ¹⁷³, spin-orbit coupling ^{176–178} and on-state currents in TMDC transistors ^{168,179,180}. Thus, strain engineering is a viable approach for the realization of various types of electronic, optoelectronic, electromechanical and spintronic devices with tunable characteristics ¹⁸¹.

Heterostructures formed by vertically stacking different TMDCs are also expected to be

strongly affected by strain^{182,183}, which could originate from the interlayer interactions and from lattice mismatch. As in the case of monolayers, strain could be used to modulate the bandgap of hybrid bilayers¹⁸³ and multilayers. Other theoretical studies investigated the effect of strain on anisotropic TMDCs¹⁸⁴, of which ReSe₂ and ReS₂ are the best known examples. Their distorted 1T phase structure gives rise to a strong dependence of the strain response on the direction in which the strain is applied. The carrier mobility might be significantly enhanced if strain is applied in the direction perpendicular to the layers.

A wide range of strategies was exploited for applying strain in nanomechanical devices incorporating 2D TMDCs. These include the use of: wet-etching¹⁸⁵ (FIG. 6a) or polymer sacrificial layers¹⁸⁶ for the fabrication of suspended devices; transfer on a substrate with pre-patterned holes or trenches¹⁸⁷; tailored nanopatterns¹⁸⁸; flexible^{189–191} or pre-stretched¹⁹² substrates (FIG. 6b); and thermal¹⁹³ or piezoelectric expansion¹⁹⁴. Optical techniques, such as photoluminescence spectroscopy^{188–191,194,195}, Raman spectroscopy^{189,191,194,196} and absorption spectroscopy¹⁹⁰, have been used to monitor the effect of strain on the optical bandgap and vibrational modes of 2D MoS₂ and other TMDCs^{197,198}. Photoluminescence measurements¹⁹⁰ confirmed theoretical predictions that strain could reduce the bandgap¹⁶³ and revealed a redshift of $\sim 70\text{meV}/\%$ strain for the direct gap transition and of $\sim 110\text{meV}/\%$ strain for the indirect gap transition in bilayer MoS₂. However, photoluminescence spectroscopy can only be used on mono and bilayer samples. Raman spectroscopy showed that the strain-induced symmetry breaking shifts the Raman modes in mono- and bilayer MoS₂, splitting the doubly degenerate in-plane vibrational modes¹⁸⁹.

Spatially inhomogeneous strain profiles, generated, for example, by depositing TMDCs on pre-patterned substrates¹⁸⁸, can create a spatially varying bandgap in an initially homogeneous material, and can result in the appearance of the funnel effect, in which optically excited electron-hole pairs drift to areas of the sample where the bandgap is lower before recombining (FIG. 6c). This effect can be exploited to produce light-emitting devices that can be locally configured using strain¹⁸⁸.

The strain-induced modulation of electrical transport can be attributed mainly to the piezotronic and piezoresistive effects, which originate from the piezoelectric effect and from the strain-induced bandgap tuning in TMDCs, respectively. 2H polymorphs of 2D TMDCs with an odd number of layers are piezoelectric because of broken inversion symmetry^{199,200}. Both the conversion of strain to voltage²⁰¹ and of voltage to strain (actuation)¹⁸⁶ have been reported for MoS₂. In this context, the piezotronic effect arises owing to piezoelectric polarization charges appearing at the sample edges, which increase or decrease the Schottky barrier height at the contact depending on the direction of the polarization field. Unlike the piezoelectric effect, the piezoresistive effect, which is due to the strain-induced modulation of the bandgap, appears both in odd and even-layered

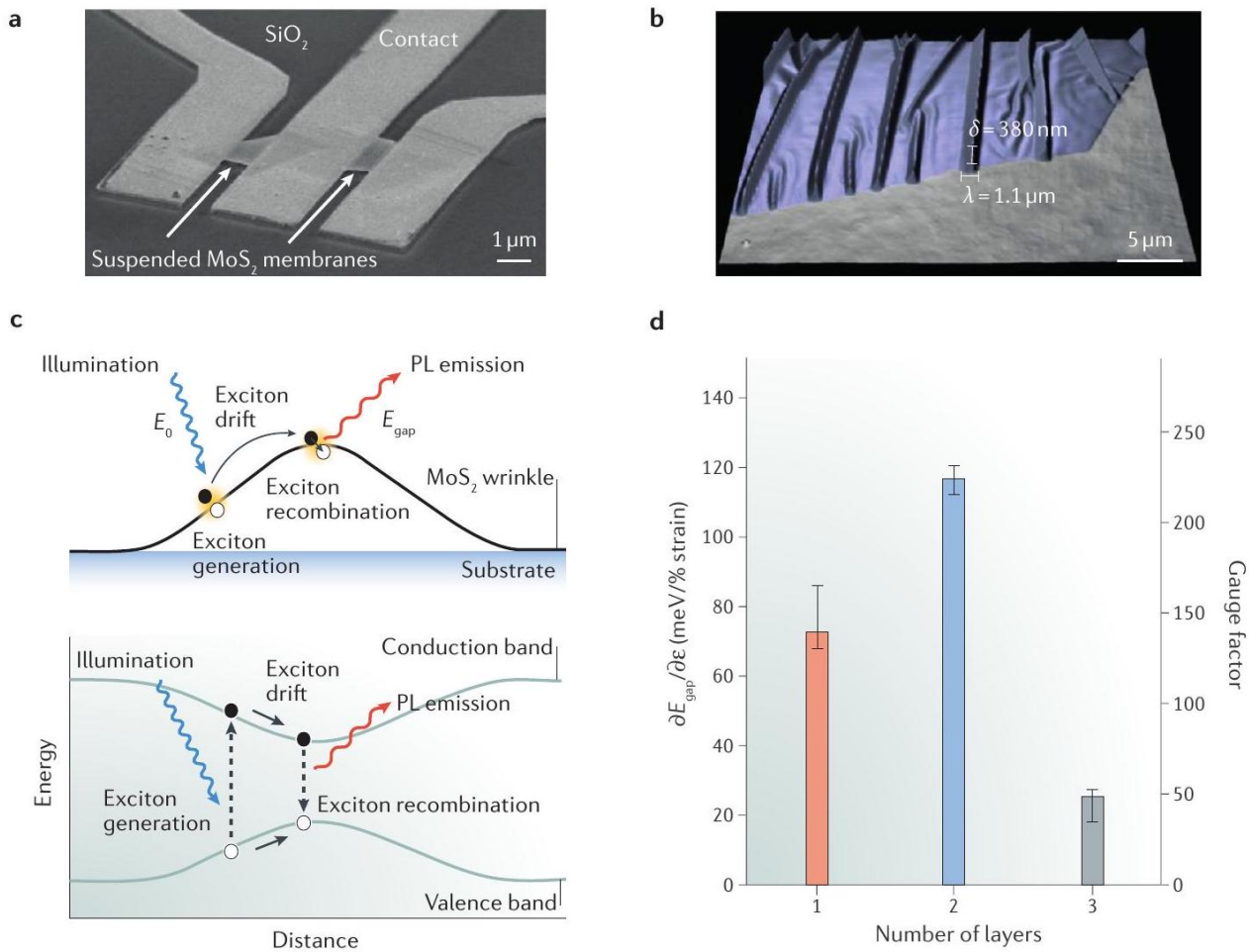


Figure 6 | Strain engineering in TMDC-based devices.

a | Scanning electron microscope image of a device with a suspended MoS_2 channel; electrical contact electrodes clamp the suspended membrane. The suspension is achieved by wet-etching the underlying oxide substrate and ensures the mechanical degree of freedom required for applying strain using a probe.

b | Three-dimensional rendering based on an atomic force microscope image of a wrinkled few-layer MoS_2 flake. An elastomeric substrate is stretched before the deposition of MoS_2 . The strain is then released, producing a buckling-induced delamination of the MoS_2 flakes, which results in a localized strain profile.

c | Schematic depiction of the funnel effect due to the localized strain profile in MoS_2 . Owing to the application of local strain (top panel), the bandgap of the material is locally modified (bottom panel), giving rise to the funnel effect: excitons drift hundreds of nanometres to recombine in the regions of the sample with a lower bandgap. This results in the formation of areas exhibiting strain-induced localized emission.

d | Strain-induced bandgap tuning and piezoresistivity due to mechanical deformation of the MoS_2 membrane for mono-, bi- and trilayer MoS_2 devices. The graph shows experimentally extracted values for the bandgap change rate and for the piezoresistive gauge factor. ϵ , strain; E_0 , energy of incoming photon; E_{gap} , bandgap energy; PL, photoluminescence; TMDC, transition metal dichalcogenide. Panels **a** and **d** are adapted with permission from REF. 185, American Chemical Society. Panels **b** and **c** are adapted with permission from REF. 192, American Chemical Society.

atomically thin TMDCs. Electromechanical experiments on locally strained, suspended MoS₂, in which electrical conductivity measurements are performed in parallel with mechanical deformation applied using an atomic force microscope, can quantify the piezoresistive effect. The resulting gauge factors (the ratio of the relative change in electrical resistance to the strain) are greater than 100 for mono- and bilayer MoS₂ (REF. 185) (FIG. 6d). The piezoresistive coefficients for mono- and bilayer MoS₂ are comparable to those of state-of-the-art silicon strain sensors²⁰² and two orders of magnitude higher than that of graphene^{203,204}. However, MoS₂ has a much higher fracture strain (as high as 11%)¹⁶⁰ than silicon (0.7%)²⁰⁵, thus it would be more suitable for flexible strain sensors for use on curved surfaces and highly deformable objects, such as biological tissue. The presence of both piezoresistive and piezoelectric effects in MoS₂ makes this material a promising candidate for ultralow power piezoelectric transduction logic devices^{206,207}. The exploitation of these effects has been demonstrated in MoS₂-based flexible photodetectors, in which the optical response could be modulated using piezophototronic effects²⁰⁸.

The combination of high breaking strain and favourable electrical and optical properties makes 2D TMDCs highly promising materials for the realization of large-area, high-performance flexible devices and circuits. Research on flexible 2D TMDC devices started in 2012 and has achieved performances superior to those of organic, amorphous and metal oxide thin-film transistors. Learning from the experience with graphene, the top-gate device structure was avoided for flexible TMDC transistors^{209–211}, preventing the reduced yield and weaker performance caused by complications related to the fabrication of the gate stack on flexible substrates²¹². Instead, for TMDC thin-film transistors, the gate structures and channel regions were fabricated separately and transferred together later²¹³, or embedded gate structures^{210,211} and ionic gel gating^{209,214} were used. It is also important to note that the concept of flexible devices extends to stretchability in addition to bendability, making TMDCs particularly suitable for these applications. Stretching flexible TMDC transistors would allow piezoresistive strain sensing^{215,216}. Recently, TMDC-based integrated circuits on flexible substrates were also realized²¹⁷.

3.0.5 Conclusions

We have summarized some of the recent key results on the electronic properties of 2D TMDCs, and in particular of MoS₂, which is the most studied TMDC material because of its robustness and the high availability of the raw material.

Owing to their wide range of electrical properties, the atomic-scale thickness of their single layers and the possibility of obtaining a direct bandgap in semiconductor TMDCs, these materials display a rich physics and hold promise for a wide range of applications in low-power electronics, flexible electronics, optoelectronics, straintronics or spintronics.

Furthermore, TMDCs show promise for biophysics applications, such as DNA sequencing and personalized medicine, because nanopores based on atomically thin membranes of TMDCs were shown to provide a rapid, high-resolution method for DNA sequencing.

Although the atomic thickness of TMDC-based nanopores enables the necessary spatial resolution for nanopore DNA sequencing, the fast translocation speeds of DNA across such ultrathin membranes limits the detectability of single nucleotides.

This issue has been addressed by using ionic liquids to create a viscosity gradient that can control the DNA translocation across MoS₂ nanopores^{218,219}.

The rapid progress of the field of TMDCs is reflected in the large number of scientists working on these materials and in the fast rise in the number of publications. However, the field is in many ways still in its early stage, with a large number of TMDC materials that

have not been seriously studied or even synthesized yet and which promise many more exciting discoveries.

4 On the origin of charge-density waves in select layered transition-metal dichalcogenides by Rossnagel

(select= like selected, but not the ones which we selected, but ones that are a subset, it it nearly the same word)

Abstract

The occurrence of charge-density waves in three selected layered transition-metal dichalcogenides (1T-TaS₂, 2H-TaSe₂ and 1T-TiSe₂) is discussed from an experimentalist's point of view (it has many theoretical discussions, actually) with a particular focus on the implications of recent angle-resolved photoelectron spectroscopy results.

The basic models behind charge-density-wave formation (= the mess of some theoretical ideas is presented) in low-dimensional solids are recapitulated, the experimental and theoretical results for the three selected compounds are reviewed, and their band structures and spectral weight distributions in the commensurate charge-density-wave phases are calculated using an empirical tight-binding model (finally, how exactly it is done???) .

It is explored whether the origin of charge-density waves in the layered transition-metal dichalcogenides can be understood in a unified way on the basis of a few measured and calculated parameters characterizing the interacting electron-lattice system. (abstract sentence, nothing is useful in it, we already know that they try to describe the CWD)

It is found that the predictions of the standard mean-field model agree only semi-quantitatively (how is it, semi-quantitatively??) with the experimental data and that there is not one generally dominant factor (which dominant factors???) driving charge-density-wave formation in this family of layer compounds.

The need for further experimental and theoretical scrutiny (what exactly should be measured and researched??) is emphasized.

4.1 Article

4.1.1 6. Summary and conclusions

Our goal has been to understand the formation of CDW/PLDs in the layered transition-metal dichalcogenides quantitatively and comprehensively. (It wasn't achieved)

We first recapitulated the 1D weak-coupling mean-field theory (this is that main model in ch.2, a question why is it called so is already in that section) on which much of our understanding is based and, with particular relevance for the layer compounds, restated that our understanding is poor for 2D, anisotropic systems in the strong-coupling regime (this article reviews that they don't understand much) .

In our analysis of real CDW/PLD materials, we then focused on the three prominent layer compounds: 1T-TaS₂, 2H-TaSe₂ and 1TTiSe₂.

We briefly reviewed the large body of experimental and theoretical work on these materials, concentrating on the key signatures of a CDW/PLD: the lattice distortion, the energy gap and the Kohn anomaly.

An important conclusion was that the CDW/PLDs observed in the layer compounds are genuinely intermediate coupling to strong coupling in nature (why intermediate coupling to strong coupling???? where is the value of coupling in this theory?) .

To resolve uncertainties regarding the magnitude and location of the CDW energy gap (location in the energy band) , we turned to ARPES, which has recently provided an accurate

and virtually complete picture of the band structures near the Fermi level, both in the normal phases and in the CDW/PLD phases. (how? read the article)

We demonstrated that a simple empirical tight-binding model (how does it look like??? formula) captures the essential aspects of the ARPES spectral weight redistribution and of the underlying band structure changes.

We corroborated (=provide new evidence) that, contrary to the simple Peierls model, the electron band energy lowering that stabilizes (how is it, stabilizes in terms of formulas?) the CDW/PLD does not result from the opening of a uniform gap at the Fermi vector, but from subband splittings and shifts over extended parts of the Brillouin zone. (electron band lowering originates from subband splittings and shifts ????? read about it in the article)

Finally, we set out to explain CDW/PLD formation in the three selected layer compounds in a unified way(unified way?? or course, we should have the same theory for all the materials, but how it can be done in another way, with purely different theories? I think, it is always "by unified way") on the basis of the simple (knowingly deficient) weak-coupling and strong-coupling mean-field models. (why the MF models are very deficient???)

Not unexpectedly, the agreement with the experimental data was, at best, semi-quantitative. (how exactly they agree?)

It turned out that simple considerations based on the geometries of Fermi surfaces or local chemical bonds may serve as qualitative explanations only. (and which exactly predictions considerations based on the geometries of Fermi surfaces give??)

Moreover, a generally dominant factor driving CDW/PLD formation could not be identified (maybe because there are just different factors and this is all? there shouldn't be a dominant one) , although strong electron-phonon coupling and an appropriate density of states near the Fermi level are certainly important. (which factors give the electron-phonon coupling and density of states near the Fermi level??)

The major conclusion, then, is that the simple, commonly applied theoretical framework, which specifically assumes k -independent interactions (k -independent electron-phonon coupling) (why is it so important?) , fails to describe the situation adequately. (what exactly we can't describe???)

At this point, a significant advance in our understanding of CDW/PLD formation in quasi-2D seems to require greater theoretical and experimental scrutiny. (have some answers appeared after this publication?)

Theory should deliver accurate band structure calculations, providing 3D Fermi surfaces and the $\mathbf{k}$ -dependent electron-phonon coupling. (why Fermi surfaces and $\mathbf{k}$ -dependent coupling? Can't we just calculate measurable quantities and this is all?)

Also, an accurate treatment of electron-electron and electron-hole interactions is needed. (does it play role?)

On the other hand, experiment, ARPES in particular, is expected to provide the reality check: accurate and complete band structure data from which accurate experimental maps of the electronic susceptibility can be obtained [85]. (wasn't it done? I thought, it was done already)

It is also foreseen that femtosecond timeresolved ARPES will help to disentangle the relative roles of the various involved interactions in the time domain [14]. (why? read about femtosecond timeresolved ARPES. they say that theory for it is a very important theory, right?)

In our view, there is reason to believe that it is only difficult and not impossible to understand CDW/PLD formation in the layered transition-metal dichalcogenides quantitatively and comprehensively.

4.1.2 1. Introduction

(SUMMARY: there is such CDW, but there are a lot of open questions)

Charge-density waves (CDWs) in low-dimensional solids are a rather old [1-8] but still vital and alluring [9-17] research topic.

It is now some 35 years since CDWs in the transition-metal dichalcogenides were discovered (who and when discovered it?) and since this class of layered crystals consisting of three-atom-thick chalcogen-transition metal-chalcogen sandwiches initiated the popularization of the concept of a CDW [18] (=people started studying CDW in TMDCs) .

Yet, although much has been learnt about the structural and electronic properties of 'the layer compounds' and about the nature of their various CDW phases [18-24], we are still far from understanding how and why the CDWs in these quasi-twodimensional systems are formed. (again they say that they don't know some important answers)

Some important aspects of the CDW phase transition in these materials are captured qualitatively by models coming under different names (=different models) : Peierls instability, giant Kohn anomaly, Fermi surface nesting, band Jahn-Teller effect (I don't think that there is something called "band Jahn-Teller effect") or excitonic insulator.

But a coherent and realistic microscopic theory has not yet emerged (see, however, [23] (strange citation, maybe I'll look, it is not written why we need it, I just believe that not yet emerged and this is all)) meaning that truly quantitative predictions of CDW properties are practically impossible.

This is all the more frustrating given that the 'standard model' of CDW formation (one-dimensional weak-coupling mean-field theory) provides a good quantitative explanation for the occurrence of CDWs in quasi-one-dimensional solids [25](check this comparison with experiment!) and also seems to work well for other quasi-two-dimensional systems such as the layered rare earth tritellurides [26,27] (check how it works for that materials) .

To make further progress at this point, we believe that the current situation regarding CDWs in transitionmetal dichalcogenides, which encompasses a large body of experimental and theoretical results from the pre-cuprate era(pre-cuprate era??) as well as recent high-resolution angle-resolved photoelectron spectroscopy (ARPES) results, must be looked at in greater detail and taken into account more seriously before one fills the gaps in understanding by suggesting novel, exotic CDW mechanisms. (= we should think again and more about this theory)

In this spirit, we will strictly concentrate here on the possible origin of three distinctive CDWs (which three distinctive CDWs? CCDW, NCDW and ?) in three prominent members of the transition-metal dichalcogenide family, i.e. 1T-TaS₂, 2H-TaSe₂ and 1T-TiSe₂.

Phenomena that go beyond the primary formation of the CDW, such as the dynamics of CDWs [28] (dynamics of CDWs?) or the competition between CDWs and superconductivity [29] (CDWs and superconductivity???) , will not be discussed.

Also, the many other CDW materials with one-dimensional (1D) [25], two-dimensional (2D) [30] and three-dimensional (3D) [31, 32] band structures will not be dealt with. (read them in scope of increase of general education in CDW)

For the three selected transition-metal compounds, we will specifically focus on the interpretation of the most recent, very detailed ARPES results in terms of an empirical tight-binding model (=describe ARPES results with TB model) and on the resulting implications for the microscopic mechanism underlying CDW formation (which implications for the microscopic mechanism ??? I thought we just extract parameters from the TB model) .

The working hypothesis will be that the origin of all three CDWs can be understood at least semi-quantitatively within a mean-field model, on the basis of a few measured and calculated

parameters such as the transition temperature, the wave-vector and amplitude of the CDW, the non-interacting electronic susceptibility, bare phonon frequencies, an electron-phonon coupling constant or the total band energy lowering in the CDW phase. (where do these parameters enter the model???)

The approach is that of an experimentalist (no, it is just a review, which does not include theoretical parts, it is not of an experimentalist) and, if not providing a detailed microscopic explanation, it is at least expected to reveal the weak points in our understanding of CDW formation in the layered transitionmetal dichalcogenides (and which are the weak points in our understanding?) .

(this is just a overview what will be next, nothing is informative here) The outline of the present work is as follows. In section 2 we provide the theoretical background by summarizing the basic ideas and concepts behind CDW formation in low-dimensional systems. This is done with a narrow focus on the models that are commonly used to explain the origin of the CDWs in the layered transition-metal dichalcogenides. In section 3 we briefly review the extensive experimental and theoretical results obtained for the three selected CDW compounds, before in section 4 we seek to explain the results of recent ARPES measurements by calculating the band structures and spectral weight distributions in the CDW phases using an empirical tight-binding model. Finally, in section 5, we weave the strands together (=combine all the previous evidence into one coherent conclusion) and attempt - on the basis of a few relevant parameters extracted from experiment and theory - to answer the fundamental question at the center of this work: why do CDWs occur in the layered transitionmetal dichalcogenides?

(finally, how did they attempt to answer why CDW is in the TMDCs??? maybe because of strong EP coupling and polarons, maybe this is what is needed?)

4.1.3 2. Theoretical aspects of CDW formation

Introduction to a framework of CDW

Consider a 1D metal made of a linear chain of atoms with a regular spacing a and suppose that the electron density is cosinusoidally modulated:

$$\rho(\mathbf{r}) = \rho_0(\mathbf{r}) [1 + \rho_1 \cos(\mathbf{q}_0 \mathbf{r} + \phi)] \quad (1)$$

(ρ_0 is actually not a constant, what does it equal to??? are there some particular examples?)

where $\rho_0(\mathbf{r})$ describes the unperturbed electron density, and ρ_1 , (ρ_1 should be dimensionless) $\mathbf{q}_0$ and ϕ are the amplitude, wave-vector and phase of the electron density modulation, respectively.

The last term in the square bracket is called the CDW. (this is not a standard def. I suppose, the idea is that modulation of charge is a typical example of CDW)

This standing wave has a wavelength $\lambda_0 = 2\pi/|\mathbf{q}_0|$ and it causes each ion in the chain to see a different potential so that the ions move to new equilibrium positions. (CDW influences PLD)

The resulting periodic lattice distortion (PLD) has the form

$$u_n = u_0 \sin(n|\mathbf{q}_0|a + \phi) \quad (2)$$

(why isn't it in the form of (1)??? now we have the n and sin, not cosine)

where the integer n defines the position of the ions and the amplitude u_0 is generally small compared to the lattice constant a .

Now suppose that first the ions are periodically displaced according to equation (2).

Then, the conduction electrons will try to screen the new potential (revise Kittel, learn which formula is assumed here?) and an electron density modulation of the type given in equation (1) will be created.

Thus, a CDW and a PLD always come together [6, 13] (check these papers, derive the CDW from PLD and PLD from CDW. Currently, I just believe this) (see figure 1(a)) and we will speak of a CDW/PLD throughout the paper.

A number of questions arise from this simple consideration.

(i) Although a CDW and a PLD occur simultaneously, one may ask the (philosophical) chicken and egg question: which one is the driving force? (isn't as discussed above it a useless question since anyway the second effect immediately follows from the first?)

In other words, is the CDW/PLD transition primarily an instability of the electron system or of the lattice?

(ii) The formation of a CDW/PLD clearly costs Coulomb and elastic energy (how is it, costs Coulomb and elastic energy? energy of the closed system should be conserved) .

But what are the stabilizing factors? (have we discussed ever stability? electron band energy lowering stabilizes it according to introduction, but what does it mean?)

What is the microscopic origin of a CDW/PLD? (electron phonon coupling, see Levitov Sitov)

(iii) A CDW/PLD will certainly modify the electron and phonon dispersions.

So what are the signatures of the CDW/PLD phase in both the electron (appearance of the gap) and phonon (what at all influences phonon spectra and how? polarons, scatterings maybe influence, but how?? revise these effects) spectra?

(iv) For CDWs in one dimension and in the weak-coupling limit ($u_0/a \ll 1$) a theoretical framework is available.

But can the 1 D models simply be generalized to 2D? (FSN mechanism is proposed for this generalization)

And what happens, if the coupling strength increases?

In this section some answers shall be given to these questions. (what are the answers in a nutshell?)

2.1. Peierls instability

(SUMMARY: ????)

(!!!!!!! work out Pereles effect from the note on cond matter!!!!)

(by the way, seems that for all the quasi 1D materials there should be the Peierls instability. is it the case??? why exactly we need strong EP interaction and what is the atomic origin of it???? write it in the note on electrons and phonons)

The Peierls instability of quasi-1D metals towards CDW/PLD formation is a consequence of strong electron-phonon interaction. (see theoretical formulas which prove this)

The principal idea behind the Peierls model is this [1 – 3, 6, 25, 33]:

a CDW/PLD of the type given by equations (1) and (2) sets up a potential which opens an energy gap at the Fermi surface (see figure 1(b)), thereby lowering the energy of occupied electron states and raising the energy of empty states, and since the resulting net one-electron band energy gain overcompensates the Coulomb and elastic energy cost (we calculate the change of energy, this is how we check for stability) , the CDW/PLD is self-sustaining (self-sustaining???)

Note that we use the term 'Peierls instability' here to describe the (here are just synonyms) instability of a coupled electron-lattice system, an instability which is, in essence, a structural phase transition driven by strong electron-phonon coupling.

Thus, in contrast to other definitions [13] (and what is another definition? I don't see a big difference), in this work a Peierls instability is not seen as a purely electronic phenomenon in which the lattice distortion is only an accidental by-product (see also section 2.4).

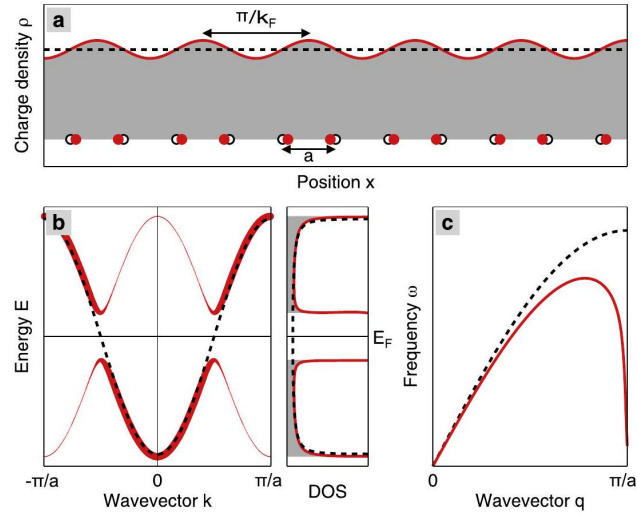


Figure 1. (here, there is a typical clear theory) Peierls instability of a 1D metal with a half-filled band.

(a) Schematic view of a CDW/PLD showing the modulations of the conduction electron density (solid red line) and ion positions (filled red circles).

The normal state is characterized by a constant charge-density (dashed black line) and an undistorted chain (open black circles).

(b) Electronic band dispersion and density of states in the metallic state above the transition temperature T_0 (dashed black lines) and in the CDW state at $T = 0$ (solid red lines).

The thickness of the red lines in the band structure plot is proportional to the spectral weight carried by the electron states in the CDW phase. (why is it so? that it is bigger in the inner part? never heard of it)

(c) Acoustic phonon dispersion well above T_0 (dashed black line) and at T_0 (solid red line). (that Khon anomaly)

The Peierls transition to a CDW/PLD ground state can be described quantitatively by a mean-field theory (what is exactly meant here by "mean-field theory"??? what is beyond this approximation?) of a 1D electron-lattice system in the weak-coupling limit (see, for example, [6, 19, 25, 34]).

The simplest approach further implies the independent electron, harmonic and adiabatic approximations. (there is no sense in thinking about what is written here? to understand description of this theory one needs anyway to read the cited literature)

The coupled electron-lattice system is then modeled by a Fröhlich Hamiltonian of the form (this is what author thinks about MFT) (the derivation of it is a big another story for the note on cond matter)

$$H_{\text{PI}} = \sum_{\mathbf{k}} \epsilon_{\mathbf{k}} a_{\mathbf{k}}^{\dagger} a_{\mathbf{k}} + \sum_{\mathbf{q}} \hbar \omega_{\mathbf{q}} b_{\mathbf{q}}^{\dagger} b_{\mathbf{q}} + \frac{1}{\sqrt{N}} \sum_{\mathbf{k}, \mathbf{q}} g_{\mathbf{q}} a_{\mathbf{k}+\mathbf{q}}^{\dagger} a_{\mathbf{k}} (b_{-\mathbf{q}}^{\dagger} + b_{\mathbf{q}}) \quad (3)$$

(why $\frac{1}{\sqrt{N}}$? check, Al. and Mott's book has something similar, or ask GPT) ($N = ?$)

((????!!!! why do we have a bold vectors in 1D model)???? (then we are told that for 2D there is another formula) maybe no one cares about this notation, but still, we should think about 1d vectors here, maybe)

where $\epsilon_{\mathbf{k}}$ refers to the energy of electron state $\mathbf{k}$ (it is calculated from 0, not from E_F) , $a_{\mathbf{k}}^+$ and $a_{\mathbf{k}}$ are the creation and annihilation operators for state $\mathbf{k}$, $\omega_{\mathbf{q}}$ is the frequency of the phonon normal mode $\mathbf{q}$, $b_{\mathbf{q}}^+$ and $b_{\mathbf{q}}$ are the creation and annihilation operators for phonon $\mathbf{q}$, $g_{\mathbf{q}}$ is an electron-phonon coupling constant (assumed to be independent of $\mathbf{k}$ (why independent on $\mathbf{k}$, and dependent on $\mathbf{q}$)) and N is the number of lattice sites per unit length.

(why not optical phonons, only acoustical??? some another paper might explain it)

((3) are we dealing with real or virtual phonons? standing waves, are they phonons at all? because nothing propagates)

In this model, a static displacement $u_{\mathbf{q}}$ of phonon mode $\mathbf{q}$ sets up a potential

$$v_{\mathbf{q}} = g_{\mathbf{q}} u_{\mathbf{q}} \sqrt{\frac{2M\omega_{\mathbf{q}}}{\hbar}}, \quad (4)$$

where M is the ionic mass. (why the formula is such???)

((4) M is the mass of Ta or S2? (for 1D TaS2) (maybe Ta+S+S))

The associated lattice strain energy is given by

$$\delta E_{\text{lattice}} = \frac{1}{2} M \omega_{\mathbf{q}}^2 u_{\mathbf{q}}^2 \quad (5)$$

(why energy of a atom is a sum over all the squares of harmonics??? it we assumed that there is only one frequency, then there would be no sum in the (3) formula. if there were a lot of frequencies, we would need first sum over their displacements and then only this formula for the oscillator. right? check it, think more about it)

and the total band energy change of the electron system due to the potential $v_{\mathbf{q}}$ is (within second-order perturbation theory)

$$\delta E_{\text{band}} = -|v_{\mathbf{q}}|^2 \chi_0(\mathbf{q}), \quad (6)$$

where $\chi_0(\mathbf{q})$ is the non-interacting electronic susceptibility defined as

$$\chi_0(\mathbf{q}) = \frac{1}{L} \sum_{\mathbf{k}} \frac{f_{\mathbf{k}+\mathbf{q}} - f_{\mathbf{k}}}{\epsilon_{\mathbf{k}} - \epsilon_{\mathbf{k}+\mathbf{q}}} > 0 \quad (7)$$

(how to derive it??!!!! I forgot, I'll learn later, it is important for a background!!!)

In this definition, $f_{\mathbf{k}}$ represents the Fermi function $f(\epsilon_{\mathbf{k}})$ and the matrix element (which matrix element???) that couples the states $\mathbf{k}$ and $\mathbf{k} + \mathbf{q}$ is, as is usually done, neglected; L is the length of the atomic chain.

From equation (6) one sees that $\chi_0(\mathbf{q})$ is a direct measure of the distortion-induced band energy gain (why gain?) .

The new CDW/PLD ground state will be stable, if $\delta E_{\text{band}} + \delta E_{\text{lattice}} < 0$ for a certain phonon mode $\mathbf{q}_0$. (what about conservation of energy in the system?)

Using equations (4)-(6), we obtain a simple instability condition for the normal state, based on microscopic parameters: (check it later, but I am assured that it is true)

$$\frac{4g_{\mathbf{q}}^2}{\hbar\omega_{\mathbf{q}}} > \frac{1}{\chi_0(\mathbf{q})} \quad (8)$$

Apparently, for a CDW/PLD to occur, a large electron-phonon coupling constant $g_{\mathbf{q}}$ and a large electronic susceptibility $\chi_0(\mathbf{q})$ are required at the (some) wave-vector $\mathbf{q} = \mathbf{q}_0$. (only one wave-vector should be enough)

(THERE IS A DISCUSSION OF THIS FORMULA WITH Q IN THE SECTION OF DISCUSSION, LOOK THERE, IT IS NOT A LITTLE TOPIC, TO UNDERSTAND WHAT IS MEANT THERE)

By including the effects of Coulomb and exchange interactions, Chan and Heine derived a similar criterion for PLD/CDW formation [6]: (read their paper, idk how to derive it?)

$$\frac{4g_{\mathbf{q}}^2}{\hbar\omega_{\mathbf{q}}} - 2U_{\mathbf{q}} + V_{\mathbf{q}} \geq \frac{1}{\chi_0(\mathbf{q})} \quad (9)$$

with the necessary hierarchy of terms:

$$\frac{4g_{\mathbf{q}}^2}{\hbar\omega_{\mathbf{q}}} > 2U_{\mathbf{q}} > V_{\mathbf{q}} > 0 \quad (10)$$

Here $U_{\mathbf{q}}$ stands for the Coulomb interaction and $V_{\mathbf{q}}$ is the screened exchange interaction. (screened exchange interaction???)

(For $4g_{\mathbf{q}}^2/\hbar\omega_{\mathbf{q}} < 2U_{\mathbf{q}}$, a spin-density wave (SDW) will set in [6].) (why? anyway it is not relevant)

A severe simplification implied in condition (9) ($\frac{4g_{\mathbf{q}}^2}{\hbar\omega_{\mathbf{q}}} - 2U_{\mathbf{q}} + V_{\mathbf{q}} \geq \frac{1}{\chi_0(\mathbf{q})}$) is that not only $g_{\mathbf{q}}$ but also $U_{\mathbf{q}}$ and $V_{\mathbf{q}}$ are assumed to be independent of $\mathbf{k}$. (what is the meaning of such independence?)

Nevertheless, the criterion (9) ($\frac{4g_{\mathbf{q}}^2}{\hbar\omega_{\mathbf{q}}} - 2U_{\mathbf{q}} + V_{\mathbf{q}} \geq \frac{1}{\chi_0(\mathbf{q})}$) reveals the important factors and it also confirms intuition: CDW/PLD formation is generally encouraged by strong electron-phonon and electron-electron exchange interaction (large $g_{\mathbf{q}}$ and $V_{\mathbf{q}}$), by a weak Coulomb interaction and a small lattice strain energy (small $U_{\mathbf{q}}$ and $\omega_{\mathbf{q}}$) (why lattice strain energy should be small???) (why Coulomb interaction should be weaker???) , and by a large non-interacting susceptibility (large $\chi_0(\mathbf{q})$) (what causes χ to be large?) .

Beside its intuitive appeal, the instability condition (9) ($\frac{4g_{\mathbf{q}}^2}{\hbar\omega_{\mathbf{q}}} - 2U_{\mathbf{q}} + V_{\mathbf{q}} \geq \frac{1}{\chi_0(\mathbf{q})}$) is also sufficiently practicable and quantitative to make contact with experimental data. (and how one can use (9) ($\frac{4g_{\mathbf{q}}^2}{\hbar\omega_{\mathbf{q}}} - 2U_{\mathbf{q}} + V_{\mathbf{q}} \geq \frac{1}{\chi_0(\mathbf{q})}$) in an experiment???)

Since the CDW/PLD ground state generally occurs in systems with strong electron-phonon interactions (and what is the reason for strong EP interaction???) (actually, I think it might be a wrong statement. we don't know if there is a strong EP interaction or no unless we do an experiment. so here they say "CDW occurs in sustems where it occurs", this is not a valuable statement) , it can be expected that both the electron and the phonon dispersions are significantly modified upon CDW/PLD formation.

In the following, we consider the archetypal (=the most typical) situation of a 1D solid with a single half-filled band.

We assume a tight-binding band dispersion

$$\epsilon_{\mathbf{k}} = -E_F \cos(ka) \quad (11)$$

with Fermi energy E_F and Fermi vector $|\mathbf{k}_F| = \pi/2a$ [34, 35]. (reminder: revise the derivation)

Electron-electron interactions are again neglected ($U_{\mathbf{q}} = V_{\mathbf{q}} = 0$). (when can we neglect them?)

For this band, when $E_F/k_B T$ is large, the non-interacting susceptibility at $\mathbf{q} = 2\mathbf{k}_F$ diverges with falling temperature T as (derive it! should we just plug something in the formula above?)

$$\chi_0(2\mathbf{k}_F, T) = \frac{1}{2}N(0) \ln \left(\frac{2.28E_F}{k_B T} \right) \quad (12)$$

where $N(0)$ is the density of electron states at the Fermi energy E_F (which we assume is the constant on the Fermi surface) (why is $N(0)$ a constant at all?? Fermi surface can have a very different shape) (in the normal phase, per atom and including both spin directions).

The sharp temperature-dependent peaking of $\chi_0(\mathbf{q}, T)$ causes a strong renormalization of the phonon frequencies in a narrow wave-vector range around $\mathbf{q}_0 = 2\mathbf{k}_F$.

This is generally referred to as a giant (word "giant" is not important) Kohn anomaly: (derive it!!!! why g is here????)

$$\tilde{\omega}_{\mathbf{q}}^2 = \omega_{\mathbf{q}}^2 \left(1 - \frac{4g_{\mathbf{q}}^2}{\hbar\omega_{\mathbf{q}}} \chi_0(\mathbf{q}) \right), \quad (13)$$

where $\tilde{\omega}_{\mathbf{q}}$ and $\omega_{\mathbf{q}}$ denote the renormalized and normal-state phonon frequency, respectively [6]. (revise this theory)

(What is the connection btw $\omega=0$ and the new state at all????)

For a non-zero electron-phonon coupling constant $g_{\mathbf{q}_0}$, we have

$$\tilde{\omega}_{\mathbf{q}_0}^2 = 0 \quad (14)$$

at a finite temperature T_0 . This complete softening of phonon mode $\mathbf{q}_0$ at T_0 (see figure 1(c)) signals a phase transition to a state with a frozen-in lattice distortion, i.e. a CDW/PLD with a wavelength $\lambda_0 = 2\pi/|\mathbf{q}_0| = \pi/|\mathbf{k}_F|$.

Since $\mathbf{k}_F$ is determined by the electron filling of the band structure in $\mathbf{k}$ space, a CDW/PLD superstructure in general will be incommensurate (=out of proportion, not matching in size or degree) with the underlying crystal lattice, as opposed to the simple commensurate scenario we discuss here. (this is why we call it superlattice)

Note that equations (13) and (14) lead to the simple instability criterion (8). (but what is the meaning of the $\tilde{\omega}_{\mathbf{q}_0}$ to turn to 0?)

With equations (12)-(14), the (mean-field) transition temperature in the tight-binding approximation becomes (how to calculate it?? should we calculate the χ ?)

$$k_B T_0 = 2.28 E_F \exp \left(-\frac{1}{\lambda} \right) \quad (15)$$

with the dimensionless electron-phonon coupling constant

$$\lambda = \frac{2g_{\mathbf{q}_0}^2 N(0)}{\hbar\omega_{\mathbf{q}_0}} \quad (16)$$

(check this formula in literature about electrons and phonons)

As for the electron bands, an important point to note is that the Brillouin zone edges of the CDW/PLD superstructure characterized by $\mathbf{q}_0$ coincide exactly with the Fermi points $\pm\mathbf{k}_F$. (is it always so for 1D materials?) (!!! think about this statement more. I thought that Fermi points are not where there the BZ is...)

Thus, since the new Brillouin zone edges entail (=involve, require) energy discontinuities, the normal-state energy band $\epsilon_{\mathbf{k}}$ splits into two branches:

$$E_{1,2}(\mathbf{k}) = \frac{\epsilon_{\mathbf{k}} + \epsilon_{\mathbf{k}+\mathbf{q}_0}}{2} \pm \sqrt{\left(\frac{\epsilon_{\mathbf{k}} - \epsilon_{\mathbf{k}+\mathbf{q}_0}}{2}\right)^2 + \Delta^2} \quad (17)$$

(!!! derive this formula)

separated by an energy gap 2Δ (why 2Δ not Δ ??) at $\mathbf{q}_0/2 = \mathbf{k}_F$.

(how this formula coincides with the plot?? I don't now imagine a plot for this formula. read literature)

The lower branch is completely occupied, while the upper branch is completely empty.

The density of states $N(E)$ diverges at $E = \pm\Delta$ (derive that it diverges) and is zero in between (see figure 1(b)), i.e. a uniform and complete (complete?) energy gap opens up at E_F .

In the model developed so far, the energy gap 2Δ is related to the displacement amplitude $u_{\mathbf{q}_0}$, the electron-phonon coupling parameter $g_{\mathbf{q}_0}$ and the unrenormalized phonon frequency $\omega_{\mathbf{q}_0}$ by [25] (derive!) (lol, in classical limit $\hbar \rightarrow 0$ we'll have a problem. what to do about it???)

$$\Delta = u_{\mathbf{q}_0} g_{\mathbf{q}_0} \sqrt{\frac{2M\omega_{\mathbf{q}_0}}{\hbar}} \quad (18)$$

(why there is not a renormalized ω , but a bare one?)

If the modified band dispersion is to be measured by ARPES, a difficulty arises from the fact that the electron states carry a $\mathbf{k}$ -dependent spectral weight. ($\mathbf{k}$ -dependent spectral weight??)

The spectral weight distribution, which for a slowly varying ARPES matrix element is approximately proportional to the measured ARPES intensity distribution (ARPES matrix element???? ARPES matrix element proportional to ARPES intensity distribution????) , is generally given by the spectral function $A(\mathbf{k}, E)$.

For the modified band dispersions (17), one obtains (how to obtain it??)

$$A(\mathbf{k}, E) = \frac{\delta(E - E_1(\mathbf{k}))}{1 + \frac{\Delta^2}{(E_1(\mathbf{k}) - \epsilon_{\mathbf{k}+\mathbf{q}_0})^2}} + \frac{\delta(E - E_2(\mathbf{k}))}{1 + \frac{\Delta^2}{(E_2(\mathbf{k}) - \epsilon_{\mathbf{k}+\mathbf{q}_0})^2}}, \quad (19)$$

where $\delta(E)$ denotes the Dirac delta function.

Figure 1(b) shows that the spectral weight of the reconstructed subbands is mostly concentrated near the original band; only near $\mathbf{k}_F$, where the energy gap has opened up, are some back-bending effects observable.

Thus, in contrast to the subband dispersions $E_{1,2}(\mathbf{k})$, the spectral function $A(\mathbf{k}, E)$ does not exhibit the novel periodicity of the CDW/PLD phase.

For $T = 0$ and $\Delta/E_F < 1$, it can be shown that the change (after creation of modulation of a lattice) in the sum of the occupied one-electron energies satisfies (why?????????)

$$\delta E_{\text{band}} \propto \frac{\Delta^2}{E_F} \ln \left(\frac{\Delta}{E_F} \right) \quad (20)$$

Minimization of the total energy change, $\delta E_{\text{band}} + \delta E_{\text{lattice}}$, then gives a zero-temperature energy gap (for the tight-binding band):

$$\Delta(0) = 4E_F \exp \left(-\frac{1}{\lambda} \right) \quad (21)$$

(check the derivation in literature!) where $\lambda \lesssim 1$ [34].

Finally, with the help of equation (15), we obtain the well-known Bardeen-Cooper-Schrieffer (BCS) relation between the zero-temperature energy gap and the (mean-field) transition temperature:

(why is it applicable at all to the Pereles transition???)

$$2\Delta(0) = 3.52k_{\text{B}}T_0 \quad (22)$$

Although the picture (if it is a one picture, then derive one should be able all from one start. I don't think that it is possible now, it looks more like a combination of many several pictures) presented through the above equations is that of a full microscopic theory, it has to be pointed out that this theory has many weaknesses connected with the various approximations made.

For example, the mean-field solution of the 1D model neglects the effects of fluctuations and predicts long-range order at a finite transition temperature, which can in fact only come about when the system is quasi-1D, i.e. when there is some finite coupling between neighboring chains [25]. (I think, this problem should be already solved. We have quasi-1D systems, so fluctuations are somehow suppressed and there is a substrate which also should be included somehow for a better description)

Also, within the independent electron approximation, it turns out that a Peierls instability will always occur at a low enough temperature, while, if electron-electron interactions are included, the 1D metal may indeed be stable [36]. (how e-e interaction makes the material stable?)

In the next two sections, we briefly summarize what happens when the assumptions of weak coupling (maybe weak coupling?? it was written before that we consider the case of strong coupling) and one dimensionality are relaxed.

2.2. Weak coupling versus strong coupling

(SUMMARY: in 1d we need weak coupling, in 2d a strong coupling. a lot is researched, learn the cited papers (finish ????, think again))

When the electron-phonon coupling strength is increased, the physics of CDW/PLD formation does not change fundamentally, but most of the formulae given above cannot be applied anymore. (why??? did we consider that case of weak coupling before??? then where was this limit of applicability?)

Compared to a weak-coupling CDW, a strong-coupling CDW is characterized by a larger distortion amplitude (I thought it is a distortion that corresponds to $2p_F$, no???) , a larger energy gap and a smaller coherence length as, for example, given by the inverse width of the Kohn anomaly in the $\omega(\mathbf{q})$ diagram.

The dividing line between the two is roughly set by the ratio $\Delta/\hbar\omega_{\text{D}} \approx 1$ (derive thee $\Delta/\hbar\omega_{\text{D}}!!!$) (with the electronic energy gap Δ and the Debye phonon frequency ω_{D}) [30, 37].

In both cases, the origin of the energy gain is electronic. (I don't think that this is a meaningful statement)

However, for a small energy gap ($\Delta/E_{\text{F}} \ll 1$), the band energy gain originates mostly near k_{F} and is of order $\Delta^2 \ln \Delta$ (equation (20)), whereas for a large gap ($\Delta/E_{\text{F}} \lesssim 1$), the energy gain is spread over the entire Brillouin zone and proportional to Δ [38]. (learn how to calculate this energy gain)

Hence, the relative importance of the Fermi surface for CDW/PLD formation is reduced as the coupling strength is increased. (is by CDW/PLD formation we mean the deviation of the χ ?)

The thermodynamic behavior near the transition temperature T_0 is also markedly different [38, 39]. (learn the thermodynamics near Pereles transition!!!! are there experiments about it??)

In a weak-coupling CDW, the thermal disordering is dominated by electronic entropy (not by lattice, like it will be for higher temperatures) (which formula tells us, why??) , arising from electronic excitations across the gap, and above T_0 the CDW/PLD vanishes completely.

In a strong-coupling CDW, on the other hand, the transition is driven by the entropy of the lattice (why transition is driven by the entropy of the lattice ??? I didn't know that there is such a big differences) and only the long-range coherence of the CDW/PLD is lost at T_0 (what is the long-range coherence?) .

Above T_0 , fluctuating short-range distortions remain and it is expected that these fluctuations smear, but do not destroy, the energy gap and cause strong carrier scattering [39] (so then how do we define T_c , if there is still a gap and everything else?) (read this theoretical derivation!) .

The undistorted state will finally be restored at a temperature well above T_0 (which is it equal?) .

In McMillan's (2D) microscopic model of strong-coupling/short-coherence-length CDW/PLDs [39] (how does this model look like?) , the (normal metal-to-incommensurate CDW (what is the incommensurate CDW?)) transition temperature is given by (derive it!)

$$k_B T_0 = 0.296 C \frac{(\pi \xi_0 u_0)^2}{2\Omega} \quad (23)$$

where ξ_0 is the coherence length, u_0 the distortion amplitude (is the u_0 a constant? should we derive it first from somewhere?) , Ω the area of the normal-state unit cell and C (in $\text{eV}\text{\AA}^{-2}$) a measure for the electron-lattice coupling. (how to calculate Ω and C ?)

This equation is to be compared to equation (15) ($k_B T_0 = 2.28 E_F \exp(-\frac{1}{\lambda})$) for the weak-coupling CDW/PLD transition temperature (in 1D). (they look very different, is it fine??)

(why did we get such a different formulas? at which point in derivation we went to two roads? where did we use a strong coupling??)

Quite generally, it can be expected that strong coupling will lead to significant deviations from the BCS equation (22), i.e. $2\Delta(0) > 3.52 k_B T_0$.

It has been suggested that in the extreme limits of weak and strong coupling two qualitatively different pictures apply [38, 39]. (how to derive them from something one?)

In the long-coherence-length picture (long-coherence-length picture???) , the CDW/PLD transition can be understood in terms of the Peierls instability (why in the long-coherence-length picture?) .

(here are abstract statements which I don't understand, it is better to forget it. The role of FS was always not clear, maybe it gives the contribution to that χ if we have a nesting vector...) As shown above, this instability is intimately connected with the Fermi surface and thus deeply rooted in $\mathbf{k}$ space, where long-range order and incommensurability are easily explained.

In the short-coherence-length picture (short-coherence-length picture??) , on the other hand, a local-chemical-bonding picture (local-chemical-bonding picture?? read the cited papers) is often more appropriate [24, 39-41].

Due to the much larger atomic displacements, nonlinear terms in the electron-lattice interaction are important. (what is known about the nonlinear terms in the electron-lattice interaction?)

The atoms then show a tendency to form pairs with shortened bonds as well as clusters and the CDW/PLDs tend to lock into the underlying crystal lattice. (this is an abstract comment

which can be skipped. the idea is that atoms become closer $\rightarrow$ stronger bonds appear $\rightarrow$ electrons feel bigger potential $\rightarrow$ they localized. but no formula is assumed here, it is just an imagination)

It should be pointed out that the two seemingly different pictures (two coherence length limits) are just two sides of the same coin, because one can pass continuously from one limit to the other [38] (learn this theory that derives both models. LOOKS LIKE A USEFUL ACTIVITY TO DO) .

The complementarity is also reflected in the common analogy between the Peierls instability in low-dimensional solids and the Jahn-Teller effect in molecules [33] (learn the analogy to Jahn-Teller effect later. it is not important to understand it) .

A theory for the intermediate-coupling regime is presently not available [42] (what is known about intermediate-coupling regime? I thought that in the first of its region we do the LLP transformation and at all work with polarons. in the latter region, yes, maybe it is not understood yet. but what about numerics?) , but it can be expected that looking at both the electronic structure in $\mathbf{k}$ space and the local chemical bonding in real space may help to understand intermediately coupled CDWs. Table 1 summarizes the different properties of weak-coupling and strong-coupling CDWs.

Table 1. Qualitative comparison of weak-coupling and strong-coupling CDWs.

	Weak-coupling CDW	Strong-coupling CDW
PLD/CDW amplitude	Small	Large
Energy gap	Small ($\Delta/E_F \ll 1$)	Large ($\Delta/E_F \lesssim 1$) (Such a big gap?)
Coherence length	Large ($\xi/a \gg 1$)	Small ($\xi/a \gtrsim 1$)
Electronic energy gain	Arising mostly near k_F ($\alpha\Delta^2 \ln \Delta$)	Spread over Brillouin zone ($\alpha\Delta$)
CDW periodicity w.r.t. original lattice	Incommensurate ($\lambda_0 = \pi/k_F$)	Tends to be commensurate (how is it?)
Thermal disordering	Due to electronic entropy	Due to lattice entropy
Electron-hole pairing above T_0	No	Yes, but pairs are incoherent
Qualitative picture	Fermi surface instability (???)	Local chemical bonding (???)

2.3. One dimension versus two dimensions

(SUMMARY: there are a lot of effects that are present in χ and in 2d they play another nontrivial role. see cited papers to master these dependences)

Dimensionality has a profound effect on two important factors in the standard theory of CDW/PLD formation: on the peaking (how dim-ty affects the peaking? it is answered in Gruner's book, read it) of the non-interacting susceptibility $\chi_0(\mathbf{q})$ and on the flatness of the Fermi surface $\epsilon_{\mathbf{k}} = E_F$ (how dim-ty affects the flatness?) .

In one dimension, it is the logarithmic divergence of $\chi_0(\mathbf{q}_0)$ with falling temperature (equation (12)) that drives the CDW/PLD transition (this is if we do $T \rightarrow 0$, so at finite temperature they mean that there is divergence?) .

It causes the phonon mode $\mathbf{q}_0$ to soften completely (soften completely??? why at all it is so??) and it ensures a large band structure energy gain to be made.

The wave-vector of the singularity becomes the wave-vector of the CDW/PLD superstructure. (wave-vector of the singularity?? I thought they are the same always)

However, as pointed out recently [13], the logarithmic divergence of the non-interacting susceptibility is not particularly robust against temperature, lifetime and momentum broadening effects (robust against temperature?????? what is it at all? learn this derivation! adding a temperature to the distortion) . (is it important at all?)

Note that momentum broadening (momentum broadening???) naturally arises in quasi-1D systems, in which interchain interactions lead to a buckling of the Fermi surface (buckling of the Fermi surface???) .

Consider then the enhancement $\chi_0(\mathbf{q}_0)/\chi_0(0)$, which is infinite for the ideal 1D case at $T = 0$.

For realistic parameters ($E_F = 0.3\text{eV}$, $|\mathbf{k}_F| = 0.5\text{\AA}^{-1}$), the infinite enhancement is easily reduced to a factor of only about three for, respectively, a temperature of 200 K, an energy broadening of 5 meV or a momentum broadening of $0.01\text{\AA}^{-1}$ [13]. (how to take into account the broadening???)

Thus, in realistic situations a sufficiently large electron-phonon coupling $g_{\mathbf{q}_0}$ is absolutely necessary for a CDW/PLD transition to occur (see equation (8)). (this conclusion if not relevant for the argument before)

What is the role of the Fermi surface with respect to the CDW/PLD transition in 1D? (I don't know)

Looking at definition (7), a large $\chi_0(\mathbf{q})$ requires a large numerator $f_{\mathbf{k}+\mathbf{q}} - f_{\mathbf{k}}$, a small denominator $\epsilon_{\mathbf{k}} - \epsilon_{\mathbf{k}+\mathbf{q}}$ and many such $\mathbf{q}$ -coupled states, i.e. a high density of states. (it is a typical argument)

The largest contribution to $\chi_0(\mathbf{q})$ is expected to arise near the Fermi surface. (why?)

In the weak-coupling limit, indeed, this is the case.

But even then, electronic states away from $\mathbf{k}_F$ (in the entire Brillouin zone) are not negligible as the factor $\ln(\Delta/E_F)$ in equation (20) is known to originate particularly from such states [13, 37]. (derive the $\ln(\Delta/E_F)$)

When the coupling strength is increased, the electronic energy gain cannot be easily localized in $\mathbf{k}$ space (localization of electronic energy gain ???) anymore and the role played by the Fermi surface effectively tends to zero.

(I have no idea if we increase EP coupling, why FS does not play a role anymore???)

For a 2D metal, the situation becomes even worse because $\mathbf{k}$ -space geometry is generally not favorable (why $\mathbf{k}$ -space geometry is generally not favorable???) .

In 3D $\mathbf{k}$ space, a 1D metal has a planar Fermi surface(planar Fermi surface ???) which can exactly coincide with the planar energy discontinuities created by the CDW/PLD, thus resulting (it can be written "in other words"..) in a uniform and complete energy gap at the Fermi level ($N(0) = 0$).

For a 2D metal, on the other hand, the Fermi surface is generally not planar so that the new Brillouin zone edges will only partly coincide with the Fermi surface. (draw an example. how they do not coincide?)

The energy gap is then also only partial ($N(0) > 0$). (partial gap???)

The best case scenario occurs when the Fermi surface is effectively 1D, i.e. when it has large flat parallel sections. (think more about the formula which is assumed here, read Gruner's book.)

The resulting possibility to displace one section of the Fermi surface by a single wave-vector $\mathbf{q}$ and to superimpose it exactly onto another section is the well-known concept of Fermi surface nesting (all should be about that formula for χ) , which, however, may only be used for a simple qualitative analysis of the electronic response in higher dimensions [13]. (so it is like "show me the FS, I'll tell you will there be a divergence"?? work out an example of this analysis)

The effect of dimensionality on the form of the noninteracting electronic susceptibility is dramatic (what about interacting susceptibility?) .

Upon the transition from perfect ($D = 1$) to weak ($D > 1$) Fermi surface nesting, the logarithmic divergence evolves into a smooth peak whose height and position critically depend on the size and curvature of the nested Fermi surface segments [43]. (how does position dependent on size and curvature of FS?)

We note that, apart from Fermi surface nesting, significant contributions to $\chi_0(\mathbf{q})$ can also arise in two dimensions from the nesting of saddle points in the band structure (nesting of saddle points in the band structure??? how is it?) , if the saddle points are very close to E_F [44].

In general, however, layered CDW materials are notoriously(= widely known) known for showing only a weak peaking of $\chi_0(\mathbf{q})$ in a rather broad wave-vector range around the experimentally observed $\mathbf{q}_0$ [13, 23, 45 – 48](why is it so?) .

The Kohn anomalies are therefore smaller and broader than in 1D materials and, consequently, the electron-phonon coupling required for the occurrence of a CDW/PLD is larger [25, 49]. (can we give some quantitative formulas for them?)

Also, in 2D systems the temperature dependence of $\chi_0(\mathbf{q})$ is generally very weak [23, 46]. (formula for $\chi_0(\mathbf{q})(T)$???)

In two dimensions, yet another problem arises. (the problem that we should use a more general form of EP coupling, see this paragraph)

If the Fermi surface is anisotropic (TOP ACTIVITY FOR GENERAL EDUCATION: UNDERSTAND WHY at all FS CAN BE ANISOTROPIC??) , the $\mathbf{k}$ dependence of the electron-phonon matrix element cannot be neglected anymore and the simple instability criteria (8) and (9) ($\frac{4g_{\mathbf{q}}^2}{\hbar\omega_{\mathbf{q}}} - 2U_{\mathbf{q}} + V_{\mathbf{q}} \geq \frac{1}{\chi_0(\mathbf{q})}$) cease to be valid. (how is the anisotropy related to the importance of k dependence?)

The expression for the electronic susceptibility has to be generalized to (derive it!!! this will show that I understand how to work in 2D)

$$\chi(\mathbf{q}) = \frac{1}{L} \sum_{\mathbf{k}} |g'_{\mathbf{k}, \mathbf{k}+\mathbf{q}}|^2 \frac{f_{\mathbf{k}+\mathbf{q}} - f_{\mathbf{k}}}{\epsilon_{\mathbf{k}} - \epsilon_{\mathbf{k}+\mathbf{q}}} \quad (24)$$

where $g'_{\mathbf{k}, \mathbf{k}+\mathbf{q}}$ denotes the $\mathbf{k}$ -dependent electron-phonon matrix element. (how to derive the $g'_{\mathbf{k}, \mathbf{k}+\mathbf{q}}$ and χ with it?? I saw only a derivation of constant g .) (how to take a non interacting limit of it and get the χ_0 ??? I don't see it at all, looks like a wrong formula)

As a rule of thumb, $g'_{\mathbf{k}, \mathbf{k}+\mathbf{q}}$ is large when $\mathbf{k}$ and $\mathbf{k} + \mathbf{q}$ are states with large and opposite band velocities [50].(example of opposite band velocities?)

In layered CDW systems, the electron-phonon matrix element depends rather strongly on $\mathbf{k}$ [23, 48, 51](THIS IS IMPORTANT. WHY IS IT SO? HAVE OTHER AUTHORS TOOK THIS INTO ACCOUNT???) , but in most cases it does not become dominant in $\chi(\mathbf{q})$: the peaking of $\chi(\mathbf{q})$ is more pronounced than the peaking of $\chi_0(\mathbf{q})$; still, it is not sharp enough to pick out the correct $\mathbf{q}_0$ [23, 48, 52].(Rosnagel references some literature, open it to understand what he means?? something else gives the main contribution to the χ)

In a nutshell, when going from one dimension to two dimensions, the role of the electronic susceptibility in CDW/PLD formation appears to be largely diminished (why electronic susceptibility is not working as it was working in the 1d case, but there is still an effect? maybe it is a purely different effect) , and the same holds for the role of the Fermi surface.

Our qualitative comparison of 1D and 2D CDW systems is summarized in table 2.

Table 2. Qualitative comparison of ideal 1D and 2D metals with respect to CDW/PLD formation.

	1D	2D
Fermi surface:		
Geometry (in 3D)	Planar	Cylindrical
Nesting	Perfect	Weak
Electronic susceptibility:		
$\mathbf{q}$ dependence ($T = 0$)	Log. divergence	Weak peaking
T dependence ($\mathbf{q} = \mathbf{q}_0$)	Log. divergence	Weak peaking
Kohn anomaly	Large, sharp	Small, broad
$g_{\mathbf{q}}$ required for CDW	Small (why??? not large???)	Large
CDW energy gap	Complete	Partial

(draw different 2D FSs!!! practice)

(draw some particular examples of χ in 2D!)

2.4. Excitonic insulator instability

(SUMMARY: if there are two bands, then the excitonic insulator phase can be created. (??? what is it??))

Up to this point, we have discussed a situation with a single metallic band and a CDW/PLD transition driven by an electron-phonon interaction. (still, how to say "hey, we add an EP interaction and give the distortion". I can't derive a lot of formulas there)

Now, we consider a two-band model with a small indirect bandgap(indirect bandgap?? see Kittel) /overlap and a 'pure' CDW transition that is driven by an electron-electron interaction - the so-called excitonic insulator instability [4, 5]. (how the CDW can be driven by electron-electron interaction? I thought it is by EP interaction, no?)

Let us assume a valence band with maximum at $\mathbf{k} = 0$ and a conduction band with minimum at $\mathbf{k} = \mathbf{q}_0$ (some $\mathbf{q}_0$, which we define here as the one where conduction band has a minima) :

$$\epsilon_{\mathbf{k}}^a = -\frac{1}{2}E_G - \frac{\hbar^2}{2m_a}\mathbf{k}^2, \quad \epsilon_{\mathbf{k}}^b = \frac{1}{2}E_G + \frac{\hbar^2}{2m_b}(\mathbf{k} - \mathbf{q}_0)^2 \quad (25)$$

where E_G is the energy gap, and m_a and m_b are effective masses, and let us consider qualitatively what may happen at the semiconductor ($E_G > 0$)-to-semimetal(isn't it a metal?) ($E_G < 0$) transition, when the Coulomb interaction is taken into account (see figure 2).

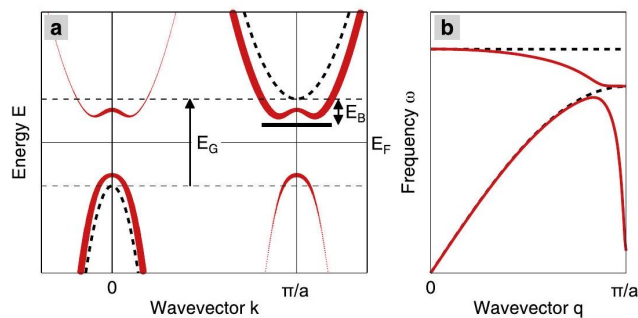


Figure 2. Excitonic insulator instability of a semiconductor with a small indirect bandgap. (indirect bandgap?)

(where are the two bands which were assumed?)

(a) Electronic band dispersion in the normal phase (dashed black lines) and in the excitonic insulator phase (solid red lines), after the bandgap E_G has become smaller than the binding energy of the exciton state E_B . (looks like the E_B is still smaller than E_G , is it right?)

The thickness of the red lines is proportional to the spectral weight carried by the electron states in the excitonic insulator phase.

(b) Exciton and phonon dispersions in the normal phase (dashed black lines) and in the excitonic insulator phase (solid red lines).

In the depicted situation, the soft (spin singlet) exciton mode interacts strongly with a phonon mode. (what would be if they interacted not strongly?)

First, we start on the semiconducting side with an energy gap $E_G > E_B > 0$, where E_B is the binding energy of the lowest-lying excitons, and reduce E_G by some external parameter. (how this E_G is dependent on some external parameters?)

During this process, E_B is expected to remain finite such that eventually a point can be reached at which the exciton excitation energy $E_G - E_B$ goes to zero. (so the upper band does down and the E_B stays approximately on the place)

Then, an electronic instability occurs due to the spontaneous formation of excitons. (I guess it means that electrons become conducting, since the gap disappears. I don't know how to understand it in another way)

Similarly, if we start with a semimetal with a small band overlap $|E_G|$, the excitation energy of a plasmon (how to derive the excitation energy of a plasmon from semimetal or not from semimetal?) can go to zero when the band overlap becomes smaller than some critical energy $|E_1|$ ($E_1 < 0$).

This instability can be connected to screening effects. (learn screening effects finally!!!)

If the number of electrons and holes in the semimetal becomes sufficiently small, the Coulomb attraction between them will be insufficiently screened so that bound states are formed, turning the semimetal into an insulator. (it is a well-known idea of a Wigner crystal)

Taken together, the normal insulating and semimetallic ground states are unstable in the range $E_1 < E_G < E_B$ [4, 5]. (check, why is it so?)

Besides the complete softening of an exciton or plasmon mode (how is this softening works in terms of formulas?), the excitonic insulator state is signaled by the formation of an electron density wave as well as by changes to the band structure, and possibly by a lattice distortion.

Depending on the total spin S of the soft mode, the superstructure in the electron density can be an antiferromagnetic SDW, for $S = 1$, or a CDW, for $S = 0$. (learn this dependence on spin!!!! never heard about it before!!! antiferromagnetic SDW???)

In both cases, the density oscillation will have the wavelength $\lambda_0 = 2\pi/|\mathbf{q}_0|$. (why exactly at $\mathbf{q}_0$??? we have defined it as where the energy is minimal)

In the case of the SDW, the soft electronic mode does not interact (why it does not interact?) with the phonon modes of the system so that the lattice period will not be modulated. (anyway, it is some exotic effect for some exotic materials)

For the CDW, on the other hand, strong mixing between the soft electronic mode and some phonon mode (both having $S = 0$) will generally occur (see figure 2(b)) and the CDW will be accompanied by a PLD with the same periodicity. (this was explained before)

In a strict sense, this CDW/PLD is in contrast to the one resulting from the Peierls instability, which is an instability of the combined electron-lattice system driven by strong electron-phonon coupling.

The excitonic insulator instability is primarily an electronic instability, the driving force is the electron-electron (not electron-phonon!) interaction (electron-hole attraction) and the lattice distortion is therefore only a byproduct resulting from a finite electron-phonon coupling. (seems that here, there is a purely different mechanism for PLD, I'll think about equations here again later if needed)

It should be pointed out, however, that although the driving force may be different the outcome of Peierls and excitonic insulator instabilities is qualitatively the same (maybe not exactly the same, a different distortion may occur, anyway, just look at the theory of this effect to find out how it works?) : a novel ground state with broken translational symmetry exhibiting a CDW, a PLD and a gap in the one-electron (word "one-electron " is redundant) spectrum.

(how to distinguish the Peierls and excitonic insulator instabilities experimentally?)

Moreover, the two scenarios are mathematically indistinguishable [53] (see table 3 for a qualitative comparison). (learn this math)

Table 3. Qualitative comparison of two basic CDW mechanisms: Peierls instability versus excitonic insulator instability. (nice table, I'll return to it if needed)

	Peierls instability	Excitonic insulator
Type of instability	Electron + lattice	Primarily electronic
Archetypal situation	1 band, odd valence	2 bands, even valence
Dominant interaction	Electron-phonon	Electron-hole
Type of density wave	CDW/PLD	CDW (SDW)
Soft collective mode	Phonon	Exciton or plasmon
Lattice distortion	Large	Small (none)

The modification of the electronic band structure in the excitonic insulator phase can be modeled by the simple effective Hamiltonian (cf equation (3)): (with two type of operators here) (where this model is used also?)

$$H_{EI} = \sum_{\mathbf{k}} \epsilon_{\mathbf{k}}^a a_{\mathbf{k}}^+ a_{\mathbf{k}} + \sum_{\mathbf{k}} \epsilon_{\mathbf{k}}^b b_{\mathbf{k}}^+ b_{\mathbf{k}} + \sum_{\mathbf{k}} \Delta_{\mathbf{k}} (b_{\mathbf{k}}^+ a_{\mathbf{k}} + a_{\mathbf{k}}^+ b_{\mathbf{q}}) \quad (26)$$

Via the last term, states in the valence and conduction band - separated in wave-vector by $\mathbf{q}_0$ - are connected. (typical hopping)

If we set $\Delta = \Delta_{\mathbf{k}} = \text{const.}$, $\epsilon_{\mathbf{k}} = \epsilon_{\mathbf{k}}^a$ and $\epsilon_{\mathbf{k}+\mathbf{q}_0} = \epsilon_{\mathbf{k}+\mathbf{q}_0}^b$ (meaning, set $\epsilon_a = \epsilon_b$), we can reuse equations (17) ($E_{1,2}(\mathbf{k}) = \frac{\epsilon_{\mathbf{k}} + \epsilon_{\mathbf{k}+\mathbf{q}_0}}{2} \pm \sqrt{\left(\frac{\epsilon_{\mathbf{k}} - \epsilon_{\mathbf{k}+\mathbf{q}_0}}{2}\right)^2 + \Delta^2}$) and (19) ($A(\mathbf{k}, E) = \frac{\delta(E - E_1(\mathbf{k}))}{1 + \frac{\Delta^2}{(E_1(\mathbf{k}) - \epsilon_{\mathbf{k}+\mathbf{q}_0})^2}} + \frac{\delta(E - E_2(\mathbf{k}))}{1 + \frac{\Delta^2}{(E_2(\mathbf{k}) - \epsilon_{\mathbf{k}+\mathbf{q}_0})^2}}$) for the reconstructed band structure and the spectral function, respectively.

Figure 2(a) illustrates the effects. The valence and conduction band parabolae are mapped onto each other, the band edges become repelled and some spectral weight is transferred from the original bands to the reconstructed ones.

The nature of the resulting state depends on the sign of the gap E_G and on whether the two bands $\epsilon_{\mathbf{k}}^a$ and $\epsilon_{\mathbf{k}}^b$ have the same or different anisotropies (in the k_x and k_y direction). (why it depends on anisotropies?)

When E_G is positive, the resulting band scheme will always be that of an insulator. (this is obvious, but the message is that we somehow need to calculate E_G)

If, on the other hand, E_G is originally negative, an insulating ground state occurs only when the band anisotropies are the same (why? think about it later, I wasn't thinking much yet) .

For different band anisotropies, the modified bands will overlap and the new ground state will be semimetallic [4]. (work out this example, of band anisotropies) (criterion for semimetallicity. and what does it physically mean?)

2.5. Application to real materials

(SUMMARY: no clear answers are given here)

Before we turn from the theoretical background to the review of the properties of the selected CDW/PLD materials, we may ask whether the presented models can indeed be applied to real materials. (= we will discuss in general applicability of theory here)

As for the Peierls instability, as detailed in section 2.1, the model with its formulae certainly helps to identify and understand, at least semi-quantitatively, CDW/PLD transitions in real materials, in particular in quasi-1D solids [25]. (give an example, like we take this material, then we this way can explain something about it)

It can also be seen as a reasonable starting point for more sophisticated microscopic theories. (and how to start from this point???)

The theory of the Peierls instability is, however, based on weak coupling (learn where in Peierls instability we use weak coupling? revise this theory) and special (1D) features of the near- E_F electronic structure and is therefore expected to become inappropriate when the electron-phonon coupling and energy gapping are large and Fermi surface geometry is not 1D-like. (from which experimental methods and higher temperatures we can check this conditions of applicability?)

Nevertheless, when realistic calculations are not available, the Peierls model provides a theoretical framework within which semiquantitative predictions can be compared with experimental data. (still it is not explained how this abstract framework can be used? how to use these semiquantitative predictions for a particular material?)

In section 5, we shall take this approach for the selected layered CDW/PLD systems. (so maybe Rossnagel writes that he'll tell it later???)

Concerning the model of the 'pure' excitonic insulator instability, its relevance for real materials is less clear. (so it is not physical theory?)

In real materials, electron-phonon coupling and electron-hole attraction are always simultaneously present such that the classification of a system as either a Peierls insulator or an excitonic insulator is generally ambiguous. (so we can call the same math with different physics words) (but what about that argument for several bands for exc. insulator to exist?)

(Note that in the Chan-Heine condition (9) ($\frac{4g_q^2}{\hbar\omega_q} - 2U_q + V_q \geq \frac{1}{\chi_0(q)}$), which will frequently be used in our analysis of the CDW/PLDs in the layered compounds, the presence of the two interactions is indicated by the parameters g_q and V_q . (it was explained already before, it is not relevant here))

It is nevertheless surprising that, while the existence of Peierls insulators is undoubted, there are only a few materials for which experimental evidence for an excitonic insulator state has been reported. (=there are a lot of Peierls (CDW) insulators, but not the excitonic insulator)

Two important examples are the rare earth compound $\text{TmSe}_{0.45}\text{Te}_{0.55}$ [54] and the layered transition-metal compound 1T-TiSe₂ [11]. (how theory of excitonic insulators is applicable for them?) (which experimental signatures tells us that they are excitonic insulators?)

For the latter material, whose electronic structure is so suggestive of the excitonic insulator instability (and which is it so it is suggestive?) , we will specifically investigate in section 4 whether evidence can be found for a strong excitonic contribution to the observed electronic structure changes (which electronic structure changes? I don't understand what R. announce?)

.

4.1.4 3. CDW/ PLDs in the layer compounds 1 T-TaS₂, 2 H-TaSe₂ and 1 T-TiSe₂

For our study of CDW/PLD formation in the family of layered transition-metal dichalcogenides, we select here 1TTaS₂, 2H-TaSe₂ and 1 T-TiSe₂ from the nine family members that are

known to undergo a transition to a CDW/PLD state (only pure compounds and 1 T, 2H and 4H_b polytypes counted [18]). (learn which also have the CDW and why they are less popular)

These three compounds are perhaps the most extensively studied ones and they are especially characterized by high transition temperatures, well above 77 K, that lead to significant and reproducible effects upon CDW/PLD formation. (which role does the the transition temperatures play? I thought it is only a consequence of the inner properties, it doesn't lead to anything...)

Besides having large amplitudes, the CDW/PLDs in 1 T-TaS₂, 2H-TaSe₂ and 1 T-TiSe₂ are also remarkably robust against imperfection as they survive transition-metal or chalcogen substitution up to the 15% level [18, 55, 56], intercalation of metal atoms up to the 5% level [9, 57] and alternating octahedral (1T) and trigonal prismatic (2 H) coordination as in the 4H_b Ta compounds [18, 58-60]. (it is not important, there is a collection of papers about imperfections here)

One may therefore expect that these CDW/PLDs can be more easily linked to a specific mechanism. (useless sentence, we are doing nearly whole this article this linking)

On the other hand, strong effects naturally imply that one leaves the solid framework of weak-coupling theory. (useless sentence, we have discussed strong coupling before)

The basic undistorted crystal structures of the 1 T and 2 H polytypes are illustrated in figure 3.

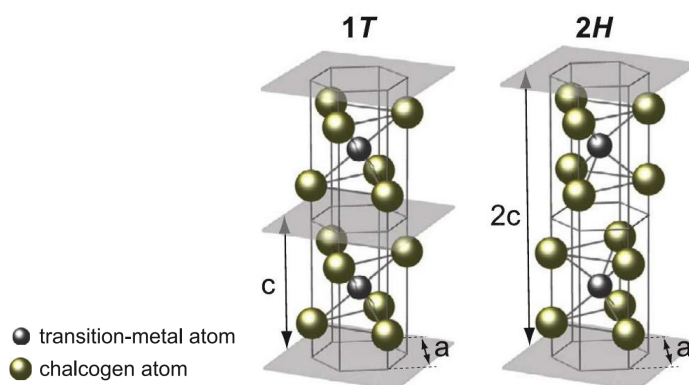


Figure 3. Schematic crystal structure of the 1 T (left) and the 2 H (right) (why are they called so?) polytype of layered transition-metal dichalcogenides.

In the 1T structure, the transition-metal atoms are octahedrally coordinated by chalcogen atoms (= surrounded by 4 atoms) and the thickness of the repeat unit in the c direction is one sandwich.

In the 2 H structure, the coordination is trigonal prismatic and the unit cell is two sandwiches thick(why two sandwiches thick???) .

3.1. Summary of observed CDW/PLD phases

We begin this brief review with 1 T-TaS₂, the compound with the richest phase diagram of all transition-metal dichalcogenides.

If we start at roughly 560 K and lower the temperature, a sequence of CDW/PLD phases with some kind of ordering close to a $\sqrt{13} \times \sqrt{13}$ superstructure will occur [18, 61]. (so it is measured experimentally that from 560 there is the CDW/PLD)

The CDW/PLD is incommensurate (period does not match the crystal lattice period by any simple integer ratio) (learn more about ICCDW) between 543 and 352 K, nearly commensurate from 352 to 183 K (from 221 to 355 K upon heating), and finally commensurate below 183 K [18, 59, 61].

The incommensurate, nearly commensurate and commensurate phases are also called 1 T₁, 1 T₂ and 1 T₃, respectively. (I think it is an exotic notation)

On the way from the incommensurate to the commensurate phase, the rotation angle of the superlattice with respect to the undisturbed lattice changes from 0° to 13.9° [61]. (how to imagine it?)

In the nearly commensurate phase, the rotation angle is about $12^\circ \pm 1^\circ$. (how to imagine it?)

In this phase, commensurate domains are present, arranged in a hexagonal 'super-superlattice' and separated by discommensurate areas [63]. (one can imagine typical images from STM, R. could have added them here)

In the commensurate phase, the Ta atoms are grouped into 13 -atom clusters with a 'Star-of-David' arrangement, as shown in figure 4 (left). The Ta atom displacements are very large, up to 0.24Å, and mostly in-plane.

The displacements of the S atoms are smaller by about a factor of two and mostly out-of-plane [62]. (how in general to find it out???)

As to a possible out-of-plane periodicity (out-of-plane periodicity??) of the CDW/PLD, it can be noted that the stacking sequence of the Ta layers has a period of three in the incommensurate (don't we have a nonperiodic sequence of CDW??) and nearly commensurate phases [61], but that it is not clear whether the stacking sequence is disordered [64-66] or has a period of 13 [63] in the commensurate phase. (what was the problem to measure it???)

A distinctive feature of the (first-order (why first-order?)) nearly commensurate - commensurate phase transition in 1 T-TaS₂ is that electron correlation effects are involved. (electron correlation effects?? learn something about this NCCDW-CCDW PT)

In the presence of the commensurate CDW/PLD, the electronic states in the partially filled Ta 5d band are regrouped such that a Mott-Hubbard transition can occur (which parameter we change, temperature?), to a state with overlapping Hubbard subbands (Hubbard subbands??) and thus a pseudogap at the Fermi level [67] (read this paper, it is not clear what is meant here) .

The few remaining states at E_F are then sensitive to Anderson localization, which is finally responsible for the observed semiconducting behavior of commensurate phase 1TTaS₂ [68]. (connection btw Anderson localization, Hubbard subbands and semiconducting behavior????)

A CDW phase with semiconducting properties is the exception in the family of transition-metal dichalcogenides. (interesting, what TMDCs have to make them one of few materials with SM+CDW state? it might be an unanswered question...)

All other CDW phases (which are left?) are metallic or even superconducting at low temperatures.

Compared to 1 T-TaS₂, the phase diagram of 2H-TaSe₂ is less complex. (look at this image from the cited paper)

Upon cooling, 2H-TaSe₂ undergoes a second-order transition at 122 K to an incommensurate phase with a modulation close to a 3×3 reconstruction, which is followed by a first-order lock-in transition at 90 K to the commensurate 3×3 state [69]. (what about dependence on pressure?)

Upon warming, a 'striped' incommensurate phase with broken hexagonal symmetry has also been found between 93 and 112 K [70] (some hysteresis is there for this material, it is not important to understand it now) .

In the commensurate phase, the Ta atoms form seven-atom clusters (and where are these 7 atoms???) , similar to the inner seven atoms of the 'Stars of David' in 1T-TaS₂ [62] (figure 4 (middle)).

At a temperature of 5 K, the in-plane Ta atom displacements are about 0.05Å, more than

five times larger than the in-plane Se atom displacements [69]. (and to which direction the Se atoms are displaced?)

As in 1T-TaS₂, the movements of the chalcogen atoms in the perpendicular direction, into the van der Waals gaps (van der Waals gaps???) between the Se-Ta-Se sandwiches, are slightly more pronounced. (perpendicular shifts are bigger than shifts in plane, which is known maybe after a measurement)

Compared to the two Ta compounds, the CDW/PLD transition in 1T-TiSe₂ is markedly different: a commensurate superlattice forms without the occurrence of an incommensurate phase (and what was before? how much there was ICCDW phase?) , the transition involves a wave-vector corresponding to a high-symmetry point of the Brillouin zone (example of high-symmetry point of the Brillouin zone) and the CDW/PLD undoubtedly shows 3D long-range ordering (3D long-range ordering???) .

At 202 K, 1T-TiSe₂ undergoes a second-order phase transition to a commensurate $2 \times 2 \times 2$ CDW/PLD [71]. (what is the $2 \times 2 \times 2$ CDW?? we are not drawing it, since it is 3D, right?)

The atomic displacement pattern within an Se-Ti-Se sandwich is shown in figure 4 (right). (in the CDW phase)

At low temperature (77 K), the metal atom displacements are again quite large, about 0.085 Å, and the ratio of Ti to Se displacements is 3 : 1 [71].

All three compounds develop a triple- $\mathbf{q}$ CDW, i.e. the charge-density modulation is given by (why such 3 modulations????)

$$\rho(\mathbf{r}) = \rho_0(\mathbf{r}) \left[1 + \sum_{i=0}^2 \rho_i \cos(\mathbf{q}_i \mathbf{r} + \phi_i) \right], \quad (27)$$

where $\rho_0(\mathbf{r})$ describes the unperturbed electron density (how does the $\rho_0(\mathbf{r})$ look like??? do we take it into account, that it is not a flat distribution??) , and ρ_i , $\mathbf{q}_i$ and ϕ_i are the amplitudes, wave-vectors and phases of the three superimposed electron density modulations (cf equation (1) ($\rho(\mathbf{r}) = \rho_0(\mathbf{r}) [1 + \rho_1 \cos(\mathbf{q}_0 \mathbf{r} + \phi)]$)).

In the commensurate CDW phases, the CDW wave-vectors can be expressed as linear combinations of the hexagonal reciprocal lattice vectors (how the expressions are such???) $\mathbf{a}_i^*$ ($i = 0, 1, 2$): $\mathbf{q}_0 = \frac{1}{13}(3\mathbf{a}_0^* + \mathbf{a}_1^*)$ or $\mathbf{q}'_0 = \frac{1}{13}(-3\mathbf{a}_0^* + 4\mathbf{a}_1^*)$ for 1T-TaS₂ (in-plane components only), $\mathbf{q}_0 = \frac{1}{3}\mathbf{a}_0^*$ for 2H-TaSe₂ and $\mathbf{q}_0 = \frac{1}{2}(\mathbf{a}_0^* + \mathbf{a}_2^*)$ for 1T-TiSe₂. (where are these $\mathbf{a}^*$ -s are located???)

The wave-vectors $\mathbf{q}_1$ and $\mathbf{q}_2$ are in each case obtained by rotating $\mathbf{q}_0$ around the k_z axis by $\pm 120^\circ$ (why by $\pm 120^\circ$???) . (I don't understand their meaning, but they are in the eq. (27))

Figure 4 shows the projected (projected?) real-space unit cells and Brillouin zones for the three materials.

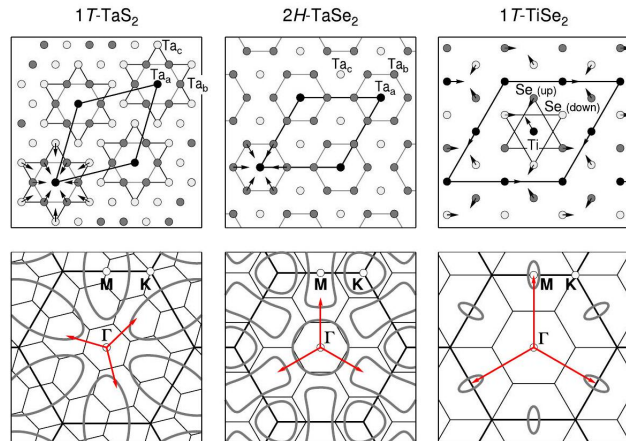


Figure 4. Real-space unit cells (top) and Brillouin zones (bottom) for the commensurate $\sqrt{13} \times \sqrt{13}$ (derive the $\sqrt{13}$) (left), 3×3 (middle) and 2×2 (right) superlattices within a single sandwich (sandwich is a redundant word) layer of 1 T-TaS₂, 2H-TaSe₂ and 1 T-TiSe₂, respectively. (why did Jaka in "configurationla electronic..." paper counted differently these states, like 0 something was there??)

In the top row, the arrows indicate in-plane displacements of the atoms from their original positions (arrow lengths are not to scale). (at the third image it is a strange displacement, but ok)

For 1T-TaS₂ and 2H-TaSe₂ only the Ta atoms are shown; there are inequivalent 'a', 'b' and 'c' Ta atomic sites in the distortion patterns (distortion patterns?? what does it mean?) .

In the bottom row, the red arrows indicate the in-plane wave-vectors of the various CDWs (can we guess these vectors from the FS image?? why are they so?) and the gray contours illustrate the topology of the equi-energy contours near the Fermi energy (= Fermi surface) for the transition-metal d-derived states (d-derived states???) in the normal phase (not in CDW phase, in it, there will be gaps, see below! the top row is for the normal phase) .

In the following, we will only be concerned with the microscopic origin of the transition from a normal undistorted phase to a (commensurate) CDW/PLD phase and not with the various transitions between incommensurate, nearly commensurate and commensurate CDW/PLD phases. (interesting approach, take the initial state and the final, neglect intermediate transitions... maybe it is also possible to do like this, but I haven't pried it ever yet)

The latter (intermediate transitions) have been successfully modeled by phenomenological Landau theory [72, 73] (read it at least 1 time) .

3.2. Characteristics of the CDW/PLD states

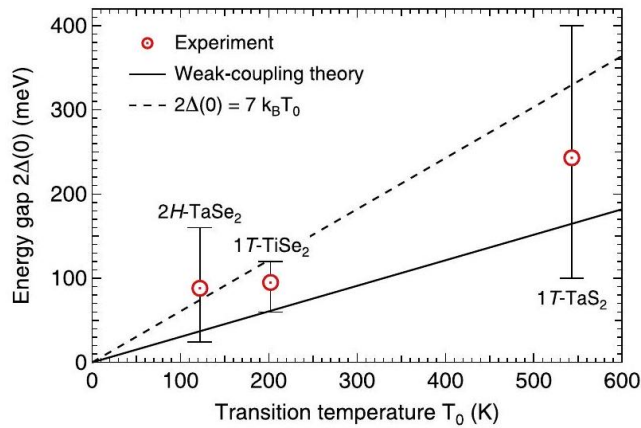


Figure 5. Experimentally determined energy gap sizes (open symbols) versus CDW/PLD transition temperatures for 2H-TaSe₂, 1T-TiSe₂ and 1T-TaS₂. (this is a strange plot which should be consider as an illustration for a theory. in real life, of course, we can't vary T₀ and get the line. note that the last measurement is meaningless, since the error is too big)

For comparison, the prediction of weak-coupling theory (solid line) and a heuristic criterion for the applicability of the strong-coupling limit (dashed line) are also indicated. (how to get these predictions??? I'll try to derive it later, maybe, looks like a good practice)

Beginning in the mid-1970s [18], a broad variety of experimental and theoretical studies have been performed on 1T-TaS₂, 2H-TaSe₂ and 1 T-TiSe₂. (what was their main outcome?)

(next, there is an overview of methods) The experimental techniques used include X-ray,

neutron and electron scattering to determine structural changes and angle-resolved photoemission, scanning tunneling and optical spectroscopy as well as specific heat and transport measurements to characterize the electronic properties and the changes in the electronic spectrum.

On the theoretical side, density-functional theory within the local density approximation (LDA) (learn DFT + LDA) has provided quite accurate results on the electronic structure near the Fermi level, at least for the unreconstructed phases.

Table 4 summarizes selected experimental and theoretical results. From these, a number of conclusions can be drawn.

(i) First of all (here is a confusing sentence. CDW are just seen, and they are predictive also, this is the main idea), there is strong evidence for the occurrence of a CDW/PLD transition in all three compounds because in each case the presence of the three most important signatures - a periodic lattice distortion (PLD is signature for PLD, it can't be, just forget these words "PLD" here) and an energy gap below a certain transition temperature (check the ref. in table 4 about energy gap) and a Kohn anomaly (check the ref. in table 4 about Kohn anomaly) above that temperature - is consistent with the experimental data.

(ii) For all three systems, the electron-phonon coupling is strong (SO WHY DID R. WRITE A THEORY FOR A WEAK COUPLING CASE BEFORE???) , as can be concluded from several experimental results.

First, the amplitudes of the PLDs are large; for the maximum displacement of the transition-metal atoms relative to the lattice constant one finds $u_{\max}/a = 1.5 - 7\%$. (how to find out, what is a large amplitude?)

Second, the depression of the phonon frequency at the CDW/PLD wave-vector due to the Kohn anomaly appears to be significant: $1 - \omega_{\mathbf{q}_0}/\omega_{\mathbf{q}_{\max}} \approx 0.2 - 0.7$, where $\omega_{\mathbf{q}_{\max}}$ is the maximum phonon frequency in the branch that shows the softening. (I understand this as "the Kohn anomaly is indeed detected and significant")

And, third, although there is some uncertainty about the precise values (why uncertainties are so big???) , the average experimental energy gaps in the electronic spectra are large, both with respect to the Fermi energy and the transition temperature: $\langle 2\Delta(0) \rangle / E_F \approx 0.15 - 0.5$ and $\langle 2\Delta(0) \rangle / k_B T_0 = 5.56 \pm 1.20 \gtrsim 3.52$ (see figure 5). (and how does it connect to large EP coupling?)

(The average experimental energy gaps $\langle 2\Delta(0) \rangle$ are (they are presented on the fig. 5) $243 \pm 113 \text{ meV}$ (1 T-TaS₂), $88 \pm 53 \text{ meV}$ (2H-TaSe₂) and $95 \pm 25 \text{ meV}$ (1T-TiSe₂).)

Large energy gapping is also indicated by a significant reduction of the density of states at the Fermi level: $N(0)^*/N(0) < 0.5$, (how is the DOS related to the gapping?) where $N(0)^*$ denotes the low-temperature value derived from specific heat measurements (how to get the $N(0)^*$ from specific heat measurements???) and $N(0)$ comes from band structure calculations performed for the undistorted phases. (how to get $N(0)$ from the band structure calculations???)

For the strong-coupling limit to apply, it has been suggested [39] that $2\Delta(0)/k_B T_0 > 7$. (learn this connection of srt. c. with this criterion!!(???))

As can be seen in figure 5, the measured gap sizes place the three materials somewhere in the intermediate to strong-coupling regime. (why the weak coupling is also a line?)

(iii) A strong interaction between electrons and phonons is also suggested by the relatively high electrical resistivity above the transition temperature. (connection with EP coupling and resistivity???)

For all three compounds, $\rho \geq 0.1 \text{ m}\Omega \text{ cm}$, which is roughly 50 times larger than the resistivity of Cu at 373 K [102]. (why do they compare it with Cu at 373 K???)

Such high carrier scattering rates above T_0 have been interpreted as being caused by fluctuations of a strong-coupling CDW/PLD [103]. (read this theory to understand this, some advance derivation of resistivity tells us this connection)

(iv) Using the inverse width of the Kohn anomaly $1/|\Delta\mathbf{q}|$ as a measure for the coherence length (why is it a measure for the coherence length?? why does this eq. exist?) , we obtain $\pi/|\Delta\mathbf{q}|\lambda_0 \approx 1$ (and what is it $\pi/|\Delta\mathbf{q}|\lambda_0 \approx 1$???) for all three systems, where λ_0 is the wavelength of the observed CDW/PLD ($\lambda_0 = 2\pi/|\mathbf{q}_0|$, we deduce it from this equation) .

This implies that the coherence lengths are as short as they can physically reasonably be, which again suggests that the short-coherence-length (strong-coupling) limit applies. (why short-coherence-length is the strong-coupling?)

(v) It is not surprising that all three compounds can be regarded as quasi-2D ($2 < D < 3$), when comparing resistivity measurements parallel and perpendicular to the layers. (and how the $\rho_{\parallel}/\rho_{\perp}$ tells us that they are quasi 2D??? I don't know this criterion)

However, the anisotropy ratio (what is the anisotropy ratio? why it wasn't discussed before?) covers two orders of magnitude, $\rho_{\parallel}/\rho_{\perp} \approx 2.5\text{-}500$ (why??) , which implies qualitative differences between the compounds.

1 T-TaS₂ should be regarded as a 2 D system, while 1 T-TiSe₂ is almost 3 D, and 2H-TaSe₂ is somewhere in between. (why???) (importantly, they are not 2D as I thought) (dis we discuss CDW theory for 3D materials before??)

(vi) Finally, an interesting observation is that the maximum atomic displacement (some atoms are displaced bigger and some are stronger, they oscillate also, but here it is meant maximum constant displacement) appears to scale linearly with the transition temperature: $u_{\max}/a \approx 1.27 \times 10^{-4} T_0$ (K) (why the units are such?? shouldn't it be unitless??) (check it from table 4, is there enough data to conclude it???) , with T_0 referring to the transition between the normal phase and the first CDW/PLD phase reached upon cooling (an incommensurate CDW phase for 1T-TaS₂ and 2H-TaSe₂ and a commensurate CDW phase for 1 T-TiSe₂).

It is not clear whether this is accidental or implies a common underlying mechanism. (any-way, I don't understand the derivation of it here)

However, if we combine the linear transition temperature dependences of the energy gap $\Delta(0)$ and of the maximum atomic displacement $u_{\max}$, we obtain a 'universal' electron-phonon coupling parameter $\Delta(0)/u_{\max} = (0.55 \pm 0.13) \text{ eV}\text{\AA}^{-1}$. (was it used somewhere? can we used it somewhere??? looks like a link to some strange transformation, which is not used ever...)

Table 4. Selected experimental and theoretical parameters for the layered CDW compounds 1T-TaS₂, 2H-TaSe₂ and 1T-TiSe₂.

	1 T-TaS ₂	2H-TaSe ₂	1T-TiSe ₂
Transition temperatures			
T_{ICDW} (K)	543 ^a	122 ^b	-
T_{CCDW} (K)	183-221 ^a	90 ^b	202 ^c
Lattice distortion			
Superstructure	$\sqrt{13} \times \sqrt{13}^{\text{d}}$	$3 \times 3^{\text{b}}$	$2 \times 2 \times 2^{\text{c}}$
Displacement u_{max}/a	7% ^e	1.5% ^f	2.4% ^c
Energy gap			
$2\Delta(0)$ (meV)	100 – 400 ^g	24 – 160 ^h	60 – 120 ⁱ
Kohn anomaly ^j			
$\hbar\tilde{\omega}_{\mathbf{q}_0}$ (meV)	4.8 ^k	7.0 ^b	5.4 ¹
$1 - \tilde{\omega}_{\mathbf{q}_0}/\tilde{\omega}_{\mathbf{q}_{\text{max}}}$	73% ^k	22% ^b	42% ¹
$ \mathbf{q}_0 - \mathbf{q}_{\text{max}} \left(\text{\AA}^{-1} \right)$	0.32 ^k	0.26 ^b	0.44 ¹
LDA band structure			
E_{F} (eV)	$\sim 1.3^{\text{m}}$	$\sim 0.6^{\text{n}}$	$\sim 0.2^{\text{n}}$
$N(0)$ (states/eV u.c.)	1.4 – 1.7 ^o	5.2 ^o	0.9 – 1.5 ^p
Specific heat			
$N(0)^*$ (states/eV u.c.)	0.2 – 0.6(1.8) ^q	1.9 – 2.2 ^r	0.08 ^s
Θ_{D} (K)	249 ^q	201 ^r	251 ^s
Electrical resistivity			
ρ (m Ω cm) ^t	$\sim 0.2^{\text{u}}$	$\sim 0.1^{\text{v}}$	$\sim 1^{\text{w}}$
$\rho_{\perp}/\rho_{\parallel}$	$\sim 500^{\text{x}}$	$\sim 25^{\text{v}}$	$\sim 2.5^{\text{w}}$
Lattice constants ^y			
a ($\text{\AA}$)	3.365	3.435	3.536
c ($\text{\AA}$)	5.883	2×6.359	6.004

^a Thermal and transport measurements [59].

^b Neutron scattering [69]. ^c Neutron scattering [71].

^d Electron diffraction [18]. ^e X-ray diffraction [62].

^f Neutron scattering [69, 74].

^g ARPES, scanning tunneling spectroscopy, optical conductivity and tight-binding simulations [75-79]. The value range does not necessarily reflect the size of the CDW gap because below ≈ 180 K there is also a Mott-Hubbard-type gap.

^h ARPES, scanning tunneling spectroscopy and optical spectroscopy [80-85].

ⁱ ARPES [11, 86-89]. ^j Near room temperature.

^k X-ray thermal diffuse scattering at 360 K [90].

¹ X-ray thermal diffuse scattering at 295 K [91].

^m Reference [92]. ⁿ For a semimetallic normal phase [93].

^o Reference [94] and references therein.

^p Reference [95] and references therein.

^q References [18, 96]. ^r References [18, 97].

^s Reference [98]. ^t Above T_{CDW} . ^u At 550 K [12].

^v At 300 K [99]. ^w At 300 K [71]. ^x Reference [100].

^y Average values from references compiled in [101].

Summary

Summing up, the key experimental observations - an electronic energy gap and a periodic lattice distortion (PLD shouldn't be here, because PLD does not suggest PLD (see next part

of the sentence)) at low temperatures as well as a Kohn anomaly at high temperatures - suggest a Peierls-like CDW/PLD instability in the three layer compounds 1 T-TaS₂, 2H-TaSe₂ and 1 T-TiSe₂. (the conclusion is well-known before, but what exactly was measured??)

Yet, we foresee that the simple 1D weak-coupling mean-field theory(why this theory is described as weak-coupling mean-field theory??? I don't see it, just the standard EP theory, no?) will probably not describe the observed transitions adequately, because the materials are quasi-2D and in the intermediate to strong-coupling regime. (so the FSN idea is a failed idea? what exactly it does not explain?)

As pointed out in section 2.2 ("Weak coupling versus strong coupling") , strong coupling implies that models based on special features of the Fermi surface alone will not work when trying to explain the microscopic origin of CDW/PLDs. (it is not clear, what is meant??? we actually try to explain experiment with some model, so does it explain experiment?)

Instead, a detailed look at the entire band structure is necessary. (= we need to take some other approach)

In addition, there is some uncertainty related to the sizes of the measured energy gaps, not only because different methods measure different gaps in the electronic spectrum, but also because it is not evident where exactly in **k** space the energy gap(s) should open up. (aren't measurements tell us, where they should open?)

In that respect, it is also not fully transparent what a spectroscopy such as ARPES is actually seeing in the CDW/PLD phases. (what are the options what it can see?)

For these reasons, it seems necessary to investigate in detail the band structures and spectral weight distributions of the three selected materials in their reconstructed phases. (it is intro to the next section)

4.1.5 4. Band structures and spectral weight distributions of reconstructed 1T-TaS₂, 2 H-TaSe₂ and 1T-TiSe₂

In this section, our goal will be twofold:

(i) to better understand the ARPES results obtained from 1 T-TaS₂, 2H-TaSe₂ and 1T-TiSe₂ in the commensurate CDW/PLD phases

and

(ii) to find some clues to the possible CDW mechanism(s) in the electronic structure near the Fermi energy E_F . (=R. just repeats that he wants to have some ideas about the real working theory of CDW)

We will not perform (intransparent) density-functional theory calculations. (read some articles about DFT!!! I need to read at least one article about it!)

Instead, our approach is to use an empirical tight-binding model that is as simple as possible but captures the essential aspects. (intro to the section of TB models)

We start with a brief review of the available ARPES results on the three selected compounds. (are these new results or they have already been discussed before?)

4.1. Review of ARPES results

(why exactly $E < E_F$ on the ARPES, not vice versa??)

In the last couple of years, numerous ARPES studies have been performed on 1 T-TaS₂ [68, 77, 79, 92, 104-112], 2H-TaSe₂ [81, 82, 84, 85, 113, 114] and 1 T-TiSe₂ [11, 86-89, 115, 116]. (read at least some of the papers)

Here, we will concentrate on the CDW/PLD-induced changes to the single-particle energies and the accompanying redistribution of spectral weight.

Possible many-body effects on the ARPES lineshapes will not be considered. (which possible many-body effects?)

For each compound, we show in figure 6 characteristic electronic structure changes - as seen by ARPES - that occur near the Fermi level (looks like also below the Fermi level) upon entering the commensurate CDW/PLD phase.

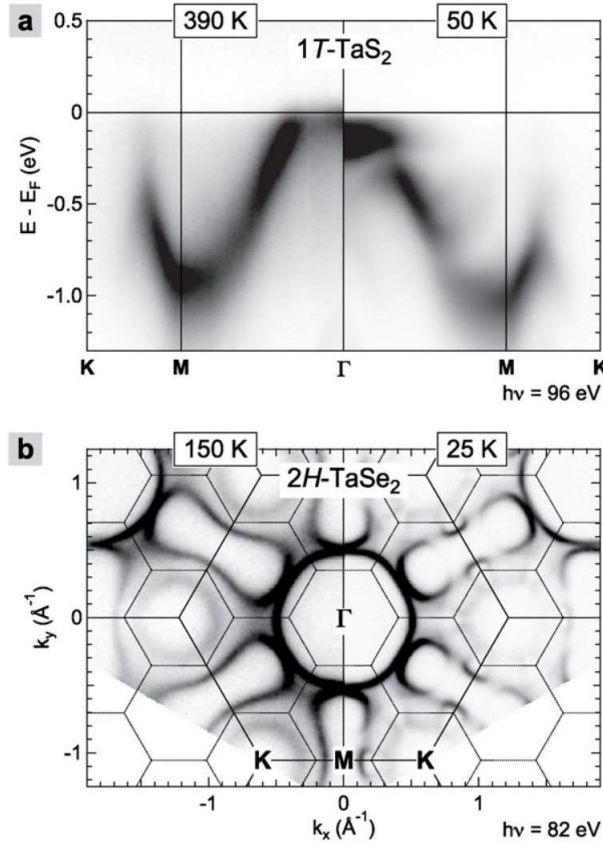
(next is info about experimental setup) The corresponding ARPES measurements were conducted at the Electronic Structure Factory endstation at beamline 7.0.1 of the Advanced Light Source in Berkeley, with an overall energy resolution of $\sim 50\text{meV}$ and with the samples heated and cooled to above and below the known CDW transition temperatures (sample temperatures and photon energies used are indicated in figure 6).

From these ARPES results and the previous (experimental) studies, we abstract the schematic view of the material-specific electronic structure changes shown in figure 7. (so fig. 7 is only from experiments, this is how I understand it)

In this figure the black lines reflect the respective band structures or Fermi surfaces in the normal and CDW phases, whereas the thick gray lines accentuate those electronic states that carry a large ARPES spectral weight (just highlight of very black areas) in the CDW phases.

We emphasize that our ARPES results (figure 6) are in good overall agreement with the most recently reported results [11, 85, 110]. (check other ARPES results to make sure how they look like)

Minor discrepancies are presumably due to matrix element effects(matrix element effects???) connected with different experimental geometries and photon energies used.



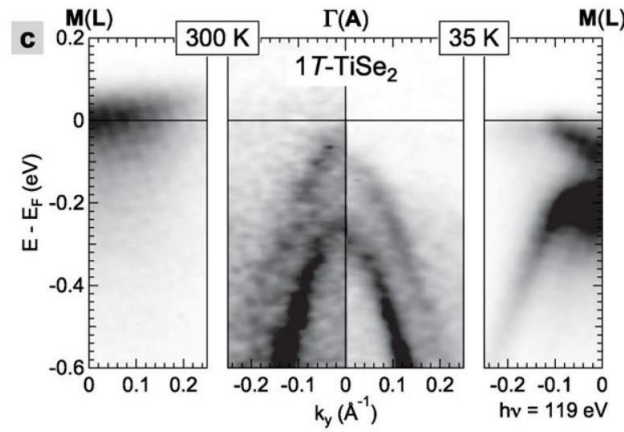


Figure 6. Experimental electronic structures (why the plots are of so different type???) of (a) 1 T-TaS₂, (b) 2H-TaSe₂ and (c) 1 T-TiSe₂ (how to understand named of points of c) is it before and after shrinking of BZ? still, what do they mean and why they are such?) , as seen by ARPES in the normal phases (left) and in the commensurate CDW phases (right).

(there is a 390K on fig. 6, but below it is written that undeformed phase is at 543K, so at what temperature?)

(next is the obvious description of the plot) The corresponding temperature and photon energies are indicated. ARPES intensity maps are shown in inverse grayscale (black corresponding to high intensity). In (b) the Brillouin zones for the 1×1 (solid lines) and 3×3 (dotted lines(it means that little hexagon, dots are not seen here, but they are assumed)) (it is also confused here, 3x3 should be solid and 1x1 should be dotted) superlattices of 2H-TaSe₂ are indicated.

Figure 7(a) reproduces the results of an early tight-binding calculation for 1T-TaS₂ [75] (check this paper, looks like THE MOST IMPORTANT CITATION FROM THIS ARTICLE. how is it possible to calculate it at all???) , on which much of our current understanding of the band structure in the commensurate $\sqrt{13} \times \sqrt{13}$ CDW/PLD phase is based.

(in fig. 7a) there is a lot of degeneration at the left, yes?)

In undistorted 1T-TaS₂, a single Ta 5d band (why 5d band??) disperses downwards from the Brillouin zone center (Γ point) toward the zone boundary (M point) and then back upwards along the zone face (what is the zone face??) (M-K direction).

It crosses the Fermi level twice to give an elliptical Fermi surface pocket centered on M (see figure 11 (b)). (I still don't understand this connection of the FS in the k-plane and the bands. how does it work???)

In the $\sqrt{13} \times \sqrt{13}$ reconstructed phase, a dramatic rearrangement is predicted to occur. (nearly nothing is left the same)

The occupied part of the Ta 5d band(why 5d band?) is split into submanifolds separated by gaps and the Fermi surface becomes 'messy', being determined by the bottom of a spaghetti-like set of bands (I thought that there is a FS and there are bands. how do bands determine the FS?) (see figure 7(a) (right)).

The results of ARPES measurements on 1 T-TaS₂ are in principle consistent with this picture. (= fig. 6 and 7. looks similar)

The existence of the submanifolds has been confirmed [75, 79, 104](how to confirm the existence of the submanifolds???) and some of the fine structure within the submanifolds, including subband dispersions, has been resolved [77, 109-111](some special properties of submanifolds were studied, read it later!) .

(WHY WE ARE NOT USING THEORY OF SUBMANIFOLDS IN THE MODELS?? I HAVEN'T SEEN THIS TAKEN INTO ACCOUNT IN THE MODELS BEFORE.)

This is illustrated in figure 7(a) by the thick gray lines. (maybe it is meant that gray areas indicate that there is a special fine structure there)

It should be pointed out, however, that relating ARPES data on 1TTaS₂ to CDW effects is not unambiguous. (= we can derive different conclusions for CDW, as was mentioned somewhere above)

First, there are no ARPES results available for the undistorted phase, which exists only in a small temperature interval (why at a small temperature interval??? I thought it is for all the temperatures above this one. Is above this temperature the structure distorted again?) above ~ 543 K (ARPES data for the highest sample temperature so far are shown in figure 6(a)).

Yet, this is not too problematic. Since spectral weight distributions reflect the original band dispersion as long as the superlattice crystal potential is small (see section 2.1)(I don't understand connection of spectral weight distributions and band dispersion), the undistorted band dispersion can practically be extracted from room temperature ARPES data, when the system is in the nearly commensurate CDW phase. (we can get undistorted ARPES results from some slightly distorted because we know some advanced theory)

In fact, even deep in the commensurate CDW phase, the spectral weight is mostly concentrated along the original band and the reconstructed band structure is only faintly (=weakly) visible [109-111] (see also figure 6(a)). (how can we see it from the theory? from experiments, we see just similar plots, right?)

Second, the transition to the commensurate phase is accompanied by (explained by) a Mott-Hubbard-type metal-insulator transition, which creates a ~ 0.4 eV gap at E_F and leads to the appearance of a rather sharp Hubbard subband (Hubbard subband??) around Γ at ~ 0.2 eV below E_F [68, 104, 110] (thick gray line in figure 7(a)(WHY THERE IS A GREY AREA WHERE THERE IS NO BLACK AREA ON THE FIG.7a?)). (how to come to this result? read the cited papers!)

Hence, strong electron-phonon coupling and electronic correlations are simultaneously present in 1 T-TaS₂ (we expect them, but I don't see how to come to this conclusion?) and this, together with the 'band spaghetti', leads to broad ARPES lineshapes and the absence of sharp Fermi level crossings [105, 106, 110, 111] (figure 6(a)). (R. just describes fig. 7, nothing informative is here. Maybe he means that theory also explains the experiment...)

The experimental Fermi surface maps are diffuse (= not sharp, see the fig. 6b); if unnormalized, they show a high-intensity feature centered on Γ (maybe it is meant "with the center in Γ ", anyway it is a description of fig. 6b.) and almost no intensity near the zone boundaries [108, 111].

The conclusion then is that there is considerable uncertainty in the band diagram depicted in figure 7(a) (so it is written that the gray areas are because of fluctuations of a Fermi surface???) (what is meant here??) and in its relation to the measured spectral weight distributions (how does the measured spectral weight distributions look like?) .

ARPES cannot resolve all the predicted fine details (it is bad that we have not bands, but some smeared areas) and the tight-binding model itself may not be fully appropriate, not least because it neglects the spin-orbit interaction, which is expected to be important in the valence band structure of Ta compounds. (why SO effects are important???)

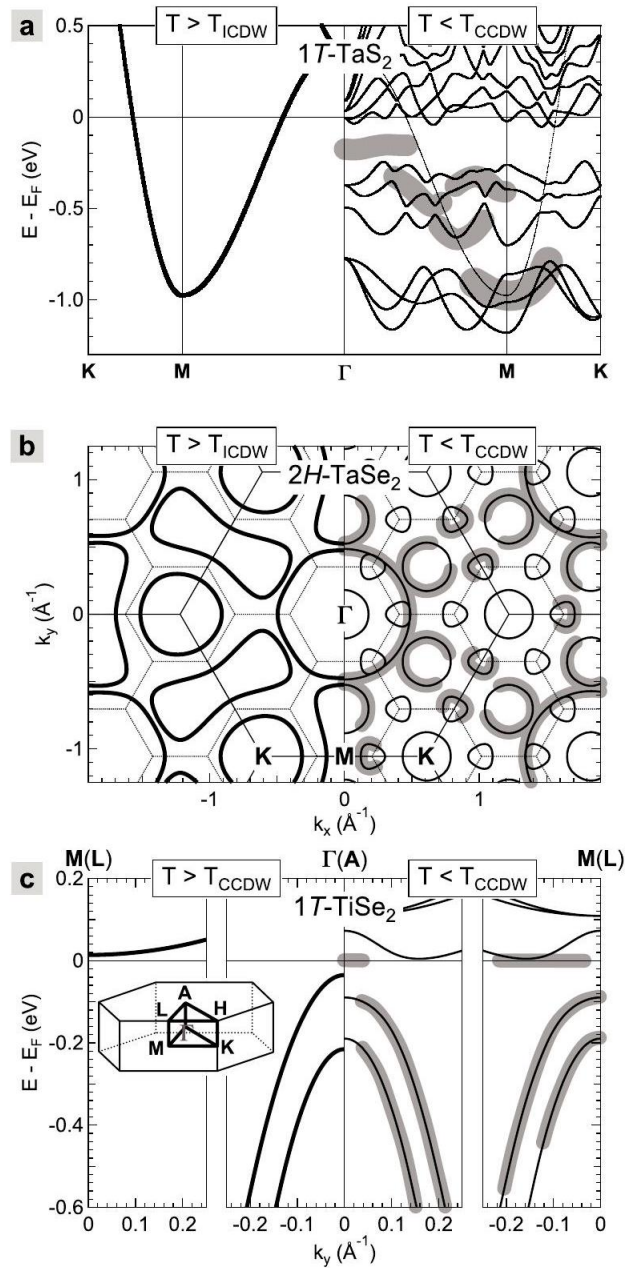


Figure 7. Schematic electronic structures of (a) 1T-TaS₂, (b) 2H-TaSe₂ and (c) 1T-TiSe₂, taken from experimental and theoretical (what is from experiments and what is from theory???) band structure results in the normal phases (left) and in the commensurate CDW phases (right). (why images are of different type for different materials, so we even can't compare them?)

(how to understand horizontal axes on the fig. 7c??? for example, there at the left the conduction band goes and then disappears, why?)

(fig. 7a, why there is a wide gray area where there are no bands????????????!!!! Where is the CDW gap??? there are several gaps!!! maybe from the top valence band to a conduction band? if yes, then why?)

(Why at right on fig. 7c we have top bands, but not at the right of 6c?)

(fig. 7b, right, what is about circles inside the big central circle? we don't see them in ARPES)

(fig. 7a) there are a lot of degenerations at the left, yes? this is how I understand it. or they appear only after folding the BZ?)

Band structure features that carry significant spectral weight in the CDW phases are highlighted by thick gray lines. (still, what is "band which carry a spectral weight?")

The inset in (c) shows the bulk Brillouin zone of the layered compounds. (how to understand

the inserted shape into the BZ?)

(fig. 7c, why there is no that softening from fig. about excitonic insulators? NOTHING IS HERE FROM THAT PLOT (FIG. 2), this is very strange)

(Om fig. 7a there are so many bands, but on fig. 6a we don't see them, I guess this is because they have a tiny spectral weight)

For 2H-TaSe₂, the situation is different.

The most recent ARPES data are extremely sharp and, therefore, allow for a quantitative analysis by fitting the data to tight-binding formulae [84, 85, 113, 114]. (learn later how it was done?)

Here, we concentrate on the CDW-induced changes to the Fermi surface. (why not on spectra? because this is what papers which he cites have decided?)

(see fig. 7b =) Figure 7(b) compares the Fermi surface topologies in the normal and commensurate CDW states, as determined with high accuracy in [85, 113, 114]. (HOW AT ALL TO OBTAIN THIS 7B FIGURE??? I HAVE NO IDEA)

(FS is like on fig. 7b =) In the normal phase (above 122 K), the Fermi surface of 2H-TaSe₂ consists of two hole-like(why hole-like?) circular pockets around Γ and around K and one electron-like 'dogbone' centered on M.

Note that this topology was not clear until recently [84](it is not important) and that it implies the existence of two saddle points in the band structure along the $\Gamma - K$ direction, one above and the other below E_F (why it implies something in band structure?) .

As a precursor of the CDW (at a temperature of ~ 180 K), ARPES finds small pseudogaps (difference btw pseudogap and gap?) on the K pocket and possibly also on parts of the M dogbone [85]. (= there is something found in the spectra at high T. see cited paper to learn more)

Upon entering the incommensurate CDW phase (between 90 and 122 K) these pseudogaps become larger, until they finally evolve into real bandgaps in the commensurate 3×3 CDW phase (below 90 K) [85]. (how to imagine a band? I imagine evolution of gap, but not gap -> pseudogap)

As a result, the K Fermi surface pocket is completely destroyed (looks like it just diminished, not destroyed) and the M dogbone is broken up at the zone face, while the Γ pocket remains fully intact [84, 85]. (why do they change? it is not explained here, read cited paper)

(here is only a description of fig. 6b, 7b) The reconstructed Fermi surface appears to consist of circular pockets centered on the Γ points of the new Brillouin zones and rounded triangles around the new K points (see figures 6(b) (right) and 7(b) (right)).

(description (without explanation) of bold black lines on fig. 6b/ gray lines on fig. 7b =) The spectral weight, however, is concentrated on the normal-state Γ pocket and on those parts of the other normal-state Fermi surface sheets that contribute to the reconstructed Fermi surface pockets [85].

In short, ARPES presents a comparatively lucid (=clear) picture of the CDW-induced changes to the Fermi surface of 2H-TaSe₂ and the results suggest that the selective, $\mathbf{k}$ -dependent energy gapping should be given closer scrutiny. (= no conclusions, one can think and maybe make some conclusion later)

In the case of 1T-TiSe₂, the relevant electronic states are the Se 4p states (why 4p states?) forming the valence band maximum in the zone center (at the Γ point) and the Ti 3d states (why 3d states?) of the conduction band minimum at the edge of the 3D Brillouin zone (what is the connection of states and the points on the bZ????) (at the L point, see the inset in figure 7(c)).

In the commensurate $2 \times 2 \times 2$ CDW phase (below 202 K), the Γ and L symmetry points

of the normal reciprocal lattice become equivalent Γ points of the smaller Brillouin zones (why exactly so?? I can't even imagine it! some point becomes another point of the modified BZ...) so that the Se 4p and Ti 3d bands can interact directly, if they are close enough in energy. (I need more education in zones to understand it, how BZ can shrink and how it leads to exactly direct interaction?)

(here is about fig. 7c, most right) Although a consensus on the magnitude and sign of the p-d gap in the normal phase has not yet been reached, the most recent ARPES results have yielded sufficiently small gap values between -20 meV (band overlap(I think it is still a band gap)) and +150 meV (bandgap) for the p-d interaction to play an important role in the band energy lowering in the CDW phase [11, 86, 87, 89, 116](which role does the band interaction play in CDW???? Nothing was explained about it) . Figure 7(c) reproduces the quantitative ARPES results of [87].

(Note that there are only two Se 4 p bands depicted at Γ , while there should be three. The third band has probably escaped detection because of the use of an inappropriate photon energy in the experiment.)(why there should be 3? why did it escape detection?)

(why the are bands above E_F on the 7c, but non of them in fig. 6c?)

Upon the transition from the normal state to the commensurate CDW state, 1 T-TiSe₂ transforms from a semiconductor with a small indirect gap of ~ 50 meV between Γ and L(why between Γ and L?) to another semiconductor with a larger indirect gap of ~ 100 meV at a slightly different location in k space (I don't see how it is consistent with fig. 7c) read the cited article! .

(but other results are different =) In other ARPES studies, similar p-band shifts to lower energies are reported [11, 86, 87, 89] (see also figure 6(c)). (why are there different results???)

(there are other modifications of bands, it we move ot CDW phase. see fig. 6(c) and 7(c) =) Besides this opening of a p-d gap, the strong p-d band interaction(I don't think that it is a strong p-d band interaction, it is just an observed change) manifests itself in the flattening of the top of the Se 4p valence bands, the suppression of spectral weight near the top of these bands, the buckling of the bottom of the Ti 3d conduction band and the appearance of remarkably intense folded Se 4p bands at L (see figures 6(c) and 7(c)). (how to explain all these effects?)

The further supposed splitting of the threefold-degenerate conduction band in the unoccupied region [87] is not observable by ARPES. (what is known at all about conduction band? Nothing is explain about it here)

Summing up, there is clear evidence from ARPES that p-d band interaction is an important ingredient for the CDW phase transition in 1T-TiSe₂.(I don't agree. It is clear that bands change, but I don't know if the origin of it is in the band interaction or no?)

(we need to develop theory for it =) Thus, if the nature of the interaction could be further clarified, this would certainly contribute to a better understanding of the transition.

It should be pointed out that in all three compounds precursors to the effects observed in the commensurate CDW/PLD phases - such as a pseudogap, diffuse shadow band intensity(diffuse shadow band intensity???) or suppression of spectral weight (what is known about spectral weight? is here a discussion of it?) - already occur well above the transition temperatures to these phases.

In addition to the experimental signatures of the CDW/PLD states discussed in section 3.2 (there was also in table 4 and ARPES measurement, so I thought that these results are included to that chapter. but it doesn't matter) , this is further evidence for the strong-coupling nature of the CDW/PLDs in these materials. (there is no sense to consider seriously this statement, nothing is written here about the connection to strong coupling, anyway one needs to read theoretical papers)

(how can we explain the ARPES results with theory from sect. 2.1? =) How do the ARPES results on the three selected layered CDW/PLD systems comply with the simple 1D weak-coupling mean-field picture described in section 2.1?

Where do the CDW/PLD-induced energy gaps actually open up? (at these points which R. wrote before, no?)

As anticipated in sections 2.2 and 2.3, strong coupling and two-dimensionality blur the image of a Fermi surface-driven instability (it is not clear, how they blur it, and what is meant by it, but something like this was written before, where I already posted questions about it) ; the CDW gap in the electronic spectrum does not necessarily open up at E_F . (and at which position does it open?)

It does so in 2H-TaSe₂, in which the K Fermi surface pocket is completely (and the M pocket partially) removed.

But in 1T-TaS₂ and in 1T-TiSe₂ the CDW gaps are not directly connected with Fermi level crossings of the undistorted bands. (connection of CDW gaps and Fermi level crossings???)

Instead, gaps open up between subband manifolds at somewhat higher binding energies. (=between different bands?)

The CDW gapping occurs in 1T-TaS₂ between subgroups of occupied Ta 5 d bands and in 1T-TiSe₂ between the bottom of the (nominally unoccupied) Ti 3d conduction band and the top of the (fully occupied) Se 4p valence band. (why between them???)

To what extent is the novel periodicity of the CDW/PLD phase reflected in the band dispersions? (good question, idk)

We have noted above that reconstructed or 'shadow' bands carry significant spectral weight only in the proximity of original bands so that spectroscopy cannot detect the whole folded-out band structure, except for faint (=brief) shadows in the regions away from the original bands. (what are these exceptions? yes, there are shadows, but what exactly is meant here?)

Although this picture is in principle confirmed by the ARPES results on the layered compounds (really? I don't see shadow bands there) , the relative strength and clarity of the shadow band effects is surprising. (strength of a shadow band?)

(here is a comment about fine structure and isolated bands, which is not clear at all) In 1 T-TaS₂, the compound with the largest lattice distortion, the fine structure in the reconstructed band structure (fine structure in the reconstructed band????) is only faintly(=weakly) visible, while in 2H-TaSe₂ and even more so in 1T-TiSe₂ clear signatures of isolated reconstructed bands(which isolated bands?) can be identified - in 2H-TaSe₂ in the Fermi surface map(I don't understand how FS map is related to band structure?) and in 1T-TiSe₂ in the band map around the L point.(I have no idea where are these isolated bands?)

Our goal will now be to understand these band structure effects on the basis of an empirical tight-binding model. (I assume that we still work with that Frolich model, but we transform it, and this is our TB model to be considered)

An important motivation is the following: if the model can reproduce the experimentally observed spectral weight distributions, it may provide access to the complete reconstructed band structure and not just the parts with a high spectral weight that are detectable by ARPES. (why??? I thought that spectral weight is one thing, but complete band structure is another thing...)

Based on such a foundation, the discussion of the possible CDW mechanisms is expected to become richer. (discussion become richer is a useless statement)

4.2. Empirical tight-binding model

Our approach to simulating the electronic structure effects upon CDW/PLD formation is based on the simplest model that incorporates the essential physics, namely the Slater-Koster tight-binding model (is the Slater-Koster model a special one?) .

The tight-binding scheme we use follows the one outlined in [75, 117-119].(check this literature)

The first step is a fit of the Slater-Koster parameters (Slater-Koster parameters???) , using a minimal basis set, to a first-principles band structure calculation [93, 117, 120]. (why to we need at all to fit something if we have already first-principles calculation?)

For 1T-TaS₂ and 2H-TaSe₂, we use only Ta 5d orbitals (why only 5d orbitals?) , and for 1T-TiSe₂ the basis consists of the three Ti 3d_{t_{2g}} and the six Se 4 p orbitals (why these orbitals?) .

In the case of 1 T-TaS₂, the Hamiltonian includes only nearest-neighbor intralayer d-d interactions (have we ever taken the intralayer interactions before into account?) , but for 2H-TaSe₂ these are augmented (=bigger, stronger) by nearest-neighbor and second-neighbor d-d interlayer interactions.(d-d interactions are even stronger for this material) (why??)

For 1T-TiSe₂, on the other hand, only nearest-neighbor p-p, p-d and d-d intralayer and interlayer interactions are considered. (why??)

In the case of the two Ta compounds, spin-orbit coupling(why do we need to add spin-orbit coupling?) is added by inclusion of the intra-atomic matrices (intra-atomic matrices???) M and N of Abate and Asdente [121] and by use of the Herman-Skillman value(Herman-Skillman value???) of the spin-orbit parameter ($\xi = 0.313\text{eV}$) [122].

In this way, we end up with reduced Hamiltonians of dimension 10 (1 T-TaS₂), 20 (2H-TaSe₂) and 9 (1 T-TiSe₂). (why such dimensions? is there an explicit form of the matrices?)

The fitted tight-binding band structures are shown in figures 8(a), 9(a) and 10(a). (why do we need to fit at all, couldn't we just work with first principle model?)

For the two 'three-dimensional' compounds 2H-TaSe₂ and 1 T-TiSe₂, we restrict our analysis to the ALH and ΓMK planes in reciprocal space, respectively(why is it restriction? why is it done at all, could we have the similar planes?) .

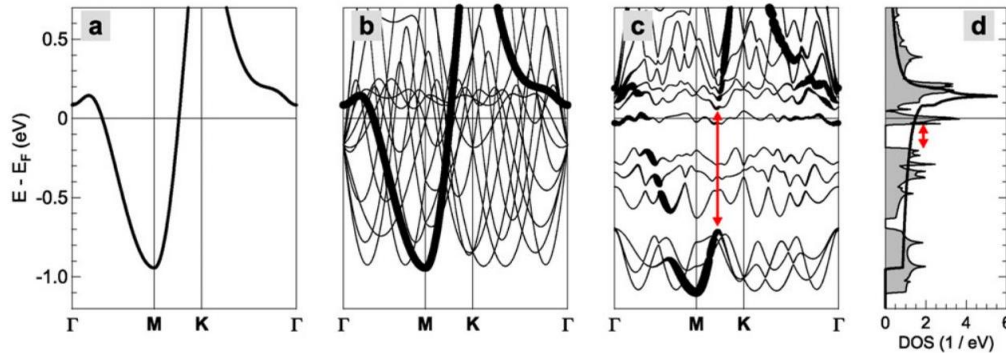


Figure 8. Evolution of the band structure of 1 T-TaS₂ from the unreconstructed(unreconstructed???) to the $\sqrt{13} \times \sqrt{13}$ reconstructed ($\sqrt{13} \times \sqrt{13}$ reconstructed ???) phase.

(a) Unreconstructed band structure. (reminder: understand these M,K, Γ later)

(all questions about it are the same as for fig. 8)

(b) Unreconstructed band structure plus umklapp bands (umklapp bands ??) generated by translation through the reciprocal lattice vectors of the reconstructed Brillouin zone(reconstructed Brillouin zone???) .

(c) Reconstructed band structure with inclusion of the bond strengthenings(bond strengthenings???) within the distortion pattern (for the observed Ta atom displacement of $0.07a$

(how does it connect to the atom displacement???)).

In (c) and (d) the symbol size(symbol size ?) is proportional to the spectral weight carried by the states.

(d) Density of states in the unreconstructed (thick solid line) and reconstructed (filled gray curve) case.

(Do I understand correctly that the area in the 8d is the same of the DOS (before/after)?)

The red arrows mark pronounced gaps in the spectral weight distribution and density-of-states curve.(how does red coincide from c) and d)?)

(WHY 8a LOOKS SO DIFFERENT COMPARING TO 7a???? THIS LOOKS LIKE A PROBLEM INITIALLY, EVEN NOT IN CDW STATE!)

The second step in our scheme is the simulation of the effects (which effects?) of the reconstruction.

This is done as previously described [75, 118, 119]. (how?)

The Hamiltonians of the unreconstructed phases are opened out(how is it, opened out?) into the larger unit cells depicted in figure 4, giving new Hamiltonians with dimension 130 (1 T-TaS₂), 180 (2H-TaSe₂) and 36 (1 T-TiSe₂). (why such dimensions?)

To simulate the reconstruction (=simulate bands in CDW case) , the Slater-Koster hopping d-d, p-d and p– p integrals (what are these integrals?? read a paper about it!) are scaled as r^{-5} , r^{-4} and r^{-3} , respectively, where r is the interatomic distance [123]. (read, why?)

Some bonds within the distortion patterns are thereby strengthened and other bonds are weakened. (the reasoning is missing, however, it is obviously so)

Since the bond-length changes are known from experiment (what we do to know these changes?) , there remain no further disposable parameters in the model.

To keep the analysis as simple as possible, we ignore any slight non-radial atomic movements [62] in the for(which effects non-radial atomic movements can give?) mation of the lattice distortion patterns and, for 1T-TiSe₂, we neglect the reconstruction in the z direction(how is it, reconstruction in the z direction?) .

The third step is to calculate the distribution of spectral weight over the reconstructed band structure. (how exactly knowledge of spectral weight is used in experiments>)

To this end, we have extended the 'spectral function' approach ('spectral function' approach ???) for the simple two-band case, as described in section 2.1, to the case with multiple reconstructed bands (see also [79, 124, 125]).

(by the way, learn about bands. which role do they play? Is a model from Alexandrov and Mott applicable for them???)

If we denote the original 'main' bands by $E_\lambda(\mathbf{k})$, the reconstructed bands by $E'_j(\mathbf{k})$ and the corresponding eigenstates by $|\lambda\mathbf{k}\rangle$ and $|j\mathbf{k}\rangle$ (with band indices λ and j), the total spectral weight carried by the reconstructed eigenstate $|j\mathbf{k}\rangle$ (having energy $E'_j(\mathbf{k})$) is given by $\sum_\lambda |\langle j\mathbf{k} | \lambda\mathbf{k} \rangle|^2$, (it should be an obvious def, if one understands the meaning of spectral weight) i.e. by the projection of the reconstructed eigenvector onto the original eigenvectors.

Thus, the spectral weight distribution function, depending on wave-vector $\mathbf{k}$ and energy ω , becomes (this could be written in scope of the previous sentence)

$$A(\mathbf{k}, \omega) = \sum_{\lambda, j} |\langle j\mathbf{k} | \lambda\mathbf{k} \rangle|^2 \delta(\omega - E'_j(\mathbf{k})) \quad (28)$$

Figures 8,9 and 10 illustrate our tight-binding approach by showing the progressive effects of the CDW/PLD reconstruction on the band structures of 1 T-TaS₂, 2H-TaSe₂ and 1 T-TiSe₂

near the Fermi level. (I don't understand these figures and how they were obtained??? how to calculate these TB effects??? what is the comparison with experiment??? (this may be explained below))

First, the original bands (figures 8(a), 9(a) and 10(a)) are opened out into the larger unit cells creating a 'spaghetti' of umklapp bands (figures 8(b), 9(b) and 10(b)). (how to calculate it?)

These 'shadow' bands are simply obtained by translation through the reciprocal lattice vectors of the smaller Brillouin zones (see figure 4). (obtain at least one of them for practice)

Then, the bond strengthenings and weakenings are introduced (but taking into account what introduces it?) (figures 8(c), 9(c) and 10(c)), which leads to considerable changes: band degeneracies are lifted, bands are shifted, energy gaps are created and spectral weight is redistributed.

Let us now discuss these effects for each compound in more detail.

4.3. Tight-binding results

(SUMMARY: if one does some TB model calculations, then one should get plots as we cited and also, there was a lot of abstract unclear and valueless statement.)

$\sqrt{13} \times \sqrt{13}$ modulation in 1T-TaS₂

(!!!!!! what are the parameters in R. TB models that fit to the experiment??? (write the formula of Hamiltonian + parameters in the 1st part))

In 1 T-TaS₂, the PLD amplitude is the largest and therefore the band structure changes are the most pronounced (the maximum Ta atom displacement is $\sim 0.07a$). (connection of PLD amplitude and band structure changes?)

The reconstructed band structure collapses into submanifolds separated by distinct energy gaps [75, 118] (see figures 8(c) and 8(d)). (why does it collapse?)

There are two low-lying three-band submanifolds, each containing six electrons. (how to check the number of electrons in a band?)

The 'thirteenth' (each Ta contributes approximately one 5d electron. we can see it from knowledge of general structure of a material) electron (there are 13Ta5 d¹ atoms in the reconstructed unit cell) resides in a distinct band at the Fermi level.

Since this band has a small width ($\sim 80\text{meV}$), it is susceptible to a Mott-Hubbard transition, as proposed originally by Fazekas and Tosatti [67] and later confirmed by ARPES [68]. (how is it, susceptible to a Mott-Hubbard transition?? what do we change and what do we see in the experiment?)

We have shown previously that reconstruction and spin-orbit interaction are both essential for the isolated band to occur [118]. (why? do we also have an isolated band somewhere?)

This band represents the important difference compared to the earlier tight-binding results [75] plotted in figure 7(a). (so 7a) was the wrong plot?)

The new results suggest that the Mott-Hubbard-type transition which is connected with (connected with = manifests itself) the nearly commensurate-CDW-commensurate-CDW transition in 1TTaS₂ appears as a consequence of the favorable electronic structure of the commensurate-CDW phase.

Since the observed Mott-Hubbard gap is relatively small [68] (check this observation), its contribution to the stabilization of the commensurate-CDW phase is presumably negligible. (how at all we can evaluate the stabilization?)

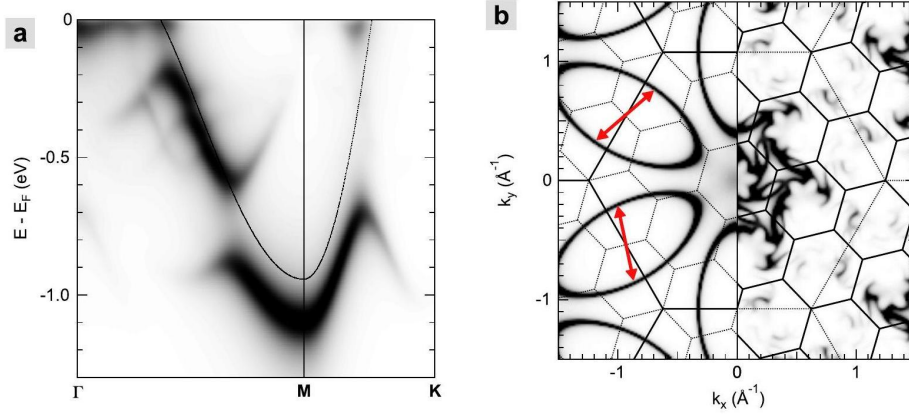


Figure 11. Simulated spectral weight distributions of 1 T-TaS₂.

(a) Band map along $\Gamma - M - K$ in the commensurate $\sqrt{13} \times \sqrt{13}$ CDW state. (how at all to obtain such a blurred plot?)

The solid line refers to the undistorted band dispersion.

(b) Fermi surface map in the normal state (left) and in the commensurate $\sqrt{13} \times \sqrt{13}$ CDW state (right). (is a blurred area a FS or not a FS?)

The Brillouin zones of the normal and reconstructed phases are indicated. (honeycomb lattice??? why is it so??? why there are dashed and non-dashed lines?)

The red arrows mark possible nesting vectors. (learn better, what does it mean? how to plug them to the χ formula?)

As expected, the calculated (how to calculate it?) spectral weight is concentrated along the original main band (figure 8(c)). (why is there a sp. w. above the main band and where there is no band?)

(see fig. 11) To facilitate a better comparison with ARPES results, we show simulated spectral weight distributions in figure 11.

These are obtained by replacing the delta function in equation (28) ($A(\mathbf{k}, \omega) = \sum_{\lambda, j} |\langle j\mathbf{k} | \lambda\mathbf{k} \rangle|^2 \delta(\omega - E'_j(\mathbf{k}))$) with a Lorentzian of 100 meV full width at half-maximum. (can we do it from physical point of view? numerically - of course, it makes sense)

Both the $A(\mathbf{k}_{\parallel}, E)$ band map along $\Gamma - M - K$ (figure 11(a)) as well as the $A(\mathbf{k}_{\parallel}, E_F)$ Fermi surface map (figure 11(b)) are in good qualitative agreement with the results of ARPES measurements (see [108-111]). (we see it for 11a, for 11b, I just believe it, I can check the cited literature)

Unfortunately, ARPES cannot resolve the predicted fine details (predicted fine details??) because of lifetime and resolution effects, although recently shadow band dispersions exhibiting the CDW periodicity have been detected [110, 111] (how this shadow band dispersions were detected and that is their meaning?) .

Two features reproduced by the simulation are remarkable: the large spectral weight gap along the M-K direction (figures 8(c) and 11(a)) (he meant $\Gamma - M$ direction) and the related strong spectral weight suppression in the Fermi surface map near the Brillouin zone boundary (figure 11(b)) (=this big change of FS) .

The tight-binding simulation shows that both effects are natural consequences of the lattice distortion in the CDW phase (how to use TB model for CDW+PLD?) ; electron localization or photoemission matrix element effects (how they could possibly explain it?) are not required for their explanation [107].

It should be pointed out that the large spectral weight gap along M-K (I don't see a gap there, there is just one band...) is not the CDW gap, although it occurs in a region of $\mathbf{k}$ space

where large parallel parts of the elliptical Fermi contours are spanned by the observed CDW wave-vector (I don't see it unfortunately, I need to learn better the BZ and then find this vector k) and therefore significant Fermi surface nesting may be expected (see red arrows in figure 11(b)). (one might apply the FSN for this distortion to get the gap, but it will not work out) (why do we have two arrows, are there two wave vectors?)

The 'true CDW gaps' are rather the gaps between the subband manifolds. (how is it???)

We emphasize that it is the energy lowering of the two low-lying three-band submanifolds that stabilizes the commensurate CDW/PLD (how does lowering energy results in the stabilization of the CDW??) , and not the lowering of states at E_F .

In fact, in the tight-binding calculation the density of states at E_F even increases in the CDW phase, due to the emergence of the distinct and narrow band straddling (= sit or stand with one leg on either side of) the Fermi level (figure 8(d)). (narrow band = small kinetic energy, so potential energy is bigger and electrons localize)

By summing over all occupied states, we find a relatively large total electronic energy gain of 160 meV per Ta atom for the experimentally observed PLD amplitude. (and when then the rest energy going when PT occurs? to the heating of the system?)

3×3 modulation in 2 H -TaSe₂.

(!!!!!! what are the parameters in R. TB models that fit to the experiment??? (write the formula of Hamiltonian + parameters in the 1st part))

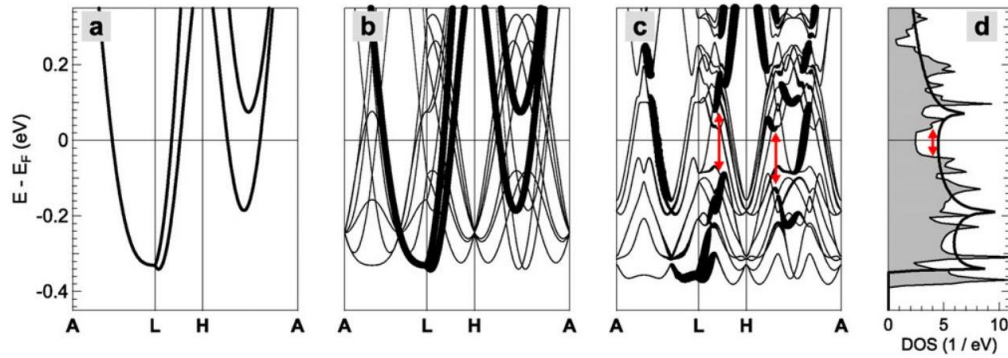


Figure 9. Evolution of the band structure of 2H-TaSe₂ from the unreconstructed to the 3×3 reconstructed phase. (same as fig. 8, but for another material and also without DOS, but with strange x2 distortion)

(a) Unreconstructed band structure.

(all questions about it are the same as for fig. 8)

(b) Unreconstructed band structure plus umklapp bands generated by translation through the reciprocal lattice vectors of the reconstructed Brillouin zone.

(c) Reconstructed band structure with inclusion of the bond strengthenings within the distortion pattern (for the observed Ta atom displacement of $0.015a$).

In (c) and (d) the symbol size is proportional to the spectral weight carried by the states.

(d) Density of states in the unreconstructed (thick solid line) and reconstructed (filled gray curve) case. The red arrows mark pronounced gaps in the spectral weight distribution and density-of-states curve.

(why fig. 9 has ALH and fig. 8 has MKT?)

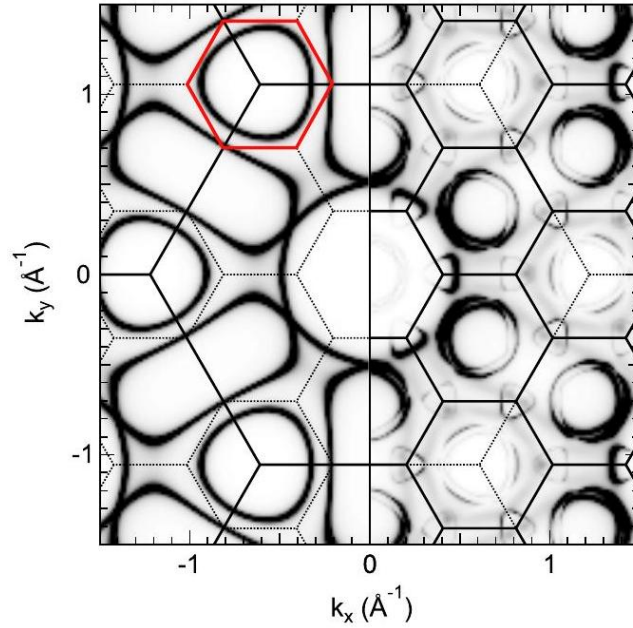


Figure 12. Simulated Fermi surface maps of 2H-TaSe₂ in the normal state (left) and in the commensurate 3×3 CDW state (right). (what lead to such differences wrt TaS₂?)

The Brillouin zones of the normal and reconstructed states are indicated. (as before)

The small Brillouin zone highlighted in red emphasizes the near match with the normal-state Fermi surface pocket centered on the K(H) point. (and what are these consequences of such match??? I don't understand them)

(why fig. 7b and left of fig. 12 are so different????!!!!!! the TB model gives a very approximate results?)

In 2H-TaSe₂, the maximum displacement of the Ta atoms in the CDW phase ($\sim 0.015a$) is about a factor of five smaller than in 1T-TaS₂. (I suppose it is known from some measurement which was cited in the precious page)

Consequently, the electronic structure changes are less dramatic. (is it explained?)

The reconstructed band structure does not collapse into submanifolds (figure 9) (I don't see it, looks like they still collapse to submanifolds) and the reconstructed Fermi surface (in the repeated zone scheme) retains much more resemblance to the original Fermi surface (figure 12) (so what? the change in FS is still big) .

Nevertheless, the PLD-induced changes are significant. (it was already written)

The Fermi surface pocket around K(H) is destroyed (red arrows in figure 9(c)) (why red arrows mean that Fermi surface pocket is destroyed?) , the M(L) dogbone is broken up (figure 12) and the new Fermi surface consists of (doubly degenerate) pockets centered on the new $\Gamma(A)$ points (why on $\Gamma(A)$ points? basically it is a question of connection fig. 12 and fig. 9) and of small rounded triangles around the new K(H) points (figure 12).

(why at all R. writes two points? like K(H))

Note that the calculated spectral weight distribution at E_F shown in figure 12 agrees remarkably well with the ARPES results (figures 6(b) and 7(b)) (I would say, to some extent, they agree) .

It is tempting to associate the occurrence of the 3×3 CDW/PLD in 2H-TaSe₂ with the near coincidence of the K(H) Fermi surface pocket with the edges of the new Brillouin zone (see the red hexagon in figure 12) (what is tempting to do??? why???) .

This scenario would be in direct analogy with the Peierls instability (I don't know how possibly to use that theory, so I can't comment much) in one dimension, where, however,

the coincidence between Fermi surface and new Bragg planes(Bragg planes?? it is first time mentioned here) is exact (see section 2.1).

Since gaps are created in the band structure near the new Bragg planes, the K(H) pocket will readily disappear when the 3×3 PLD sets in. (understanding a connection btw FS and gaps is needed to understand this)

The opening of the pseudogap in the density of states near E_F (marked by a red arrow in figure 9(d)) is the consequence. (I have no idea why is it so?)

Yet, one cannot claim that the CDW/PLD instability is purely Fermi-surface-driven, because the occupied states well below E_F contribute significantly to the total electronic energy gain (see figure 9(d)). (are there some formulas for contribution of energy from different bands? how to derive it?)

For the experimentally observed PLD amplitude, the calculated band structure energy lowering is 20 meV per Ta atom (how to calculate it? $\delta E(u_{max})$???) , in good agreement with the value of 26 meV per Ta atom reported in [126] (check there this plot, since in this paper there is no experimental plot, only a theoretical one for bands for this material) .

2×2 modulation in $1T - \text{TiSe}_2$.

(!!!!!! what are the parameters in R. TB models that fit to the experiment??? (write the formula of Hamiltonian + parameters in the 1st part))

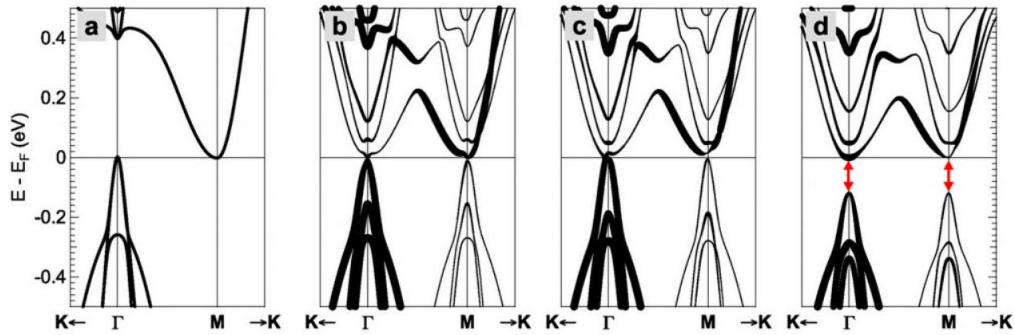


Figure 10. Evolution of the band structure of $1T - \text{TiSe}_2$ from the unreconstructed to the 2×2 reconstructed phase. (same as fig. 8, but for another material)

(a) Unreconstructed band structure.

((b)-(d)) Reconstructed band structure with inclusion of the bond strengthenings within the lattice distortion pattern:

(b) zero distortion amplitude,

(c) the observed distortion amplitude (corresponding to a Ti atom displacement of $0.024a$)

and (d) twice the observed distortion amplitude.

In (b)-(d) the symbol size is proportional to the spectral weight carried by the states.

The red arrows highlight the opening of the Se 4p-Ti 3d bandgap.

In $1T - \text{TiSe}_2$, the maximum displacement of the transition metal is $\sim 0.024a$, about 1.5 times larger than in $2H - \text{TaSe}_2$ and about a factor of three smaller than in $1T - \text{TaS}_2$. (it is known from some experiment reported in some article)

The relevant electron states (of Se 4p and Ti 3d character) are confined to small volumes(confined to small volumes??? how and why???) in $\mathbf{k}$ space in the center and on the face of the Brillouin zone.

The CDW superlattice unit cell is the smallest for the three compounds so that the number of umklapp bands is the lowest. (connection of length of unit cells and number of bands?)

Nevertheless, the band structure changes due to the PLD(why due to the PLD?) are not less intricate (=having many small parts) .

For undistorted 1T-TiSe₂, we assume the band line up depicted in figure 10(a).

There are three hole-like Se 4p bands around Γ – two degenerate Se 4p_{x,y} bands comprising the valence band maximum and one Se 4p_z band at lower energy – and one electron-like Ti 3d band around M(L). (again, the question about names of bands)

Note that spin-orbit coupling and band dispersion in the layer-perpendicular direction are neglected in the calculation. (how the formulas for the case of spin-orbit coupling and band dispersion should look like?)

The indirect Se 4p - Ti 3d bandgap is set to zero, as a compromise between the latest ARPES results [11, 86-89, 115, 116] (I understand it like they tune TB parameters such that this initial band structure is there) .

In the folded-out band structure, the Ti 3d band becomes threefold-degenerate, as there are three independent M(L) points(three independent M(L) points ????) in the first Brillouin zone.

Remarkably, this degeneracy and also the Se 4p_{x,y} degeneracy at Γ are lifted (I assume R. means that bands go lower, but the other bands are upper comparing to the lowest one?) in the reconstructed band structure already for zero distortion amplitude (figure 10(b)).

There are now three separate Se 4p bands and three separate Ti 3d bands at the equivalent Γ and M(L) points(on the fig. 10 there are way more than 3 conduction bands, why??) , but the p-d gap remains zero.

It even stays zero when the PLD amplitude is increased to the experimentally observed value (figure 10(b) (it is meant 10(c))), the major effect being that the relative band edge positions within the Se 4p and Ti 3d manifolds are changed.

For twice the observed distortion amplitude(twice the observed distortion amplitude??) , however, a p-d gap of ~ 100 meV opens up, as indicated by the red arrows in figure 10(d).

This gap value is in good agreement with ARPES measurements (figure 7(c)). (in 7c, there are 2 valence bands, here we have 3, why????)

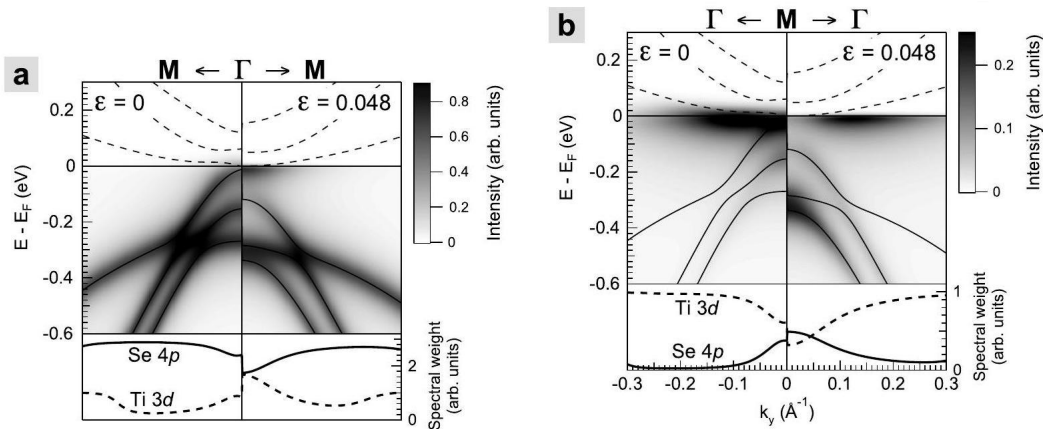


Figure 13. Simulated spectral weight distributions of 1 T-TiSe₂ for the commensurate 2×2 CDW state:

- (a) around the Γ point and
- (b) around the M(L) point.

On the left, the Ti atom displacement relative to the in-plane lattice parameter is zero; on the right, it is 4.8% (i.e. twice the experimentally observed value).

The spectral weight functions are multiplied by a Fermi-Dirac cutoff(multiplied by a Fermi-Dirac cutoff???) .

Se 4p bands are denoted by solid lines and Ti 3d bands by dashed lines.

In the bottom panels, the total spectral weight carried by each band manifold is shown. (how to calculate a sp. weight?)

(description of change of bold lines:) Upon increasing the maximum Ti atom displacement from zero to $0.048a$, spectral weight is continuously transferred from the Se 4 p to the Ti 3 d states at Γ and vice versa at M(L) (figures 10(b)-(d)).

For better comparison with ARPES results, figure 13 shows calculated spectral weight distributions for the interesting regions around the Γ and the M(L) point.

The qualitative agreement between the measured and simulated band maps is good (see figure 7(c)) (except upper than E_F bands) .

Among the key features that are reproduced by the tight-binding model are-near Γ (figure 13(a)) - the flattening of the Se 4 p valence bands (we can't see it from fig. 6 and fig. 13, we need to believe it) , the loss of spectral weight near the valence band maximum, the appearance of Ti 3d spectral weight near E_F and-near M(L) (figure 13(b)) - the occurrence of intense folded valence bands and an E_F intensity maximum away from the symmetry point [11].

A striking result is the strong spectral weight transfer at the high-symmetry points (i.e. to a point M, I don't see many points there) (see the bottom panels of figures 13(a) and (b)).

For a Ti atom distortion (calculated distortion ??? how to calculate it??) only twice as large as the observed one, the total spectral weight carried by the shadow bands at Γ and at M(L) is larger than that of the original bands.

This is in contrast to [11], where it has been argued that the atomic displacements in the CDW phase of 1TTiSe₂ are far too small to produce significant spectral weight transfer to the shadow bands (why distortions are connected to a sp. w. transfer?) .

What are the implications of these results on the CDW mechanism(mechanism???) in 1T-TiSe₂ ?

In principle, the tight-binding model confirms the scenario proposed in [87](check this paper!) (figure 7(c)). (=explains well experiment)

The PLD causes a splitting of the degenerate Ti 3d conduction band and Ti 3 d-Se4p band repulsion leads to a lowering of the top of the valence band and thereby of the total band energy. (wqhy??? which formulas are assumed by "band repulsion leads to band lowering"???)

A novel feature revealed in the present study is the PLD-induced splitting of the top two Se 4p bands (so people were not detecting the splitting of the top two Se 4p bands???) .

Note that in ARPES studies this splitting has commonly been attributed to spin-orbit interaction alone [127]. (lear SO for TB models for bands)

Since CDW fluctuations are known to affect the normal-phase band structure (CDW fluctuations affect band structure????) of 1T-TiSe₂ as seen by ARPES, it seems not unreasonable that there is a significant CDW-induced contribution to the observed p-band splitting (CDW-induced contribution to band splitting ?????) even at room temperature.

As to the origin (don't believe R., when he speaks about "origin", he never gives a clear answer about it) of the CDW/PLD in 1T-TiSe₂, two issues are the most pressing (=urgent) .

First, as the $\mathbf{k}$ -space volume involved in the transition($\mathbf{k}$ -space volume involved in the transition???) appears to be small, one may ask whether the observed changes in the electron energies near E_F are sufficient to drive the transition. (again, nothing is clear, which "driving" is meant?)

By summing over all occupied states in the energy range from -0.6 eV to $E_F = 0$, we obtain a band energy gain of $\sim 20\text{meV}$ per Ti atom. (try to sum over all occupied states later for practice)

This value agrees fairly well with the 27 meV per Ti atom reported in [23] (check the band energy gain in it) and it is comparable to the value obtained for 2 H TaSe₂ (and what is the band energy gain for this material?) , the compound with somewhat similar PLD amplitude and transition temperature.

So, stabilization of the CDW/PLD by the one-electron total energy change appears to be possible. (link to this conclusion is missing)

The second question is whether the PLD is solely responsible for the observed changes ('pure' Peierls instability) or whether there is a significant excitonic contribution (significant excitonic contribution??? what is the formula??) (combined Peierls-excitonic insulator instability [128-130]).

Our tight-binding results suggest the latter.

The most significant ARPES result for reconstructed 1T-TiSe₂ is the opening of the relatively large p-d gap and this is not reproduced by the present model until the Ti atom displacement reaches twice the experimentally observed value. (IMPORTANT CONCLUSION WHICH I MISSED, THAT WE NEED TO INPUT THIS X2 DISPLACEMENT AND THEN WE'LL GET GOOD PREDICTION WITH TB MODEL. LOOKS LIKE A COINCIDENCE.) (HOW WELL THIS WAS TESTED???)

Summary

(SUMMARY: we see many changes in bands, and there are some ideas, which R. believes in and there are cited papers which explain them better)

(something is known now=) To sum up, the magnitude, **k** dependence and origin of the CDW gap in the layered transition-metal dichalcogenides were at the focus of many ARPES studies in the past.

(fig. 7 summarizes main features) For the three selected compounds 1T-TaS₂, 2H-TaSe₂ and 1T-TiSe₂, quantitative results, when available, have been summarized in figure 7.

We find it remarkable that the key features (what exactly can be reproduced?) of these results can be reproduced by empirical tight-binding calculations.

Considering the simplicity of the model, the similarity between simulated spectral weight distributions and measured ARPES intensity maps is striking. (aren't we just fitting the TB model to experimental results by the way?)

The tight-binding results corroborate (=give extra proof) that CDW gapping in the three compounds is large, not restricted to a small interval around the Fermi energy and strongly **k**-dependent. (I did not understand the reasoning of it from this article, see cited papers)

There is not one uniform gap opening up at the Fermi energy (how to derive it from theory?) ; rather subbands are shifted over extended parts of the Brillouin zone.

The results also demonstrate that the observed band structure changes lower the total energy of the electron system significantly and that they are a natural consequence of the observed atomic distortion patterns. (again, link btw atomic distortions and band structure changes is missing)

The concept of Fermi surface nesting was not relevant in the analysis (forgot, why exactly it is not working?) , although some connection between the band structure near the Fermi level and the observed CDW/PLD wave-vectors can be drawn for all three compounds.

4.1.6 5. Why do CDW/PLDs occur in the layer compounds?

(abstract intro=) One can try to understand the occurrence of CDW/PLDs in the layered transition-metal dichalcogenides, in general, on different levels of sophistication.

In the simplest approach, the observed CDW/PLD wave-vectors may be rationalized from the $\mathbf{k}$ -space geometry of the electronic structure in a narrow energy window around E_F (I guess it is meant here that unclear idea about that red vectors that somehow will contribute later to χ more) or the CDW/PLD formation may be qualitatively explained by analyzing the observed lattice distortion patterns (I guess it is meant that TB recalculation of energy bands from a new distortion. Nothing is new is written here.) .

On a higher level, the question of whether a CDW/PLD should occur at all may be answered by considering the balance between band structure energy gain and elastic energy cost (this is a well-known method, discussed before) within simplified zero-temperature models. (is it known how to generalize this analysis for a finite temperature?)

But finally, for a prediction of the CDW/PLD transition temperatures, a full microscopic theory at finite temperatures is necessary (= it means basically "a better approach is needed") .

Here, we will proceed along this line, from the simple to the more sophisticated explanations. (= we'll try to develop a microscopic mechanism)

(we all know that there are a lot of factors =) We emphasize that there need not be one underlying CDW mechanism for the compounds we have concentrated on; the formation of the different CDW/PLD superstructures may easily be caused by different driving forces, particularly because the electronic structures and resulting transport properties of the three selected materials are so different.

(here is some motivation:) Yet, a unifying explanation would be nice and, eventually, all three CDW systems belong to the same family of compounds and electron-phonon coupling is strong in all of them.

(abstract useless sentence:) As has been pointed out previously [131, 132], the general occurrence of CDW/PLDs in these materials makes it seem reasonable that the phenomenon is based on general features rather than specific and subtle properties of the band structure.

Our working hypothesis will thus be that the physical picture provided by the Peierls model, as detailed in section 2 (DIDN'T R. WRITE A LOT OF TIMES THAT NO, THIS IS A BAD MODEL????) , is in principle correct for 1 T-TaS₂, 2H-TaSe₂ and 1 T-TiSe₂ and that the occurrence of the CDW/PLDs can be understood on the basis of a few measured and calculated parameters, such as T_0 , $\mathbf{q}_0$, u_0 , $\chi_0(\mathbf{q}_0)$ and $2g_{\mathbf{q}_0}^2/\hbar\omega_{\mathbf{q}_0}$.

(I promise you, I'll tell you soon something valuable:) Naturally, this semi-quantitative approach is still overly simplistic, but it may be instructive anyway, given that the involved concepts and arguments are so commonly applied.

(I promise, I'll do a summary which maybe one day someone will use:) It is an approach reflecting an experimentalist's view and the hope is that a hierarchy of factors determining CDW/PLD formation in the layered compounds can be established.

5.1. Qualitative explanations

Qualitative explanations of CDW/PLD formation are typically based on two extreme limits of the same physical phenomenon (of electron phonon interaction. anyway, it is intro to what is below) [38, 39] (see section 2.2). (how to write these limits as a formula????)

When the CDW/PLD amplitude is small, a metallic bonding picture applies (how to tell in formulas that we have a metallic bonding picture?) ; the coherence length is long, the energy gap small, the CDW/PLD often incommensurate and the transition is driven by an instability of the Fermi surface (transition is driven by an instability of the Fermi surface???) .

At the other extreme, when the CDW/PLD amplitude is large, an ionic-covalent bonding picture (ionic-covalent bonding picture???) is more appropriate; the coherence length is short,

the energy gap large, the CDW/PLD tends to be commensurate and the driving force of the transition (I don't understand which formula is meant by "driving force btw transition") is a tendency to form shortened bonds between neighboring atoms such that the sum of the energies of shortened and lengthened bonds is lower than the energies of the normal bonds(how to understand it in formulas) .

The tight-binding results presented in the previous section can essentially be understood in the spirit of such a local-chemical-bonding picture. (GPT says that local-chemical-bonding is another name for a TB model, I'll check later)

1 T-TaS₂ is an example for how one passes from one extreme to the other by lowering the temperature. (it is a paraphrasing that we have a PT)

For the incommensurate CDW/PLD in the hole-doped compound 1T-Ta_{1-x}Ti_xS₂ ($0 \leq x \leq 1$), electron diffraction has revealed a direct relationship between the size of the Fermi surface(why the size of the Fermi surface is that x ???) and the CDW/PLD wave-vector $\mathbf{q}_0$, $|\mathbf{q}_0| \propto \sqrt{1-x}$ [56]. (it is a very strange dependence!!!! check it!!! why is it so????? I have no idea how to take into account impurities in this model)

(I don't understand this comment below about driving force from the formula formula the previous sentence) As such a correlation(which correlation???) is expected for a nesting vector across the M centered elliptical Fermi surface pocket (see figure 11) shrinking as a function of hole doping x (why shrinking as a function of x ????) , the experimental finding strongly supports the idea of Fermi surface nesting as the driving force of the normal-to-incommensurate CDW/PLD phase transition.

On the other hand, X-ray photoelectron spectroscopy [133] and scanning tunneling microscopy [134] measurements as well as model calculations [75] suggest that 1 T-TaS₂ in the commensurate phase can be regarded as a mixed valence compound(mixed valence compound???? is it important? why "from other hand"?) since there are inequivalent Ta sites differing by up to $0.4e^-$ per atom.

(similar abstract unclear statement to statements before:) This indicates a dominant role of the local bonding properties in the transition.

(reminder of what we already know:) In terms of local bonding energies, the transition is understood as follows: 13 Ta atoms form a star-shaped cluster (figure 4) in such a way that the occupied Ta $5d_{xy}$ levels split into three submanifolds with collectively lower energy [24, 67, 75, 118](check citations!) (figure 8).

For 2H-TaSe₂, similar explanations can be given.

ARPES measurements [84, 85, 113] suggest that the observed CDW/PLD wave-vector is consistent with partial nesting of the K(H) Fermi surface pocket with the M(L) dogbone and with the Γ (A) pocket (see figure 12). (maybe this is how this works: we find some ellipses in FS, then find a vector that connects parts of the ellipses, and this is the CDW vector and the gap will be on it? maybe this was this main idea of looking at the BZ plot?)

(reminder of new FS, which we have discussed =) Moreover, figure 12 illustrates that the Fermi surface around the K(H) point is very near to the faces of the novel Brillouin zone produced by the PLD.

This is in close analogy to the archetypal 1D scenario of perfect nesting, in which a Peierls instability is bound to occur (see figure 1). (I wasn't thinking about it in these terms... how does this typical 1D scenario look in ideal case for 2d system?) (maybe the idea is that FS is on the new BZ, so that is why the gap appears and the new DOS are below this FS?)

Since Brillouin zone faces are planes of energy discontinuity (why planes of energy discontinuity??) , one expects large energy gapping on the K(H) pocket (this is about this circles around K points, they appear and they have a gap at the like of initial BZ) and this is indeed

what is observed [84, 85](check articles) .

On the other hand, the occurrence of the 3×3 CDW/PLD may also be explained by looking at the lattice distortion pattern in the Ta plane [24] (figure 4). (I don't think that we explain something here, it is just a confirmation of the PLD by direct measurement)

There, nine-atom(why nine-atom ???? I see 7 in the fig. of their change...) clusters are formed, leading in the electronic structure to a splitting of the Ta 5 $d_{x^2-y^2,xy}$ manifold (why exactly of this manifold?) into two submanifolds. (trace this statement to the plot, I don't yet imagine it)

The lower one is associated with shortened and the upper one with lengthened metal-metal bonds. (how does a submanifold connect to the change of length of a bond???)

(we calculate energy of the final CDW state, it is lower, however one can save another less clear description of it:) Since the Fermi level falls in the (pseudo-)gap between the two corresponding density-of-states peaks (see figure 9), the distorted structure is energetically more favorable.

In 1 T-TiSe₂, the situation is different. (we will be told that now there is an interaction between bands)

(FST is impossible for this FS =) The Se 4p and Ti 3d Fermi surface pockets (if they exist at all) are small and exhibit different sizes and anisotropies so that Fermi surface nesting can be ruled out.

Nevertheless, the band structure topology is suggestive of the observed CDW/PLD wave-vector, since $\mathbf{q}_0$ connects the Se 4 p valence band maximum at Γ with the Ti 3 d conduction band minimum at L (I guess it is meant in "M", since on fig. 10, there are only Γ , K, M points) . (I have no idea how to get the CDW vector from BS. I'll ask someone for examples later)

The resulting direct p-d interaction is a key element in the CDW/PLD transition. (how is the p-d interaction included in the transition???)

Because the band edges are close in energy, p-d hybridization (hybridization?) occurs and the occupied p states are pushed to lower energies, thereby stabilizing the CDW/PLD state. (I guess it means that there is a repulsion of electrons on a near bands,so the push lower electrons even lower and the energy decreases) (how to describe it mathematically?)

The often discussed question is whether the p-d interaction is phononic [23, 24, 47, 135, 136] or electronic (excitonic) [11, 137-140] in origin (= overview of approaches to this effect) .

When the coupling occurs via phonons (coupling occurs via phonons???) , the transition is seen as a (Peierls-like) Jahn-Teller band instability and the one-electron total energy change connected with the PLD is the driving force.

In terms of chemical bonding, the Se 4p band energy lowering can then be linked to the Ti-Se bond shortening in the observed distortion pattern [24] (figure 4). (here is an idea about chemical bonding picture, to understand it, I need to read this article about this approach!)

(but excitonic insulator model is also applicable =) If, on the other hand, the p holes and d electrons are coupled via direct Coulomb interaction, one has the excitonic insulator scenario described in section 2.4 and the exchange-correlation energy change associated with the CDW is an important factor (exchange-correlation energy change associated with the CDW???) .

The instability is then primarily electronic, even though it will be accompanied by a PLD due to finite electron-phonon coupling (= for some reason, the lowering of electronic energy is way bigger than the increase in the deformation energy) .

Both models (Jahn-Teller band instability and excitonic insulator model) can qualitatively explain the CDW/PLD phase transition in 1T-TiSe₂. (learn, what is meant by these models???)

(maybe here is meant "to develop better theory that uses strong EP, it is better to start with Jahn-Teller band instability ":) In view of the strong electron-phonon coupling in

this material, however, the Jahn-Teller band instability seems more natural, although our tight-binding calculations have indicated that the experimentally observed lattice distortion amplitude is not sufficient to produce the p-d gap seen by ARPES.

This leaves room for a significant excitonic contribution [128-130]. (maybe here is meant "and excitonic contribution should also be there". it contradicts the previous sentence, but no one cases)

In summary, the ideas presented here may have some merit (=good quality, value) in qualitatively explaining why the observed CDW/PLD phases may occur in the three selected compounds.

It is clear, however, that their success originates in knowing beforehand what is going to be explained. (yes, this is the important idea of this articles, that we already know parts of the results and reproduce only another part)

The concepts of Fermi surface nesting and local chemical bonding have very limited predictive power regarding the CDW/PLD wave-vectors and they definitely cannot predict whether the CDW/PLD phase transitions should occur at all. (important statement! FSN and LCB give only the change of a spectra. it is well-known, prediction of the transition itself is an unsolved problem)

Also, in a general situation, it does not seem reasonable to separate Fermi surface and local bond contributions (how we could have separated them??) [131] or, with regard to 1T-TiSe₂, one-electron and exchange-correlation energy (how we could have separated them??) contributions [38].

Consequently, we now move on to less specific, more quantitative microscopic models. (which?)

5.2. Existence of a CDW/PLD at $T = 0$

If a CDW/PLD is to occur at all, there must be a total energy gain(gain= the system in CDW should have a lower energy) resulting from distorting the lattice at $T = 0$: The electronic energy gain $\delta E_{\text{electrons}} < 0$ arising from the band structure and exchange-correlation energy change has to overcome the lattice energy cost $\delta E_{\text{lattice}} > 0$, (why the signs are such? I am not sure) i.e. $\delta E_{\text{total}} = \delta E_{\text{electrons}} + \delta E_{\text{lattice}} < 0$.

Whether the energy balance is indeed negative can, for example, be tested by using the Chan-Heine criterion, equation (9) ($\frac{4g_{\mathbf{q}}^2}{\hbar\omega_{\mathbf{q}}} - 2U_{\mathbf{q}} + V_{\mathbf{q}} \geq \frac{1}{\chi_0(\mathbf{q})}$) (and how???) , or by comparing the calculated one-electron band energy change with a phenomenological lattice energy term(I understand that we need to compare them, but it is not written, how???) .

Here we will do both.

The first approach has the advantage that it includes all relevant factors (which factors?) ; but the electronic energy change is derived from perturbation theory and $\mathbf{k}$ dependence is neglected.

In the second approach, on the other hand, the band structure energy change is more realistic (more realistic????) ; but the effects of electron-electron interactions are neglected (are electron-electron interactions important?) .

In order to check the Chan-Heine condition (9) ($\frac{4g_{\mathbf{q}}^2}{\hbar\omega_{\mathbf{q}}} - 2U_{\mathbf{q}} + V_{\mathbf{q}} \geq \frac{1}{\chi_0(\mathbf{q})}$) , we have to estimate the involved microscopic quantities (another thing is to extract the U and V from the microscopic quantities, how??) for the three selected materials: 1T-TaS₂, 2H-TaSe₂ and 1T-TiSe₂.

The results, from this work and compiled from the literature, are summarized in table 5.

The values for the electronic susceptibility $\chi_0(\mathbf{q}_0)$ are derived from calculated or measured band structures (don't understand, derive the $\chi_0(\mathbf{q}_0)$) and the electron-phonon coupling term $2g_{\mathbf{q}_0}^2/\hbar\omega_{\mathbf{q}_0}$ (don't understand, derive the $2g_{\mathbf{q}_0}^2/\hbar\omega_{\mathbf{q}_0}$) is deduced from the measured superconducting transition temperature T_{SC} .

(below it is written that the idea is that we can take the EP coupling for Tc if we had an SC transition, but it is there only for higher pressures, so we'll estimate it for this case and then think that at lower pressure where there is an insulating state, the EP coupling is the same. This is a really bad approach, because EP coupling might change drastically, we don't know it, no arguments are provided for it. but technically we measure Tc and then use McMillan's formula to extract λ)

This approach follows [49]. (check it)

Note that 1 T-TaS₂ and 1 T-TiSe₂ are not superconducting under 'ambient' conditions, but that superconductivity can be induced by hydrostatic(hydrostatic? I thought it was from air, not from liquid. check) pressure in 1T-TaS₂ [12] and by Cu intercalation in 1T-TiSe₂ [9] - in both cases via suppression of the CDW/PLD phase (via suppression of the CDW/PLD phase? it means that we have a CDW and SC at the same time?) .

We assume here that the novel superconducting states are somewhat characteristic of the pristine, undistorted compounds.

Table 5. Microscopic parameters for the layered CDW compounds 1 T-TaS₂, 2H-TaSe₂ and 1 T-TiSe₂, as determined from theory and experiment: the non-interacting electronic susceptibility as determined from band structure (how to get this χ_0 ?) , electron-phonon coupling parameters as derived from the superconducting transition temperature T_{SC} and band versus lattice energy terms from simple models. (how for example this table can be used???)

	1 T-TaS ₂	2H-TaSe ₂	1T-TiSe ₂
Electronic susceptibility			
$\chi_0(\mathbf{q}_0)/\chi_0(0) - 1$	58% ^a	35% ^b	<3% ^c
$1/\chi_0(\mathbf{q}_0)$ (eV/ state) ^d	0.7-0.9	~ 0.6	1.3-2.2
Electron-phonon coupling			
T_{SC} (K)	5 ^e	0.15 ^f	4.15 ^g
$\lambda_{\text{McMillan}}$ ^h	0.85	0.49	0.80
$4g_{\mathbf{q}_0}^2/\hbar\omega_{\mathbf{q}_0}$ (eV/ state) ⁱ (what is $\omega_{\mathbf{q}_0}$??)	1.0 – 1.2 ^j	1.3 – 1.5 ^k	1.6 ^l
Band versus lattice energy			
$-\Delta E_{\text{band}}$ (meV) ⁱ	160 ^m	20 – 26 ⁿ	20 – 27 ^o
$-\Delta E_{\text{band}}/\langle u \rangle^2$ (eV Å ⁻²) ^p	3.4 ^q	11.3-15.3	3.7-5.0
$\frac{1}{2}M\omega_{\mathbf{q}_0}^2$ (eV Å ⁻²) ^r	10.0	6.5	2.7

^a Reference [45]. ^b Reference [114]. (task for practice: check some values from this table!!!) ^c Reference [47].

^d Per transition-metal atom; using $\chi_0(0) = \frac{1}{2}N(0)$ with $N(0)$ values from table 4.

^e For $p > 3\text{GPa}$ [12]. ^f Reference [18]. ^g For Cu_{0.08}TiSe₂ [9].

^h Using McMillan's formula, equation (29) [141], with $\mu^* = 0.2$.

ⁱ Per transition-metal atom.

^j Using $N(0)$ from LDA, table 4.

^k Using $N(0)^*$ from specific heat, table 4.

^l Using $N(0)^* = 1.8$ states /eV u.c. from specific heat [9].

^m This work. ⁿ This work and [126]. ^o This work and [23].

^p Per transition-metal atom; $\langle u \rangle^2$ is the average squared displacement of the transition-metal atoms in the CDW/PLD state. ^q See also [142].

^r Using the mass of the transition-metal atom for M and the Debye frequency for $\omega_{\mathbf{q}_0}$.

The possibility to estimate the electron-phonon coupling term $2g_{\mathbf{q}}^2/\hbar\omega_{\mathbf{q}}$ (why $\omega_{\mathbf{q}}$ is included already?) from T_{SC} arises because this term appears in the formula for the electron-phonon coupling parameter λ for both the Peierls instability (equation (16) ($\lambda = \frac{2g_{\mathbf{q}_0}^2 N(0)}{\hbar\omega_{\mathbf{q}_0}}$)) and BCS superconductivity [141]. (but how do we know that BCS model is applicable for this material?? maybe some generalization is applicable?)

In the case of a CDW/PLD, however, the term is taken at the specific wave-vector $\mathbf{q} = \mathbf{q}_0$, while for superconductivity it is an average over all wave-vectors. (this is what I don't understand. In SC we have just g , not $g_{\mathbf{q}}$. I don't know a derivation with $g_{\mathbf{q}}$, but okay, intuition tells me that it will be the averaging)

We assume that the difference is not substantial. (anyway, R. writes that they don't care about this detail)

For all three compounds, the measured superconducting transition temperatures are listed in table 5 together with the electron-phonon coupling parameters $\lambda_{\text{McMillan}}$ obtained from the formula [141] (how to derive it? is it the standard formula for BCS+ Coulomb repulsion? Why 1.04 is here? it is more about the theory of SC, since in Levitov Shitov there is another formula and I wasn't thinking enough about it)

$$\lambda_{\text{McMillan}} = \frac{1.04 + \mu^* \ln \left(\frac{\Theta_D}{1.45T_0} \right)}{(1 - 0.62\mu^*) \ln \left(\frac{\Theta_D}{1.45T_0} \right) - 1.04} \quad (29)$$

To determine $\lambda_{\text{McMillan}}$, we assume a Coulomb pseudopotential $\mu^* = 0.2$ (why $\mu^* = 0.2$??) and use the Debye temperatures Θ_D listed in table 4. (check that values later, derive some of them for practice)

From $\lambda_{\text{McMillan}}$, in turn, $4g_{\mathbf{q}_0}^2/\hbar\omega_{\mathbf{q}_0}$ is estimated via equation (16) ($\lambda = \frac{2g_{\mathbf{q}_0}^2 N(0)}{\hbar\omega_{\mathbf{q}_0}}$) using appropriate values of the density of states at the Fermi level, $N(0)$ (and how to get the $\omega_{\mathbf{q}_0}$???)

These ($N(0)$) are determined from calculated band structures or specific heat measurements (example, how?) and in each case reflect the nature of the state that becomes superconducting (with either an existing or a suppressed CDW).

The remaining terms in condition (9) ($\frac{4g_{\mathbf{q}}^2}{\hbar\omega_{\mathbf{q}}} - 2U_{\mathbf{q}} + V_{\mathbf{q}} \geq \frac{1}{\chi_0(\mathbf{q})}$) are the Coulomb repulsion $U_{\mathbf{q}_0}$ and the exchange energy $V_{\mathbf{q}_0}$.

These two parameters are not well known, but estimates of $U_{\mathbf{q}_0} \approx 0.4\text{eV}$ and $V_{\mathbf{q}_0} \approx 0.4\text{eV}$ (how to get them??? check cited paper) are consistent with relation (10) ($\frac{4g_{\mathbf{q}}^2}{\hbar\omega_{\mathbf{q}}} > 2U_{\mathbf{q}} > V_{\mathbf{q}} > 0$) and seem reasonable for all three compounds [49].

When all estimated values are finally plugged into relation (9) ($\frac{4g_{\mathbf{q}}^2}{\hbar\omega_{\mathbf{q}}} - 2U_{\mathbf{q}} + V_{\mathbf{q}} \geq \frac{1}{\chi_0(\mathbf{q})}$), it turns out that the criterion for CDW/PLD formation is not easily fulfilled for all three systems. (what does it mean? we see the CDW in all three of them, right?)

Judging from the differences between the left- and right-hand sides of condition (9) ($\frac{4g_{\mathbf{q}}^2}{\hbar\omega_{\mathbf{q}}} - 2U_{\mathbf{q}} + V_{\mathbf{q}} \geq \frac{1}{\chi_0(\mathbf{q})}$), the tendency towards CDW/PLD formation is strongest in 2H-TaSe₂, intermediate in 1T-TaS₂ and weakest in 1T-TiSe₂ (see table 5). (if it is about the first row with %s, then why do we compare them with "1"???? is there somewhere $\chi_0(0)$?? I don't understand why such conclusion is made?)

On the other hand, the term $4g_{\mathbf{q}_0}^2/\hbar\omega_{\mathbf{q}_0}$, which is large when the electron-phonon coupling is strong and the lattice easily deformable, is the largest for 1T-TiSe₂. (see ref in table 5 to find out, why?)

It seems rather important to achieve a small value of $1/\chi_0(\mathbf{q}_0)$. (since this will make easier to obey the criterion)

Since the nesting enhancement of $\chi_0(\mathbf{q})$ at $\mathbf{q}_0$ is generally weak, a high density of states at the Fermi level, $(\chi_0(2\mathbf{k}_F, T) = \frac{1}{2}N(0) \ln\left(\frac{2.28E_F}{k_B T}\right))$ $N(0)$, is required.

For $N(0)$, the order from high to low is again 2H-TaSe₂ - 1 T-TaS₂ - 1 T-TiSe₂ (see table 4).

Note, however, that the experimentally observed transition temperatures and CDW/PLD amplitudes suggest the distinct order (from high to low): 1T-TaS₂ - 1 T-TiSe₂ - 2H-TaSe₂. (are there some consequences from it??)

(known intro:) In section 4, we have calculated the band structures and spectral weight distributions for the commensurate CDW/PLD phases of 1T-TaS₂, 2H-TaSe₂ and 1T-TiSe₂, using a simple tight-binding scheme.

(TB is a good model, as we have discussed =) Since the calculated effects are largely consistent with ARPES results, we dare to assume here that the tight-binding band energy changes, δE_{band} , resulting from the PLDs are somehow realistic.

The δE_{band} values obtained for the experimentally observed distortion amplitudes are listed in table 5, together with published values, if available. (= we somehow input the lattice distortion to a TB model, then we get δE_{band} .)

When the results are normalized (what is this idea of normalization?) to the average squared transition-metal atom displacement in the distortion pattern, it is found that the electron-lattice coupling (band energy lowering in $\text{eV}\text{\AA}^{-2}$) (why electron-lattice coupling is the band energy lowering?) is particularly large in 2H-TaSe₂ and by a factor of 3 – 4 smaller in 1 T-TiSe₂ and 1 T-TaS₂. (check if there was nothing contradictory written before? I hear first time that this EP coupling is such)

The counteracting increase in the elastic energy can be modeled by equation (5) ($\delta E_{\text{lattice}} = \frac{1}{2}M\omega_{\mathbf{q}}^2 u_{\mathbf{q}}^2$).

If we insert the mass of the transition-metal atom for M and the Debye frequency for the unrenormalized phonon frequency $\omega_{\mathbf{q}_0}$, we can estimate the force constant $M\omega_{\mathbf{q}_0}^2$. (it was discussed before)

The corresponding values are also given in table 5.

Since the Debye frequency will be larger than the frequency of the relevant phonon mode, the estimated force constants should be regarded as upper limits. (and how to get this Debye frequency???)

Comparing the electronic and lattice energy terms, we find that at $T = 0$ a harmonic CDW/PLD instability should definitely occur for 2H-TaSe₂ and 1T-TiSe₂, but not for 1T-TaS₂, the material with the highest transition temperature and the largest CDW/PLD amplitude. (HOW TO GET THIS RESULT????) (R. SAYS THAT FOR TAS2 THERE IS NO TRANSITION AT ALL BASED ON THE THEORY WHICH HE WORKED WITH!!!! THIS IS SO STRANGE, THIS CONTRADICTS THE BASIC KNOWLEDGE ABOUT TMDCs... THIS IS VERY BAD, ISN'T IT?)

We can also estimate the force constants(force constants???) from equation (18)($\Delta = u_{\mathbf{q}_0} g_{\mathbf{q}_0} \sqrt{\frac{2M\omega_{\mathbf{q}_0}}{\hbar}}$).

Using the 'universal' value $\Delta(0)/u_{\text{max}} = 0.55 \pm 0.13\text{eV}\text{\AA}^{-1}$ and the $4g_{\mathbf{q}_0}^2/\hbar\omega_{\mathbf{q}_0}$ terms from

table 5, we obtain values for $\frac{1}{2}M\omega_{\mathbf{q}_0}^2$ that are smaller than $2 \text{ eV}\text{\AA}^{-2}$ (why $\text{eV}\text{\AA}^{-2}$?) for all three compounds.

In this case (it is not clear, in which case???) , harmonic CDW/PLD instability is also attained for 1 T-TaS₂.

(I propose to forget this sentence, because it is too unclear:) But the trend is still inconsistent with the experimental data.

We emphasize that not much confidence should be given to the numbers presented in this section.(example?)

All estimates are based on crude models and strong approximations and the error bars of some of the involved microscopic parameters are rather large. (example: gap and comparison them on the plot of T_c , this looks like a meaningless idea)

The goal was to establish trends and identify generally important factors. (and which important factors can we distinguish?)

(here is unclear sentence, but the idea is that something important can't be predicted using theory before:) Unfortunately, the actual order of CDW/PLD strength (order of CDW/PLD strength???) , as given by the observed transition temperatures or CDW/PLD amplitudes, is reflected neither by the Chan-Heine condition nor by the comparison of band energy and lattice energy changes.

The compound with the lowest T_0 , 2H-TaSe₂, appears to exhibit the strongest tendency towards CDW/PLD formation (what is the tendency towards CDW/PLD formation???) .

(abstract useless sentence:) The major lessons, then, are that the occurrence of CDW/PLDs in the layered compounds depends on a delicate balance of several factors, that there is not one generally dominant factor (such as $4g_{\mathbf{q}_0}^2/\hbar\omega_{\mathbf{q}_0}$ or $\chi_0(\mathbf{q}_0)$) and that the simple criteria used here do not account for what is experimentally observed.

5.3. Transition temperatures

One may speculate that the Chan-Heine condition (9) ($\frac{4g_{\mathbf{q}}^2}{\hbar\omega_{\mathbf{q}}} - 2U_{\mathbf{q}} + V_{\mathbf{q}} \geq \frac{1}{\chi_0(\mathbf{q})}$) fails to provide a coherent picture for the three selected compounds because it is derived in the weak-coupling limit, while, as we have shown in section 3.2, the materials are actually in the intermediate to strong-coupling regime. (not only this criterion should fail, but all the theory from sect. 2...)

Here, we will briefly investigate whether the strong-coupling model developed by McMillan for 2H-TaSe₂ (why at all it was developed only for this compound? I thought it is approximately general model of strong coupling...) [39] is in better agreement with the available experimental results. (answer is no, it is not, since fig. 14 shows that there is no match)

We focus on a comparison of the transition temperatures predicted by equations (22) ($2\Delta(0) = 3.52k_B T_0$) and (23) ($k_B T_0 = 0.296C \frac{(\pi\xi_0 u_0)^2}{2\Omega}$) , both temperatures being calculated from parameters listed in tables 4 and 5. (calculate some of them for practice)

To simplify the calculation of the strong-coupling T_0 via equation (23), we assume the shortest possible coherence length, $\pi\xi_0 = \lambda_0$ (why is it so?) , and that the electron-lattice coupling parameter C is given by $|\delta E_{\text{band}}| = Cu_0^2 \ln |E_F/\Delta|^2$ [39]. (nothing is clear here, see [39] for all the explanation)

(see fig. 14 =) In figure 14, the predicted and measured T_0 are plotted against the relative lattice distortion u_0/a .

Note, again, that there is a conspicuous linear relationship between the experimentally determined T_0 and u_0 . (I don't agree. there are only 3 materials, take 10 materials, check for them, I bet it will not be there)

It has been argued that the conventional weak-coupling theory leads to severe inconsistencies in describing the experimental data for the layered compounds [39]. (I still don't understand, which experimental data exactly?)

However, figure 14 shows that this statement is exaggerated. (why at all we plot T_c versus latt. dist. to check the influence of coupling?)

Despite the extremely short coherence lengths, the weak-coupling transition temperature, $2\Delta(0)/3.52$ (isn't it for 1D, not for 3D?), is only by a factor of ~ 1.6 larger than the experimental values. (it is about the upper dashed line on a plot 14.)

The reformulated model, in which the strong-coupling limit is assumed, does not, on the whole, provide better agreement. (important conclusion: discussion about strong coupling is anyway useless)

Both models predict the correct order of magnitude of the transition temperature. (how to do this prediction at least from some theory? I have asked it already)

(here is one of many guesses about possible construction of the theory, not valuable =)

The observed quantitative discrepancies may be due to the mean-field approximation [39].

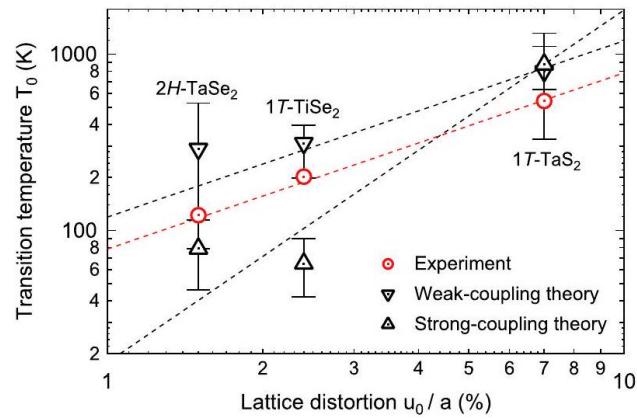


Figure 14. (why at all we plot T_c versus latt. dist. to check the influence of coupling?!!!!) Measured (open circles) and predicted (how to predict the transition temperature for a particular material???) (what is this strange vertical scale?????????) (open triangles) CDW/PLD transition temperatures for 2H-TaSe₂, 1 T-TiSe₂ and 1 T-TaS₂, plotted against the observed relative lattice distortion (u_0 : maximum transition-metal atom displacement, a : lattice constant). (what is the meaning of a line here??? why should a line at all be? for strong coupling the line makes no sense at all)

The dashed lines are guides to the eye in the spirit of the weak-coupling ($T_0 \propto u_0$) and strong-coupling ($T_0 \propto u_0^2$) theory. (how to obtain them???) (what is the value of the couplings that is there? should we have this one border that separates them?)

In conclusion, although the wave-vectors of the observed CDW/PLD distortions in 1T-TaS₂, 2H-TaSe₂ and 1T-TiSe₂ may somehow (wave vectors may fit to the geometry of the electronic structure ??) fit to the geometry of the electronic structure near E_F and although a local-chemical-bonding picture (local-chemical-bonding picture ??) may provide some clues as to why Ta clusters (Ta clusters ?) are formed in 1 T-TaS₂ and 2H-TaSe₂ and why the TiSe₆ octahedra distort in a particular way in 1T-TiSe₂, these approaches promote qualitative understanding only.

(we can't say something precise because we don't have a really working theory=) Unfortunately, if we want to explain the observed CDW/PLDs in a unified and more quantitative way, we have to rely on simple microscopic theories because realistic total energy calculations are not yet available.

(out theories are capable for at least something=) For the individual materials, the simple microscopic models and instability criteria are in semi-quantitative agreement with the available experimental data. (still, how to understand this statement in terms of formulas???)

(but it still our theories do not work well) But the generic trends are not correctly predicted (what exactly wasn't correctly predicted?) and a coherent explanation in terms of a few $\mathbf{k}$ -independent parameters has not emerged.

(it is a paraphrase of a sentence before) Apparently, the CDW/PLDs in the layered compounds are governed by a delicate balance of several factors and, in view of the strongly anisotropic electronic structures, the $\mathbf{k}$ dependence of these factors cannot be neglected. (why??? of which factors?? EP coupling?) (I don't think that it is truth. first of all, there were very bad arguments for this $\mathbf{k}$ -dependence. second, there are articles which just use some model and do some prediction of effect and they report some success without any $\mathbf{k}$ -dependence. I'll think later about it.)

(we need to think more (another reminder)=) Further theoretical scrutiny is clearly needed for a quantitative understanding of CDW/PLD formation in the layered transition-metal dichalcogenides.

4.2 Discussion

4.2.1 My Conclusion about the Article

(It is a very unclear article. It is not a surprise that there is a mess in theory about CDW, because this review is a mess itself. Yes, there are good ideas, cited papers, but it is a very bad starting point for a really productive research)

(also, the article can be 1/3 times smaller if it didn't have a lot of useless abstract statements that approximately repeat themselves)

(They overlook polarons, so this is strange, all this can be maybe described just with polarons)

(they repeat many times "we don't know how it works")

(think about that here PLD and CDW are together, but then there are works that electronic superlattices is put on top of the atomic lattice and no distortions of the latter are taken into account. is it a big overlook????? see Jaka's works where distortion of AL is neglected.)

(feels like chaos in R.-s understanding is reflected in the quality of the theory in the paper. it is not consistent and a lot of links between statements are missing)

4.2.2 My Main Questions about Main Statements in the Article

What is the conclusion about TaS₂ or other materials? Which properties should have their models to make them applicable for them?

(!!!!???? this is a very important question, I am still not ready to drive a conclusion!!!)

I still don't understand this idea of folding of BZ, why it happens?

(?!!!! I need to learn some basics!!!)

Is it a good idea to model TaS₂ without bands?

(???? some other articles do not work with bands. how wrong is this approach?)

Example of application of Peierls instability for a particular 2D material**What is the connection of TB model and Pireles model?**

(???? learn it better later!!!!)

What was improved in scope of all this theory after publication?

(??? a lot of years have passed, so we have some answers on the questions there?)

(I asked Jaka, he didn't answer, he said that there were minor developments and people started just working with models with polarons, but he didn't specify if any particular question here was answered?)

How for example, qualitatively explaining why the observed CDW/PLD phases may occur in some particular 2D material?

(!!?!?!?! I don't understand it!!! important question)

Why at all if the BZ shrinks, the bands overlap like a spaghetti?

(???? this is what is stated typically, but why is it so?)

What is the CONNECTION BETWEEN ORBITALS AND BANDS?

(this is a very important question for TB model, I'll look later)

To calculate the electronic gap, should we take into account that the phonon frequency is renormalized (Khon anomaly)?

(??? this question shows that I don't understand how to calculate the gap. Maybe we need the TB model, where the phonons are neglected at all. anyway, check later this)

What is that q in Chan–Heine criterion?

(answer from GPT)

The wavevector $\mathbf{q}$ in the Chan–Heine criterion labels a possible phonon mode and hence a possible periodic lattice distortion,

$$u(\mathbf{r}) \propto \cos(\mathbf{q} \cdot \mathbf{r}).$$

The criterion is not summed over $\mathbf{q}$. Rather, it is tested separately for every possible wavevector:

$$\frac{4g_{\mathbf{q}}^2}{\hbar\omega_{\mathbf{q}}} - 2U_{\mathbf{q}} + V_{\mathbf{q}} \geq \frac{1}{\chi_0(\mathbf{q})}.$$

In the harmonic approximation, the quadratic energy change may be written schematically as

$$\delta E^{(2)} = \sum_{\mathbf{q}} K_{\text{eff}}(\mathbf{q}) |u_{\mathbf{q}}|^2,$$

where the normal phase is stable only if

$$K_{\text{eff}}(\mathbf{q}) > 0 \quad \text{for all } \mathbf{q}.$$

If, for some wavevector $\mathbf{q}_0$,

$$K_{\text{eff}}(\mathbf{q}_0) < 0,$$

then the corresponding phonon mode is unstable and a CDW/PLD with wavevector $\mathbf{q}_0$ may form.

Equivalently, $\mathbf{q}_0$ is the wavevector for which the Chan–Heine inequality is first satisfied, or for which the instability is strongest. In a fully predictive calculation, one should evaluate all quantities

$$g_{\mathbf{q}}, \quad \omega_{\mathbf{q}}, \quad U_{\mathbf{q}}, \quad V_{\mathbf{q}}, \quad \chi_0(\mathbf{q})$$

throughout the Brillouin zone and determine $\mathbf{q}_0$ from the maximum instability.

In Rossnagel’s analysis, however, the criterion is evaluated only at the experimentally observed wavevector $\mathbf{q}_0$. Therefore the calculation tests whether the known distortion is energetically plausible; it does not predict $\mathbf{q}_0$ from first principles.

How to use Chan–Heine criterion for a particular material?

(answer from GPT)

For a given candidate CDW wavevector q_0 , the instability criterion is

$$\frac{4g_{q_0}^2}{\hbar\omega_{q_0}} - 2U_{q_0} + V_{q_0} \geq \frac{1}{\chi_0(q_0)}.$$

Rossnagel estimates

$$U_{q_0} \approx V_{q_0} \approx 0.4 \text{ eV},$$

hence

$$-2U_{q_0} + V_{q_0} \approx -0.4 \text{ eV}.$$

The remaining quantities,

$$\frac{4g_{q_0}^2}{\hbar\omega_{q_0}} \quad \text{and} \quad \frac{1}{\chi_0(q_0)},$$

are taken from Table 5.

- **1T-TaS₂:**

$$1.0\text{--}1.2 - 0.4 = 0.6\text{--}0.8, \quad \frac{1}{\chi_0(q_0)} = 0.7\text{--}0.9.$$

The criterion is only marginally satisfied.

- **2H-TaSe₂:**

$$1.3\text{--}1.5 - 0.4 = 0.9\text{--}1.1, \quad \frac{1}{\chi_0(q_0)} \approx 0.6.$$

Since

$$0.9\text{--}1.1 > 0.6,$$

the criterion predicts a CDW instability.

- **1T-TiSe₂:**

$$1.6 - 0.4 = 1.2, \quad \frac{1}{\chi_0(q_0)} = 1.3\text{--}2.2.$$

Since

$$1.2 < 1.3\text{--}2.2,$$

the criterion does not predict a CDW instability.

Therefore, within this simplified weak-coupling approach, the predicted tendency towards CDW formation is

$$2H\text{-TaSe}_2 > 1T\text{-TaS}_2 > 1T\text{-TiSe}_2,$$

which is inconsistent with experiment. This demonstrates the limited predictive power of the weak-coupling mean-field theory for these materials.

What is special in TMDCs, such that there is a CDW in them and there is no CDW in many other 2D materials?

(???? I don't know, anyway I need to read at least 5 papers about first principle calculations of the bands)

What FSN mechanism can give us and what can't?

(??? I am confused about real results of FSN, does it give them or no?)

how do we know that BZ shrinks 3 times or 2 times?

(maybe look at STM and calculate it? I haven't ever done this)

what really useful TB model gives us? if anyway we fit it to experiment?

(I'll try to speculate later)

Why FSN mechanism at all makes sense, if in CDW state the FS is changed drastically?

(????? so in the new FS, there will be new nesting vectors, we first need to know them, then input them to the χ , and only then look at the divergence. right? but there is no way to learn what are the FS in CDW without experiment)

what about state of SC+CDW? Can it be? if so, what about 5.2, where it is written that it can't be?

(??? I'll check later)

How do polarons fit at all to this picture????

(????????????!!!!!! This is a very hard question, which involves deep understanding of both models, I'll approach it later)

Can one derive a Khon anomaly and PLD with polarons????

(??? I don't know how to do it, I'll try later)

4.2.3 My Questions about Assumed Physics

What is a CDW wave vector? there are a lot of them, I suppose? But how to get them from the STM measurement?

(?? I am confused about 2d)

Why $\sqrt{13} \times \sqrt{13}$ lattice?

(it is from GPT, check it)

Let the primitive lattice vectors of the hexagonal lattice be

$$\mathbf{a}_1, \quad \mathbf{a}_2,$$

with

$$|\mathbf{a}_1| = |\mathbf{a}_2| = a, \quad \mathbf{a}_1 \cdot \mathbf{a}_2 = a^2 \cos 60^\circ = \frac{1}{2}a^2.$$

The commensurate CDW unit cell is generated by

$$\mathbf{A} = 3\mathbf{a}_1 + \mathbf{a}_2, \quad \mathbf{B} = -\mathbf{a}_1 + 4\mathbf{a}_2.$$

The length of $\mathbf{A}$ is

$$\begin{aligned} |\mathbf{A}|^2 &= (3\mathbf{a}_1 + \mathbf{a}_2)^2 \\ &= 9a^2 + a^2 + 2(3)\frac{1}{2}a^2 \\ &= 13a^2, \end{aligned}$$

thus

$$|\mathbf{A}| = \sqrt{13}a.$$

Similarly,

$$|\mathbf{B}| = \sqrt{13}a.$$

The area ratio between the reconstructed and primitive unit cells is

$$\det \begin{pmatrix} 3 & 1 \\ -1 & 4 \end{pmatrix} = 13,$$

so the reconstructed unit cell has an area 13 times larger and therefore contains 13 Ta atoms.

Hence the CDW supercell is denoted $\sqrt{13} \times \sqrt{13}$.

What is the origin of the deformation energy?

If δE_{band} is dependent only on χ_0 , what do we change? χ is the constant, it is the same even without any change?

(same for lattice change of energy, think why is it so?)

Why FS is deformed and how???? and why is it distorted so much???

(??? I don't understand even the initial non-spherical shape of FS. why is it such?)

Can it be that we have a FS nonisotropic, but there will be no interactions btw electrons and phonons???

(another question about FS, I don't know)

What is an indirect gap?

(revise SM theory!)

How the FS looks for quasi-1D materials? (if FSN was fully working)

(?? ideal example of FSN? write it here)

why exactly spectral weights are needed?

(because they give the intensity. but it is a reminder here to work out the concept of spectral weight, see examples how it is used?)

Why do we have a shrinking of BZ at all????

(we say, because unit cell decreases, but I don't see this connection. what limits BZ? Revise this origin of BZ)

Is CCDW a semiconducting or insulating phase?

(??? I don't know, check literature)

Which materials here are semiconductors and what is the criterion for them?

(??? maybe all of them, or how? I am confused, I need to check all of this, how to find it out from the plots of energy bands? or from some other theory...)

Is spectral weight T-dependent?

(???????)

What is "band which carry a spectral weight?"

(ask AI or read Kittel)

If there is no EP interaction, would the FS and other pictures look like now in the normal state?

(this question is related to the question of what influences the FS?)

why there are different CDW gaps at all?

(??? was it written somewhere in the article? I'll check later)

why sometimes we use ALH and sometimes MK Γ ? Why at all such points are chosen?

Example: why fig. 9 has ALH and fig. 8 has MK Γ ?

(??? learn basics better)

why at all we want a TB model, not a free electron model?

(revise the idea of TB model and its applicability. I don't have a clear answer)

Questions about ARPES**Why exactly $E < E_F$ on the ARPES, not vice versa?**

(?????? work out ARPES)

In other words, why for TaS₂ we don't see energy bands above E_F in ARPES?

How does two plots of different type of ARPES connect?

(I'll write a detailed answer with example here, I understand it approximately, but I need to work it out more)

Why if we have a change of bands, we don't have a change in Fermi level itself? Maybe some particles go out of the system, so that E_F decreases?

(q. about revision of the basic theory)
(I don't know now, need to read Kittel)

Can we introduce holes for all conducting materials?

(it is a question in scope of general education)

4.2.4 My Questions about Details and Extra Properties

How to know, which phase to chose, 1T or 2H?

(this is a reminder to study phases more, I left this question)

Why are the uncertainties about the gap in that plot of the gaps? Can we at all believe that plot?

(???????????? this is the strange plot anyway, so it is not an important question)
Looks that no, this is a strange plot, I don't know even why there are such big uncertainties. Read the cited papers about the gap.

What is the influence of CDW/PLD to phonon spectra?

(sounds like a big another question!!! I need to read a special article about it)

Why TiSe2 is an excitonic insulator at all from experiment?

(??? I just don't see it clearly, read cited papers and give a high quality answer)

4.2.5 My Deeper Questions

what if we take Ta Se2 and add Ti and subtract Ta, how the bands will change? Can we reproduce this change with theory?

(??? I think it is a really good theory)

What if we just take a Frolich model, will we derive all the physics from it?

(we should, but maybe the problem is that no one can derive it. do I understand it correctly?)

Why at finite T we don't have a CDW state? why not (in terms of formulas, since we showed that it is energetically more favorable)?

(???? I don't understand CDW that deep)

How does ARPES results (fig. 6) look for other CDW states (NCCDW, ICCDW, hidden state)?

(search for it in some papers)

Do we use softening of phonon model which because of CDW/PLD somewhere in TB calculations or other calculations?

(??? maybe no, which is really strange, so I'll think later about it)

If excitonic insulators are a different phenomena, then what will be if we combine CDW + two bands?

(I don't understand this excitonic insulator model...)

if PLD is bigger, then will the gap be bigger? Or we can't ask this because there is only a fixed PLD for the selected material?

(????)

Maybe this leads to a bigger unit cell, and does it lead to the bigger gap?

Why q_0 is a constant as function of T?

(???????? one can imagine situation that one configuration is changed to another one if we change temperature, so this never happens or how???)

Can we calculate theoretically T_c to CDW at all?

(??? revise the CDW theory and find this answer)

what if we take some electrons out of the system, to see how lattice changes? will there be a less PLD?

(???????????????? I think that taking electrons out of the system should be analyzed separately, I have no idea how to approach this setup...)

4.2.6 Possible Next Steps for Research Using These Results

5 From Mott state to superconductivity in 1T-TaS₂ by Sipoš, Kusamartseva, Akrap, Hberger, Forro, Tutiš (2008)

Abstract

The search for the coexistence between superconductivity and other collective electronic states in many instances promoted the discovery of novel states of matter. (example?)

The manner in which the different types of electronic order combine remains an ongoing puzzle.

1T-TaS₂ is a layered material, and the only transition-metal dichalcogenide (TMD) known to develop the Mott phase.

Here, we show the appearance of a series of low-temperature electronic states in 1T-TaS₂ with pressure:

the Mott phase melts into a textured charge-density wave (CDW);

superconductivity develops within the CDW state (how???) , and survives to very high pressures, insensitive to subsequent disappearance of the CDW state and, surprisingly, also the strong changes in the normal state (which???) .

This is also the first reported case of superconductivity in a pristine 1T-TMD compound. We demonstrate that superconductivity first develops within the state marked by a commensurability-driven, Coulombically frustrated, electronic phase separation. (what is it???)

5.1 Article

5.1.1 1 Introduction

There is a long-standing enigma addressing the competition, coexistence or cooperation between various electronic collective states, in particular centring on the superconducting state.

The most interesting systems from this point of view are those of reduced electronic dimensionality, which are more prone to electronic instabilities (this Pereles transition idea, see Gruner's book) (reminder: understand better, why?) .

Prominent examples include superconductivity in high-temperature copper oxide superconductors ¹⁻³, organic charge-transfer salts ⁴, heavy-fermion compounds ⁵, superconducting cobaltate systems ⁶ and some transition-metal dichalcogenides ^{4,7,8}.

1 T – TaS₂ is a rare layered material where both the Mott state and a number of peculiar charge-density-wave (CDW) phases have been documented ⁹⁻¹², indicating that the electron-phonon and the electron-electron interactions are equally important in the shaping of its physics. (how do we use the electron-phonon and the electron-electron interactions for this material? okay, it is a topic of other articles)

Recent angle-resolved photoemission spectroscopy experiments have suggested a further antiferromagnetic ordering at low temperatures ¹³. (antiferromagnetic ordering of what, of electrons???)

The addition of superconductivity to this assortment of phases makes this material an important candidate for providing further insights into possible relations between electronic collective states in solids. (which relation, for example??)

The pressure-temperature phase diagram developed here for 1 T – TaS₂ is unique in several respects. (see fig. below)

Combining our findings with the results of previous studies at ambient pressure, we report and explain the surprising observation of a superconducting state, that remains insensitive to the marked changes developing in the normal state under pressure. (which changes in the normal?)

On the quantitative side, we show that the textured phase where the superconductivity first occurs is a state of commensurability-driven (commensurability-driven?) and Coulombically controlled (Coulombically controlled?) electronic phase separation.

In this microscopic phase mixture, one phase supports the superconductivity, whereas the presence of the second phase severely affects the normal-state properties.

(how SC is dependent on pressure at all? it is maybe an unanswered question...)

The pressure is used here as an ideal tool to influence the electronic interactions within the material without increasing the degree of internal disorder.

This provides an obvious advantage (that we don't need to rebuild the material) over the usual and often complementary method of affecting the electronic system by chemical doping.

(it is not true, it is a different mechanism. I don't think that adding disorder and pressure gives the same physics)

The past studies prove that the pressure is especially successful in inducing changes in the electronic ground states for systems with reduced dimensionality^{14–18}. (why??)

The case of 1T-TaS₂ adds to this list, with its unique features.

5.1.2 2 Experimental results

1 The starting point

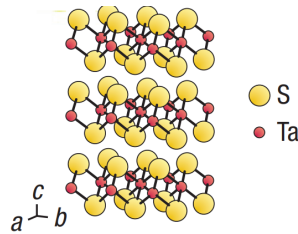
(SUMMARY: THERE IS SUCH A MATERIAL WITH DIFFERENT PHASES, CONFIGURATIONS AND RESISTIVITY)

(here, they looked on equilibrium physics and they don't measure it long in time. this is how this article can be understood consistently with other articles. Jaka was inserting some distortion, and only this way we can get some exotic configurations of DWs, which then can reconfigure very slowly. All these effects are beyond times which were considered here)

1T-TaS₂ has a simple crystal structure, composed of planes of tantalum (Ta) atoms, surrounded in an octahedral arrangement by sulphur (S) atoms, see top right inset in Fig. 1.

Even at ambient pressure, a variety of phases are present including a metallic phase at high temperatures, an incommensurate CDW (ICCDW) phase below 550 K, a nearly commensurate CDW (NCCDW)(exactly "nearly CCDW", don't confuse it with non commensurate, we don't have such a notation for "nearly CCDW") phase below 350 K and a commensurate CDW (CCDW) phase below 180 K. The CDW state in 1T-TaS₂ is mostly driven by the Fermi surface instability, resembling the ones found in Peierls (quasi) one-dimensional systems. The Peierls-like behaviour in 1T-TaS₂ is, however, substantially more complex.

$$(1 \text{ atm} \approx 1.013 \times 10^{-4} \text{ GPa.})$$



The CCDW phase is geometrically the simplest among the CDW phases in this material. (geometrically the simplest means that distortions have a simple geometry)

The displacement of the atoms leads to the formation of David-star clusters, where twelve Ta atoms within the layer move inwards towards a thirteenth central Ta atom.

The stars interlock by forming a triangular superlattice (Fig. 1, bottom left inset).

However, this deformation does not fully gap the electronic system, with only twelve out of the thirteen electrons of the new unit cell occupying the electronic states below the energy gap created by the deformation.

The 'thirteenth' electron presides above the deformation-induced gap¹⁹ (why? read the ref. I didn't read before that we break the 2d dimension in the CDW state) .

The enigma of high resistivity of this phase was resolved by pointing out that the system stabilizes by simultaneously developing a Mott insulator state from the electrons above the gap^{11,12} (why? do they derive the resistivity?) , later confirmed by other experiments including spectroscopic methods^{20,21} (do they have the same plot as here?) .

It should be noted that the formation of the David-star clusters also involves displacements perpendicular to the plane, causing a periodic swelling of the TaS₂ layers ^{22,23} (periodic swelling?) .

This CCDW Mott phase was found to be sensitive to doping ^{20,24} (how???) , disorder induced by irradiation ²⁵ (how???) and pressurization ²⁶ (how???) .

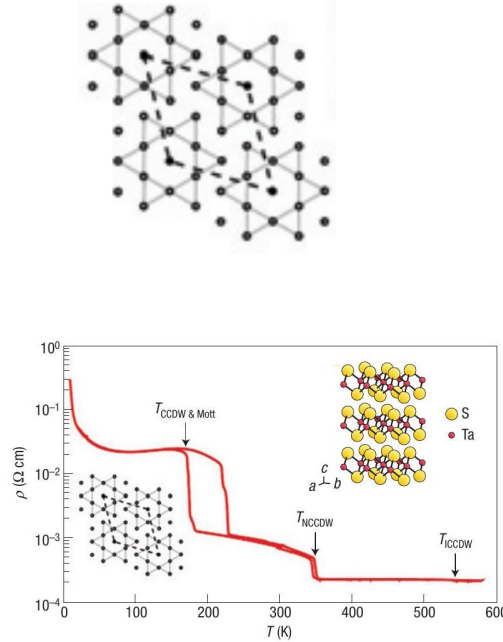


Figure 1 Ambient-pressure phases of 1T-TaS₂. (they didn't write that they got this result first themselves, but anyway they have fig. 2, which has this result in it, so this is their result)

The phases are:

- a metallic phase at temperatures above 550 K;

- an ICCDW phase above 350 K;

- an NCCDW phase above 190 K;

- a CCDW Mott phase below 190 K;

in addition there is a trigonal phase present solely during the warming up cycle between 200 – 300 K (refs 9, 10, 45) .

Also shown are the Ta atom distortions in the fully commensurate phase (bottom left inset) and the crystal structure of 1 T – TaS₂ (top right inset).

The neighbouring NCCDW phase equally contains David-star clusters, although they are arranged in a less uniform manner ⁹. (how does it look like?)

Ambient-pressure X-ray studies in 1 T – TaS₂ reveal that in the NCCDW phase several tens of stars organize into roughly hexagonal domains, locally reproducing the CCDW phase ^{10,27}.

The domains are separated by triangular regions where the amplitude of the deformation is reduced, forming the planar structure that resembles the kagome patchwork ^{10,27} (see refs about them) .

2 Experimental results

(SUMMARY: WE MEASURED RESISTIVITY AND THIS IS HOW IT DEPENDS ON PRESSURE AND TEMPERATURE, ALSO IT IS RELATED TO THE CONFIGURATIONS OF ELECTRONS)

We have carried out resistivity measurements on 1T-TaS₂ under pressures ranging from 0 to 25 GPa and temperatures ranging from 1.3 to 300 K (Fig. 2).

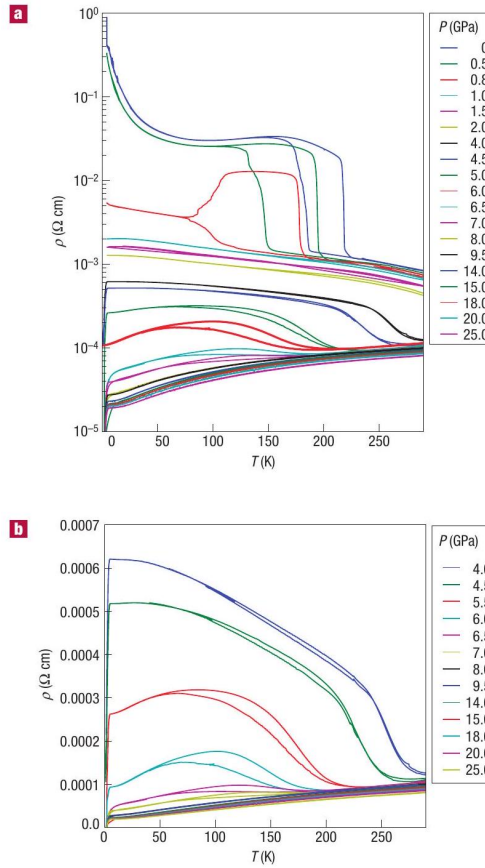


Figure 2 Resistivity in the pressure range of 0 – 25GPa and temperature range of 1.3 – 300 K.

a, The temperature dependence of the resistivity is largely non-metallic over the entire temperature range for pressures of 0 – 4GPa;

the low-temperature upturn in the resistivity that relates to the variable-range-hopping conduction in the Mott phase ^{11,12} disappears above 0.6 GPa;

first traces of the superconductivity are observed at an approximate pressure of 2.5 GPa, with a T_{Sc} of 1.5 K;

metallic-like behaviour develops for low temperatures at pressures of 4 – 8GPa;

fully metallic behaviour is present at pressures greater than 8 GPa.

b, The superconductivity first develops with pressure within the non-metallic phase. (it is the same plot as above, but in different scale)

(how is it, 0 Pa? aren't electron flying away from the material?)

(what do we mean by SC? is it when there is exactly 0 resistance??? then why do we have it at all, if always there is a nonzero resistance?)

At temperatures below 250 K, we observe a first-order transition from the NCCDW to the CCDW phase (THERE IS A TYPO HERE, THEY MEANT "FROM METALLIC TO NCCDW STATE TRANSITION". I see only a slight increase of the resistivity) , which melts with a pressure of 0.8 GPa (and a superconductor appears) .

At low temperatures, the resistivity saturates to finite residual values that shift lower and lower as the pressure is increased.

The transition from the incommensurate to the nearly commensurate CDW phase appears as an increase in the resistivity in the temperature range of 120 – 300 K for the whole pressure range.

The first confirmed signatures of superconductivity appear at 1.5 K and 2.5 GPa (we need to believe it, because it is not written explicit on the plot) .

The superconductivity arises from the nonmetallic low-temperature phase (arises from the nonmetallic low-temperature phase???) , which continuously evolves from the NCCDW state at ambient pressure. (it is clear from the plot what is going on, I think that this statement is just a bad and wrong one)

In addition, at around 4-5 GPa, the resistivity saturates to a plateau-like temperature dependence below 50 K. (I consider it as a bad sentence, actually there is no such 4-5 GPa, and there is no 50K milestone. All happens smoothly.)

The value of this low-temperature residual resistivity drops as the pressure is increased, and a metallic-like signature (metallic-like signature?) stabilizes in the low-temperature ranges (it is meant that the resistivity is changed slowly, but then it does not change much) .

Above 8 GPa, the resistivity is metallic over the entire investigated temperature range, although the temperature dependence remains unconventional (the conventional is $\rho(\text{high}T) \sim \rho_0 + \alpha T$, $\rho(\text{low}T) \sim \rho_0 + AT^2$) (derive the conventional one. revise cond matter) . (what is it here??? it is not answer in the article)

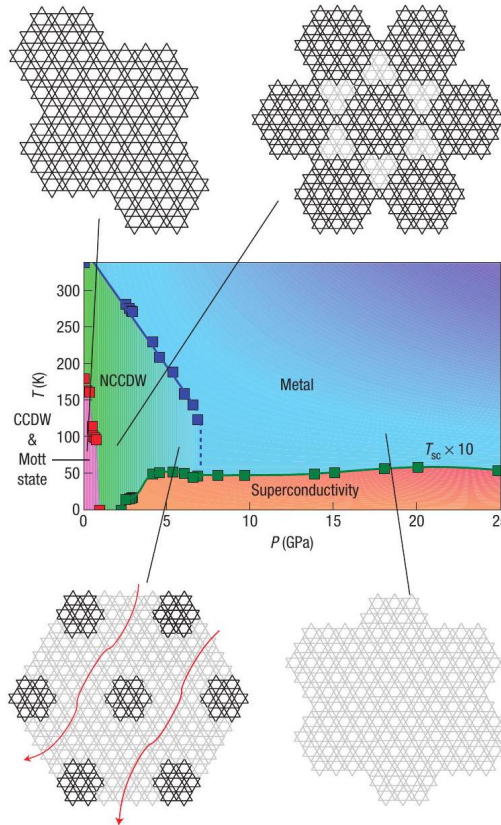


Figure 3 The temperature-pressure phase diagram of 1 T – TaS₂. The Mott localization is suppressed, closely accompanied by the melting of the CCDW phase at a pressure of 0.8 GPa; the lattice structure in the latter phase is composed of interlocking David stars.

(above, there is a ICCDW phase) (what is the phase transition line btw metallic and ICCDW phase???)

The NCCDW phase extends over the pressure range of 1 – 7GPa, and may be visualized as roughly hexagonal domains suspended in an interdomain phase, indicated in grey.

The first signatures of superconductivity appear from the NCCDW state, and remain roughly at 5 K throughout the entire pressure range of 3 – 25GPa. (so on the plot it is multiplied by 50 times! this is strange, since it is not clear what happens with other scales above Tsc? okay, maybe they are also slightly rescaled...)

In the pressure range of 8 – 25GPa, the system is metallic over the investigated temperature range when above the superconducting transition temperature.

The drawings above and below the phase diagram indicate the probable deformation patterns in the system at low temperature, as discussed in the text.

Darkly shaded parts denote the parts with the static deformation in the form of David stars, whereas in the light-shaded areas the deformation is considerably reduced or completely suppressed. (so the undeformed areas are the symmetric cells, this is how I understand it. no glass, no chaos in them.) (but what about other states? do other states appear only if we add extra electrons, which is not the case here?)

(what does these white lines mean on the blue and green areas?)

We summarize our findings in a pressure-temperature phase diagram (Fig. 3). The Mott localization and the CCDW phase are fully suppressed at pressures of about 0.8 GPa.

The NCCDW phase persists to pressures of 7 GPa (there is no such border, it is an approximate value) and may be visualized as roughly hexagonal CDW domains suspended in an interdomain phase^{10,27}. (read the cited papers, interesting, what do they tell?)

The domains are expected to become progressively smaller as the pressure increases.

The first signatures of superconductivity appear in the NCCDW phase and remain roughly at 5 K throughout the entire pressure range of 3 – 25GPa.

For pressures of 8 – 25GPa, the system is metallic over the investigated temperature range when above the superconducting transition temperature. (what is the criteria that is used to say the "system is metallic"?)

Recent preliminary field measurements indicate that the critical magnetic field would be of the order of 1.5 T, in the lower-pressure ranges. (which measurements?? ref for them??)

The questions that emerge from this new phase diagram address the melting of the CCDW Mott state, the origin of the textured NCCDW phase in relation to that state and the appearance of superconductivity in a pristine 1T system, which remains apparently insensitive to both pressure and the melting of the charge order. (insensitive to the melting of the charge order???)

(so they ask, why did they get such results and below there will be a list of their ideas about it)

5.1.3 3 Discussion

(SUMMARY: THIS IS A USELESS SECTION WITH JUST SOME IDEAS WHICH MIGHT LEAD TO THE EXPLANATION OF THE BEHAVIOR OF RESISTIVITY)

The exceptional assembly of electron-phonon coupling, nesting effects and Coulomb interaction combine to construct the elaborate phase space of 1 T – TaS₂. (so only these three are used to explain the phenomena)

To understand the many complexities of this system, it is important to consider the microscopics of the different phases at ambient pressure and their possible evolution under pressure. (basically, this is what)

We will address each of the above posed questions separately.

3.1 Meltdown of the Mott phase

(SUMMARY: WE USE HUBBARD'S MODEL, IN WHICH PRESSURE AFFECTS t AND U .)

The standard way of influencing the Mott phase is to affect the ratio between the Coulomb repulsion and the bandwidth. (below it is proposed to influence the t and U parameters by pressure and temperature)

(or maybe we need a purely new model???)

These two relevant energy scales correspond to the parameters U and t of the single-band Hubbard Hamiltonian, usually used to consider the Mott transition,

$$H = -t \sum_{\langle i,j \rangle, \sigma} \left(c_{i,\sigma}^\dagger c_{j,\sigma} + c_{j,\sigma}^\dagger c_{i,\sigma} \right) + U \sum_i n_{i,\uparrow} n_{i,\downarrow}$$

where $c_{i,\sigma}$ and $c_{i,\sigma}^\dagger$ are the destruction and creation operators of an electron at site i and with spin σ , and $n_{i,\sigma} = c_{i,\sigma}^\dagger c_{i,\sigma}$ is the occupation operator.

For the special case of the triangular lattice of David stars in 1 T – TaS₂, t and U map to the overlap of the electronic wavefunctions defined by the deformation localized at David stars, and the Coulomb interaction of the electrons above the gap within the same David star, respectively. (isn't it the case for all the materials) (I understand it like: t is because of overlap of the WF, U is because of the Coulomb repulsion. This sentence can be written more clearly) (do we really need to say "above the gap"?)

(by the way, how to derive this model?? it is a famous one, I know)

The qualitative understanding of the observed phase transition comes from the insight that pressure changes both (both means t and U) the relevant energy scales, by decreasing the swelling of the planes related to the David-star deformations in the CDW state. (swelling of the planes??? how is it???) (stupid sentence, of course, if we have only this model and pressure influences, then of course, it influences from the change of the constants. But it is not clear if this model is applicable at all?)

In particular, by reducing the deformation, the pressure diminishes the CDW gap and increases the screening capacity of the electrons below the gap (that is, the interband contribution to the dielectric function). (why does pressure increase the screening capacity??? and diminishes the CDW gap? looks like just paraphrasing the existing experiment)

Similarly, the pressure also weakens the potential that defines the local wavefunction, thereby increasing its extension and the wavefunction overlap integral. (it was written recently before)

Both these mechanisms simultaneously increase t and decrease U , leading to a decrease in the ratio U/t . (it was written recently before)

The Mott-state melting occurs naturally at a critical value of this ratio²⁸. (it is well known) (how to derive it?)

(I don't know, if this is indeed true, I wasn't ever told that pressure weakens the potential. which formula is used for it??? why it is not purely another physics? see the refs)

3.2 Nature of the textured phase

(SUMMARY: IN THE TEXTURED PHASE, THERE IS A STRANGE GAP AND STRANGE COULOMB ENERGY.)

The NCCDW phase has been subject to numerous experimental and theoretical investigations at ambient pressure. (and what are the results of them?)

Previous theoretical approaches invoked mainly phenomenological treatments, based on sophisticated versions of the Landau-type functional, leaving out the microscopic details^{29,30}. (learn these methods, haven't yet herd about them)

However, the main mechanism behind the creation of the textured phase has been established to lie in the tendency of the system to maximize the electronic gap at a given deformation

amplitude by (inter)locking the deformations at (three) commensurate wave vectors, counteracted by the remnant part of the electrons in the states above the gap. (why to "maximize the electronic gap"???) (why this is related to the NCCDW??? learn about NCCDW)

This leads to a microscopic mechanism for domain formation, common to many electronic systems with (charge- or spin-) density waves close to commensurability³¹. (it was written above, not a useful sentence)

Essentially, the discommensurations in the textured phase host the electrons that do not fit below the gap that exists in the commensurately ordered domains.

Notably, however, the size of the domains in 1T-TaS₂ is substantial, containing several hundred TaS₂ units within each layer.

Therefore, long-range Coulomb forces are expected to control the charge transfer involved in the domain size and organization³².

This important aspect was omitted in former theoretical treatments of the NCCDW phase in 1T-TaS₂.

(how the purely Coulomb interaction affects the dynamics??? everything here should be from Coulomb interaction, no??? what is meant by it at all???)

We fully include the Coulomb aspect of this charge transfer, when considering the formation of domains in the NCCDW phase in 1 T – TaS₂.

The two limiting degrees of this charge relocation leave the domains either as a lightly (self-)doped Mott state (lightly (self-)doped??) , or fully depleted. (fully depleted???) (it means that Coulomb interaction can move electrons somehow and change their positions, which will affect the resistance)

We compare the Coulomb energy per particle involved in the formation of fully depleted domains, E_c , with the electronic energy gap Δ in the domains. (it is no clear, how the E_c and the Δ influence resistance at all??? maybe they influence the CDW distribution of electrons, which is felt by other electrons?)

The case of $E_c \sim \Delta$ implies a Coulomb-controlled textured phase.

The alternatives, unrestricted by the long-range Coulomb forces, relate to $E_c \ll \Delta$ and $E_c \gg \Delta$ signifying fully depleted and slightly doped Mott phase domains, respectively. (physically what are they??)

Figure 4 shows the results of a calculation, for different domain sizes and organization in successive layers.

The calculation (see the Methods section) is carried out for a kagome patchwork with two different stacking alignments. (I still have no idea how did they calculate it???)

Stacking A considers an axial alignment of domains and interdomain triangles in successive layers, and has been experimentally observed in 1 T – TaS₂ (see Fig. 4, Stacking A). (how do they look experimentally??)

The shifted positions of the domains between adjacent planes resemble a closely packed face-centred-cubic structure²⁷.

Stacking B refers to a hypothetical case of an exact axial superposition of the domains between the planes, for comparison (see Fig. 4, Stacking B). (how would it look like in STM??)

We show that the deviation from the observed Stacking A structure induces a big change in the Coulomb energy.

The calculations demonstrate that the experimentally observed stacking and sizes of the domains support Coulomb-controlled texturing and depletion of the domains. (what is the Coulomb-controlled texturing??)

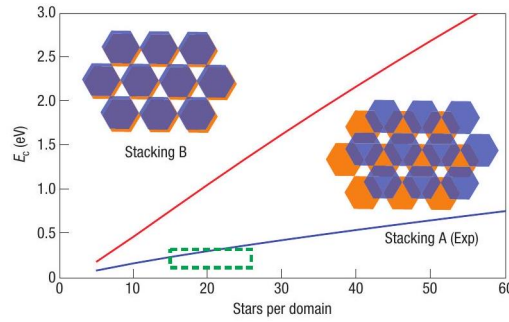


Figure 4 The results for the Coulomb energy calculation for two different domain stackings as a function of domain size. (I don't understand what is important about this plot? some strange parameter is calculated in a strange way...)

(why is this energy linear?)

The lower line (blue) corresponds to an axial arrangement of domains (hexagonal) and inter-domain spaces (triangular) between adjacent layers (stacking A), as deduced from experiment²⁷ (which experiment??) ;

the upper line (red) shows for comparison, the Coulomb energy for a hypothetical axial domain stacking between successive layers (stacking B).

The green dashed rectangle depicts the values of domain sizes that were experimentally observed in the NCCDW phase at ambient pressure. (why exactly this region is for the ambient pressure???)

We note that the Coulomb energies calculated for these values are comparable to the energy of the gap, hinting at a possible Coulomb-controlled phase separation. (what is at all the Coulomb-controlled phase separation???)

We conclude that the NCCDW phase of 1T-TaS₂ at ambient pressure is an example of a Coulombically controlled and commensurability-driven electronic phase separation. (wrong sentence, phase can't be a phase separation) (it was obvious from before that it is not clear what do they mean here at all???)

This state extends to very low temperature on pressurization, where superconductivity occurs.

3.3 Superconductivity in the textured phase

(SUMMARY: FOR UNKNOWN REASON, THERE IS ALSO A SC IN THE NCCDW PHASE)

Within the conventional picture (it is still not explained, how to describe both phenomena using some one general framework, this is meant by "conventional picture") , the CDW and superconducting ground states compete against each other, because both result in a gapping of the single-particle electronic spectra at the Fermi level.

Indeed, the superconductivity in 1 T – TaS₂ appears as soon as the fully commensurate CDW phase is suppressed at low pressures of 0.8 – 1 GPa, suggesting a mutual exclusion of each other. (no, they showed on the Fig. 3 that there is no SC at less then 2 GPa pressure)

On the other hand, no notable competition is observed in the pressure range of 1 – 7 GPa within the NCCDW phase where the CDW and superconductivity coexist (how is it when they coexist? we have distinct regions there) .

To illustrate this point, we consider the behaviour of the normal-state resistivity as a function of pressure (Fig. 5). Technically, we take the normal-state or the residual resistivity to be the resistivity at 6 K above 1 GPa. (this is their "normal state". 6K is the fixed temperature!) (what is the residual resistivity???)

Below that pressure, the resistivity is dominated by a variable range-hopping regime in the Mott state (see Fig. 2a). (I don't know what is the variable range-hopping mechanism, see a book on SM)

The residual resistivity decreases gradually above 1 GPa until an approximate pressure of 4 GPa.

This may be explained by the shrinking of the CDW domains with pressure and an increased fraction of electrons in the interdomain phase. (how are they connected, shrinking and the gradual decrease?)

(how at all to derive the resistivity of the CDW state?)

In the pressure range of 4 – 7 GPa, we see a shoulder-like anomaly in this effective residual resistivity.

This probably indicates a complete dissociation of the CDW domains into a uniform, fluctuating background of weak distortions. (looks indeed so)

Above 7 GPa, the pressure dependence of the residual resistivity is less significant.

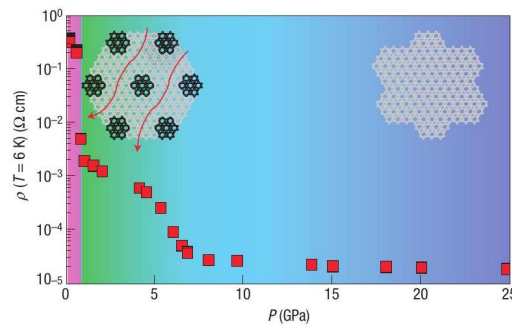


Figure 5 Resistivity taken at a temperature of 6 K as a function of pressure. (here, we explicitly see what is meant on fig .3)

A sharp decrease in resistivity accompanies the suppression of the Mott-localized phase;

linear residual resistivity pressure dependence accompanies the gradual melting of the CDW domains in the NCCDW phases;

a shoulder-like anomaly in the pressure range 4–7 GPa may be associated with the complete dissociation of the CDW domains with pressure;

above 7 GPa, the residual resistivity again behaves linearly with pressure (actually, does not change much at all) .

The scattering of electrons on the CCDW islands dominates the resistivity below 7 GPa (how to describe the scattering of electrons on the CCDW islands?)

Naturally, we propose the assumption that the superconductivity forms within the metallic interdomain spaces of the NCCDW phase. (so the NCCDW is living its life, but metallic part of it changes to the SC)

Thereby, remarkably, the competition between the CDW and superconductivity is avoided in the NCCDW phase through a phase separation in real space on a microscopic scale.

Thus, the superconducting state remains rather insensitive to the size, and even the disappearance of the domains brought on by the pressure change.

On the contrary, we may assume that the domains appear as scatterers of the electrons in the normal state, which would explain the manifest sensitivity of the normal-state resistivity to the collapse of the CCDW domains around a pressure of 7 GPa (Fig. 5) (explain the end of this fall of the resistivity) . (this is an abstract statement, there is no formula which will support it. why?)

(by the way, why no hysteresis is here??)

We may postulate that the electron-phonon coupling that is inherent in the CDW state vastly helps the superconductivity in undeformed parts of the system. (useless abstract sentence, it is well-known that the EP coupling is contributing to SC)

Combined with the phase separation on the microscopic level (phase separation on the microscopic level?), this would lead to the conclusion that the same parts of the Fermi surface are being affected by the CDW and the superconductivity transitions. (not clear, how exactly?)

This has recently been observed in $2H - NbSe_2$ (ref. 33) - another member of the transition-metal dichalcogenide compounds, where an analogous indifference of the superconductivity with respect to the CDW transition has been detected ⁴ (it is not clear, what was observed?), with some evidence for a textured phase based on a triple CDW state ^{34,35}.

It may be informative to consider the effect of intercalation (insertion of a foreign molecule between layers) on the charge-density wave in this material. (don't confuse with insertion of extra electrons which was studied by Voded et al.)

Intercalation increases the spacing between layers, which may be beneficial for the deformation related to the Mott-state phase (deformation related to the Mott-state phase???) and at the same time introduces spurious (not genuine) charge carriers which are likely to suppress this Mott-state phase. (extra electrons from extra molecule become also some conducting electrons) (why do they suppress it?)

Whether the intercalation would give rise to the currently observed superconducting phase is unclear. (there are a lot of parameters, like temperature, pressure, now if we insert another molecule, we need to measure again a lot of them. authors say that they just don't know, I also don't know, I don't have a model for this phenomena)

3.4 Compete or coexist?

(SUMMARY: SC IS LIKELY TO BE A PSEUDOGAPPED ONE)

There are several pictures relating charge ordering and superconductivity that exist in the literature.

These prove inconsistent with our phase diagram. (why?)

We rule out the possibility of superconductivity rooted in a manner of a self-doped Mott phase ^{2,36}. (what is it???)

This scenario is unlikely because of a significant charge transfer from the CCDW domains to the interdomain space within the NCCDW phase, and the insensitivity of the superconductivity to the disappearance of the CDW state. (???)

For that same reason, no signs of charge or spin-ordering fluctuations facilitating superconductivity are established to be present in $1T - TaS_2$ contrary to some other low-dimensional materials ^{37,38} (charge or spin-ordering fluctuations?) (for me, it is just some idea which is not true anyway, but it is interesting to learn it better) .

On the other hand, our phase diagram of $1T - TaS_2$ is remarkably similarly to that of some of the organic layered superconductors κ -(BEDTT-TTF)₂X (κ -(bis(ethylenedithio)tetrathiafulvalene)₂X; ref. 18), although on a different pressure scale. (add this article, learn what is there?)

Recent studies have uncovered numerous similarities, especially those revolving around the appearance of the pseudogap, between the layered organics, the superconducting cuprates and several dichalcogenide superconductors, advocating separate origins for the pseudogap and the superconducting gap ^{39,40}.

$1T - TaS_2$ may be sited within this framework by the presence of two types of order presumably accompanied by two distinct gaps in the pressure region between 1 GPa and 7 GPa. (how is it, two gaps???)

In addition, the relation between the electronic phase separation (electronic phase separation???) and superconductivity has been extensively considered for the cuprate systems in the form of stripes ^{3,41,41–43}, and recently observed by scanning tunnelling microscopy ⁴⁴.

Summary

In summary, the coincidental occurrence of both the Mott-state CCDW phase and superconductivity in 1T-TaS₂ presents unequivocal opportunities to investigate these collective states of matter in relation to each other.

The balance between these several regimes, spanning from the localized CCDW Mott phase to unconventional metallic states is readily and controllably tunable by the application of external pressure.

Although the superconductivity in 1 T – TaS₂ shares a few common features with the superconductivity in a number of layered superconductors that have been subject to extensive interest in recent years, there are a number of key differences. (which differences exactly?)

The remarkable insensitivity of the superconducting phase to the changes in the normal state;

the development of a Mott phase at low pressures as well as an exceptional variety of CDW phases, among those the textured non-metallic phase that hosts superconductivity, all combined stress the underlying importance of this material in the still perplexing field of electronic collective phenomena.

In the future, 1 T – TaS₂ would particularly benefit from further clarification of the normal and the superconducting states under pressure, using X-ray structural studies, Raman and infrared studies.

5.1.4 4. Methods

(SUMMARY: A FEW COMMENTS ABOUT EXPERIMENTAL SETUP AND USELESS CALCULATION OF SOME COULOMB ENERGY)

4.1 Measurements

The resistivity was measured using a standard four-point technique, with an a.c. current of 5 mA and a frequency of 16.98 Hz. (why these parameters?)

(what if they took other parameters?)

Pressure measurements in the low-pressure range 0 – 2GPa were obtained in a standard piston-cylinder pressure cell.

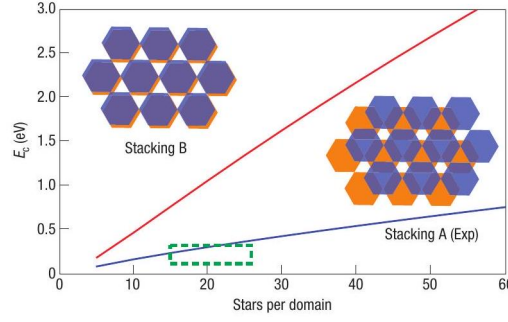
Pressure measurements in the pressure range 2 – 25GPa were carried out in an opposed-anvil Bridgeman-type pressure cell with tungsten carbide, sintered diamond anvils and quasi-liquid steatite medium. (quasi-liquid?)

Pressure was determined using a standard lead pressure gauge.

A pumped helium cryostat was used to achieve base temperatures of 1.3 K.

4.2 Calculating Coulomb energy

(I just don't understand what is going on here, I'll look later)



The Coulomb energy related to the charge transfer within the superstructure shown in Fig. 4 is calculated starting from the usual expression,

$$E_{\text{Coul}} = \frac{1}{2} \int_{\text{s.c.}} d^3\mathbf{r} \int d^3\mathbf{r}' \frac{1}{4\pi\epsilon_0\epsilon_r} \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|},$$

(forgot the exact origin of $\frac{1}{2}$, is it from double counting or what?)

where the first integral goes over the supercell in the TaS₂ plane, whereas the second integral goes over the whole space. $\rho(r)$ stands for the charge density produced by the charge transfer from domains to interdomain space.

E_{Coul} stands for the energy per supercell in the TaS₂ plane, and the energy E_c per electron transferred is obtained by dividing E_{Coul} by the number of David stars in the domain. Given the particular shape of the textured phase, we choose to calculate the integral in direct space, but with some simplifications.

First, being only interested in the long-wavelength aspect of the charge transfer, we do not consider the details of the charge distribution vertically within the layer, or on the scale of the basic TaS₂ cell.

Accordingly, the Coulomb potential is regularized below distance d , of the order of the separation between two neighbouring Ta atoms, and the planar charge density is assumed smooth on that scale.

The latter is set within the domain by the requirement of one electron lacking per David star, and the requirement that each supercell remains neutral.

In addition, no variation in planar charge density is allowed within domains or within the interdomain space. The former integral then transforms into the three-dimensional sum of convolutions of planar integrals over pairs of planar supercells.

The sum is rapidly converging on choosing the high-symmetry supercell, and all integrals are numerically calculated by subdividing the planar supercell into small triangles (size of the order of d).

(the following sentences give an idea how to get the ϵ_r)

The requirement that the states above the gap in domains are kept void, determines the contributions to the dielectric constant ϵ_r that enters the calculation.

Specifically, the contribution from electrons from metallic, 'triangular' parts should be excluded, and only the contributions that relate to gapped CDW should be included.

As these contributions also determine the screening of the electron-electron interaction in the Mott phase, the approximate value for appropriate ϵ_r may be determined from the proximity of that phase.

The collapse of the Mott state on triangular lattice²⁸ is known to occur at $U/t \sim 10$. (derive it for the purpose of general education!)

The value of U is given by $e^2/r_{\text{DS}}\epsilon_r$, where r_{DS} is of the order of the radius of the David star in 1 T – TaS₂, $e^2/r_{\text{DS}} \sim 2\text{eV}$.

The transfer integral t relevant for the Hubbard model may be read from the relevant bandwidth W in the band-structure calculation¹⁹, $W = 8t \approx 0.1\text{eV}$. This leads to $\epsilon_r \sim 10$, used in our calculation.

(check the band structure paper, it might be a useful one!!!)

5.2 My Discussion

5.2.1 Possible Next Steps for Research Using These Results

5.2.2 Questions

(there are many questions, but there is no sense right now to discuss them here, it is way more productive just to remember statements and move to another article)

Why at all they measure current and drive a conclusion about the state? Why not to use only the STM?

(it is very not clear how the state is connected to the amount of the current that passes through it. how are they connected???? sounds like a question for theoretician, has this been researched???)

Is there a theoretical explanations of at least some resistance dependence here?

(I'll ask someone, I don't know now)

What wasn't known before this article was published?

how much was known about the resistivity? I guess that there was this plot at ambient pressure before (fig. 1).

What if we went to lower pressures?

Why do we only increase pressure from the ambient one?
Maybe nothing interesting will be?

What if we look at not a "1 T" phase of TaS₂?

(I don't know yet these phases...)

What if we do measurements on another current?

Maybe nothing interesting will be?

6 Two-dimensional Fröhlich interaction in transition-metal-dichalcogenide monolayers: theoretical modeling and first-principles calculations by Sohler, Calandra, Mauri

Abstract

(calculations of the coupling between electrons and small-momentum polar-optical phonons) We perform *ab initio* calculations of the coupling between electrons and small-momentum polar-optical phonons in monolayer transition metal dichalcogenides of the 2H type: MoS₂, MoSe₂, MoTe₂, WS₂, and WSe₂. (why did they chose H type?) (why did they chose exactly small-momentum polar-optical phonons???)

(dimensionality is important) The polar-optical coupling with longitudinal optical phonons, or Fröhlich interaction (is Fröhlich interaction indeed exactly about them? check basics!) , is fundamentally affected by the dimensionality of the system.

(some extra interaction is there which affects this coupling and it is a problem) In a plane-wave framework with periodic boundary conditions, the Fröhlich interaction is affected by the spurious(not genuine) interaction between the 2D material and its periodic images. (what do they mean???)

(they use DFPT, they tune out of plane Coulomb interaction) To overcome this difficulty, we perform density functional perturbation theory calculations with a truncated Coulomb interaction in the direction perpendicular to the plane of the 2D material.

(Fröhlich interaction is much stronger than thought before) We show that the two-dimensional Fröhlich interaction is much stronger than assumed in previous *ab initio* studies. (what do they mean? read the article!)

(so they use analytics and numerics)

(they have analytical models) We provide analytical models depending on the effective charges and dielectric properties of the materials to interpret our *ab initio* calculations. (what is useful in them?)

(screening is important, there are two regimes) Screening is shown to play a fundamental role in the phonon-momentum dependency of the polar-optical coupling, with a crossover between two regimes depending on the dielectric properties of the material relative to its environment.

(Fröhlich g is screened and decreases with momenta) The Fröhlich interaction is screened by the dielectric environment in the limit of small phonon momenta and sharply decreases due to stronger screening by the monolayer at finite momenta.

(small-momentum -> simple analytical model) The small-momentum regime of the *ab initio* Fröhlich interaction is reproduced by a simple analytical model, for which we provide the necessary parameters.

(larger-momentum -> *ab initio* calculations) At larger momenta, however, direct *ab initio* calculations of electron-phonon interactions are necessary to capture band-specific effects.

(analysis of carrier relaxation times) We compute and compare the carrier relaxation times associated to the scattering by both LO and A_1 phonon modes.

(processes are fast and dependent on a lot of parameters) While both modes are capable of relaxing carriers on timescales under the picosecond at room temperature, their absolute and relative importance vary strongly depending on the material, the band, and the substrate.

6.1 Article

6.1.1 Introduction

Among the rapidly expanding family of two-dimensional (2D) materials, monolayer transition metal dichalcogenides (TMDs) offer particularly interesting features for electronic and optoelectronic applications[1, 2, 9, 4, 5]. Thanks to high carrier mobility and a direct band gap in the visible range they can be included in 2D van der Waals heterostructures to fulfil various functionalities associated to light-matter interaction and electron transport. In this context, it is essential to reach a good understanding of carrier scattering[6, 7, 8], including the intrinsic contribution from the electron-phonon interaction. In TMDs and other polar materials, a peculiar coupling emerges between electrons and longitudinal optical (LO) phonons. Such polar phonons interact with electrons by inducing a polarization density. At small phonon momenta, this polar-optical coupling, or Fröhlich interaction, can become quite large compared to standard electron-phonon coupling (EPC). Dimensionality has an interestingly drastic effect on this interaction. Indeed, in the limit of zero phonon momentum, the Fröhlich interaction

diverges in a material with three-dimensional (3D) periodicity while it tends to a finite value in 2D materials. This effect can be traced back to the behaviour of the long-range Coulomb interaction.

Density functional perturbation theory[9] (DFPT) is a powerful tool to simulate electron-phonon interactions. Associated to analytical models[10, 11, 12], this method can be used to establish quantitative models[13] of the Fröhlich interaction in bulk materials. Such a comprehensive and quantitative study of the Fröhlich interaction is still missing in the case of 2D materials. This is mainly due to the limitations of DFPT in the 2D framework. Indeed, DFPT relies on 3D periodic boundary conditions, implying the presence of periodic images when simulating low-dimensional systems. Since long-range Coulomb interactions between periodic images arise when low-dimensional systems are perturbed at small momenta[14], DFPT fails to account for the peculiarities of the Fröhlich interaction in 2D. In addition to those computational limitations, deriving analytical models of the Fröhlich interaction is not straightforward. In particular, the screening of the Coulomb interaction in 2D materials is a complex mechanism[15, 16, 17, 18, 19] requiring careful modeling.

In a previous *ab initio* study[20] of EPC in MoS₂, the small-momentum behaviour of the 2D Fröhlich interaction was estimated by fitting a 2D analytical model on *ab initio* calculations. However, the calculations were performed at momenta too large to capture the effects of dimensionality and the analytical model only partially accounted for the complex screening occurring in 2D materials. The 2D Fröhlich interaction was found to participate only moderately to the coupling with optical phonons in MoS₂, with a small-momentum limit three times smaller than the value reported here. Consequently, it was often ignored in following *ab initio* studies of EPC in TMDs[21, 22]. As far as modeling of the interaction is concerned, a more sophisticated model[15, 16, 17, 18, 19] of screening in 2D materials was used to estimate the strength of the Fröhlich interaction in a recent work[23]. This was done in the case of an isotropic dielectric tensor for the monolayer and without the support of direct *ab initio* computation of electron-phonon interactions.

We recently implemented[24] the truncation of the Coulomb interaction between periodic images of 2D materials in the DFT and DFPT package Quantum ESPRESSO[25] (QE). This technique enables us to isolate each slab and simulate electron-phonon interactions in a 2D framework. In this work we use this approach to compute the 2D Fröhlich interaction from first principles. We focus on the 2H polytypes of MoS₂, MoSe₂, MoTe₂, WS₂, and WSe₂. We propose developments on the analytical model of the Fröhlich interaction in 2D, especially concerning its screening in the case of a monolayer with anisotropic dielectric properties and for different dielectric environment on each side of the monolayer. We use *ab initio* calculations to estimate the parameters of this analytical model. The analytical model is used to interpret and support our calculations of the coupling to LO phonons, and a simple effective model is proposed to reproduce its small-momentum limit. The analytical model is also used to estimate the effect of the presence of a substrate on the Fröhlich interaction. Finally, we compute the inverse relaxation times associated to intraband scattering of carriers by LO and A₁ phonons. Large variations are observed from material to material. The relative importance of the LO and A₁ contributions strongly depends on the band in which we consider such scattering. In any case, optical phonons (LO and/or A₁) are shown to be capable of relaxing carriers on a time scale inferior to the picosecond at room temperature.

6.1.2 *ab initio* simulations of electron-phonon coupling

We perform DFPT calculations of EPC in monolayer TMDs (2H type), using our recently developed 2D Coulomb cutoff approach[24] within the Quantum ESPRESSO[25] (QE) distribution. This approach consists in truncating the Coulomb interaction between the periodic

images of the 2D material. This was implemented for the computation of total energy, forces, phonons and electron-phonon coupling. The technique requires the periodic images to be separated by at least twice the thickness of the electronic density of the simulated layer. We use a separation of ≈ 17 Å, largely fulfilling that requirement. Within a slab of thickness ≈ 12 Å everything happens as if the monolayer was isolated. Further details about the implementation of the 2D Coulomb cutoff in the DFT and DFPT packages of the QE distribution method will be exposed in a separate publication. We use pseudopotentials from the Standard Solid-State Pseudopotentials (SSSP) library (accuracy version) with PBE functionals and kinetic energy cutoff as indicated in the library. Spin-orbit coupling is neglected. Starting from experimental lattice parameters[27], structures are relaxed to minimize the total energy in our DFT framework. The resulting in-plane lattice parameters a_0 , subsequently used in our calculations, are given in Table 4. The electronic-momentum grid is set to $16 \times 16 \times 1$. Those choices are sufficient to obtain optical phonon energies within a few cm^{-1} of experimental values (when available).

In this section, MoS_2 is used as an example. We perform calculations in bulk MoS_2 as well to highlight the impact of dimensionality on the Fröhlich interaction. For bulk MoS_2 , we use the standard QE distribution and the experimental[27] out-of-plane lattice parameter of $c = 12.29$ Å. The corresponding unit-cell includes two layers such that the interlayer distance in the bulk is ≈ 6.15 Å. Note that a rigorous study of the bulk requires the inclusion of dispersion corrections[28] to account for van der Waals interactions between layers. Since we only seek a comparison of the small-momentum behaviour of the Fröhlich interaction, however, we will ignore this aspect.

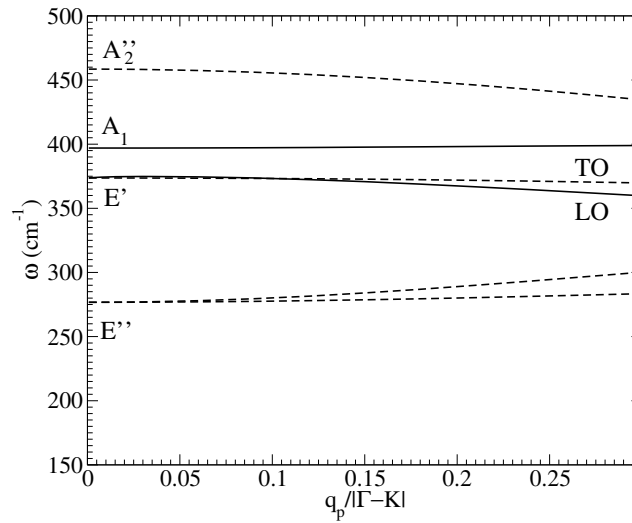


Figure 6.1: Dispersion of the optical phonons in monolayer MoS_2 at small momenta. For the modes in dashed lines, EPC matrix elements are negligible. The A_1 and LO modes, in plain lines, couple to electrons. We follow the notation of Ref. [29] for the symmetry representations of the modes at Γ . The E' mode separates into LO and TO modes.

We note $\mathbf{e}_{\mathbf{q}_p\nu}$ and $\hbar\omega_{\mathbf{q}_p\nu}$ the eigenvector and energy associated to a phonon in branch ν with in-plane momentum $\mathbf{q}_p$. The dispersions of small-momentum optical phonons in MoS_2 are shown in Fig. 6.1. Among those, only the A_1 and LO modes (plain lines in Fig. 6.1) couple to electrons. In the small-momentum limit, the A_1 mode corresponds to out-of-plane displacements of the sulfur atoms in phase opposition while the molybdenum atoms are static. The LO mode corresponds to in-plane longitudinal displacements with the molybdenum atom moving in phase opposition to both sulfur atoms. A more extensive ab initio study of phonons

in MoS₂ and WS₂ can be found in Ref. [29]. Optical phonon modes at small momenta are qualitatively similar for all the TMDs studied in this work.

We consider phonon-scattering of an electron from state $|\mathbf{k}\rangle$ to $|\mathbf{k} + \mathbf{q}\rangle$ within a given band. The associated EPC matrix element is defined as:

$$g_\nu(\mathbf{q}_p) = \sum_{a,i} \sqrt{\frac{\hbar}{2M_a\omega_{\mathbf{q},\nu}}} \mathbf{e}_{\mathbf{q}_p,\nu}^{a,i} \langle \mathbf{k} + \mathbf{q} | \Delta_{\mathbf{q}_p}^{a,i} \mathcal{V}_{\text{KS}}(\mathbf{r}) | \mathbf{k} \rangle, \quad (6.1)$$

where M_a is the mass of atom a and $\Delta_{\mathbf{q}_p}^{a,i} \mathcal{V}_{\text{KS}}(\mathbf{r})$ is the lattice periodic part of the derivative of the self-consistent Kohn-Sham potential with respect to a phonon displacement of atom a in direction i .

We consider neutral TMDs to avoid the metallic nature of the electronic screening that would occur in doped layers. Our primary goal is the study of the long-range Fröhlich interaction, involving LO phonons at small momenta ($|\mathbf{q}_p| < 15\%$ of $|\mathbf{\Gamma} - \mathbf{K}|$) and an excited electron or hole. Considering the small-momenta restriction and the energy of LO phonons, we can focus on intraband scattering. We further narrow the study to the highest part of the valence band around the high-symmetry points $\mathbf{K}$ and $\mathbf{\Gamma}$, and the lowest part of the conduction band around $\mathbf{K}$. More precisely, we compute the EPC matrix elements $g_{\text{LO}}(\mathbf{q}_p)$ for the following pairs of electronic states : (i) $\mathbf{k} = \mathbf{K} - \mathbf{q}_p/2$ and $\mathbf{k} + \mathbf{q}_p = \mathbf{K} + \mathbf{q}_p/2$ in the conduction band, noted "K cond" ; (ii) $\mathbf{k} = \mathbf{K} - \mathbf{q}_p/2$ and $\mathbf{k} + \mathbf{q}_p = \mathbf{K} + \mathbf{q}_p/2$ in the valence band, noted "K val" ; (iii) $\mathbf{k} = \mathbf{\Gamma} - \mathbf{q}_p/2$ and $\mathbf{k} + \mathbf{q}_p = \mathbf{\Gamma} + \mathbf{q}_p/2$ in the valence band, noted " Γ val". Momentum $\mathbf{q}_p$ is in the $\mathbf{\Gamma} \rightarrow \mathbf{M}$ direction to minimize LO/TO mixing.

The results of the calculations for MoS₂ are presented in Fig. 6.2. For comparison, we add the coupling $g_{A_1}(\mathbf{q}_p)$ associated to the other significant contribution of the A_1 mode. We recover the characteristic behaviours of the 2D and 3D Fröhlich interactions. In the 3D case, the interaction diverges as $\mathbf{q}_p \rightarrow \mathbf{\Gamma}$. In the 2D framework provided by our approach, however, the Fröhlich interaction tends to a constant at $\mathbf{\Gamma}$. Note that a divergence will occur when using the standard QE code, even if the interlayer distance is increased. The fact that we recover the finite limit of the coupling at $\mathbf{\Gamma}$ thus confirms that the truncation of the Coulomb interaction in QE is equivalent to simulating an isolated monolayer. The coupling to LO phonons at large momenta depends on the bands via the details of the electronic wave functions. Indeed, in that case, the variations of the polarization potential on the length scale of the width of the electronic states becomes relevant. Similar calculations were performed for monolayers of MoSe₂, MoTe₂, WS₂, and WSe₂, see Fig. ?? of the Appendix.

In Figs. 6.2 and ??, the plain lines represent analytical models discussed in the following sections. In those models, we will focus on the more general small-momentum behaviour of the Fröhlich interaction, which depends solely on the Born effective charges and dielectric properties of the material. From a modeling point of view, the existence of finite limit at $\mathbf{\Gamma}$ for the 2D interaction is easily established by considering the $1/|\mathbf{q}_p|$ dependence of the 2D Coulomb interaction in reciprocal space. The sharp decreasing of the coupling at finite- $\mathbf{q}$, however, is a more subtle screening effect that remains to be studied in details. Our numerical DFPT method provide us with a support to treat this issue in a systematic manner and establish a quantitatively accurate analytical model.

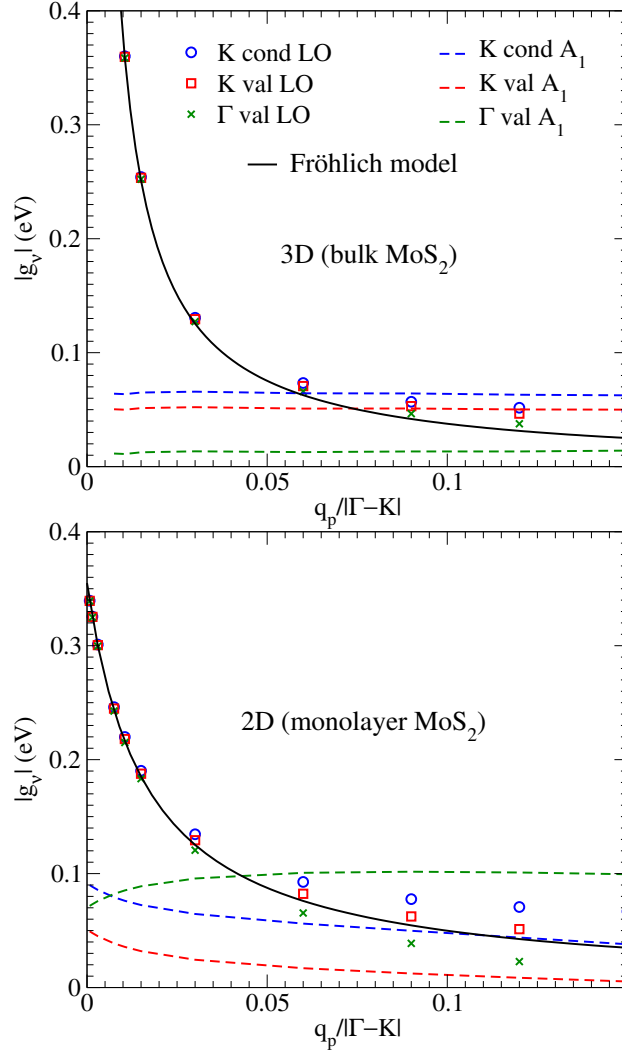


Figure 6.2: EPC matrix elements involving LO and A_1 phonon modes in bulk and monolayer MoS_2 . We consider intraband scattering of electrons or holes in the conduction band near $\mathbf{K}$ ("K cond") and in the valence band near $\mathbf{K}$ and $\mathbf{\Gamma}$ ("K val" and " $\mathbf{\Gamma}$ val", respectively). Momenta $\mathbf{q}_p$ are in the $\mathbf{\Gamma} \rightarrow \mathbf{M}$ direction. The coupling to the LO phonons includes the Fröhlich interaction. The models for three-dimensional and two-dimensional Fröhlich interactions in bulk and monolayer MoS_2 are represented in plain lines and described in the text. Dashed lines and symbols are DFPT calculations. The standard QE package was used for the bulk, while we used our implementation of the Coulomb cutoff in for the monolayer.

6.1.3 Analytical Models of the Fröhlich interaction

We now present analytical models to explain our DFPT calculations and gain better understanding on the effect of dimensionality on the small-momentum limit of the Fröhlich interaction. The tensors of Born effective charges are noted $\mathcal{Z}_a^b$ and $\mathcal{Z}_a^m$ for bulk and monolayer, respectively. The index a runs over the atoms of the unit cell. The relative dielectric permittivity tensors (simply called dielectric tensors hereafter) for bulk and monolayer are noted $\mathcal{E}^b$ and $\mathcal{E}^m$, respectively. By symmetry, the tensors are isotropic in the plane, but we allow for different properties in the out-of-plane direction. The tensors thus have the following generic forms:

$$\mathcal{E} = \begin{pmatrix} \epsilon_p & 0 & 0 \\ 0 & \epsilon_p & 0 \\ 0 & 0 & \epsilon_z \end{pmatrix} \quad \mathcal{Z}_a = \begin{pmatrix} Z_{a,p} & 0 & 0 \\ 0 & Z_{a,p} & 0 \\ 0 & 0 & Z_{a,z} \end{pmatrix}. \quad (6.2)$$

In-plane and out-of-plane variables are separated according to the notation $\mathbf{r} \rightarrow (\mathbf{r}_p, z)$ and $\mathbf{q} \rightarrow (\mathbf{q}_p, q_z)$. We use Gaussian CGS units.

Three-Dimensional bulk

We quickly recall the well-known results of the 3D case. The small momentum behaviour of the Fröhlich interaction is well described by the leading order in Vogl's model [10]

$$|g_{\text{Fr}}^{3\text{D}}(\mathbf{q}_p)| = \frac{4\pi e^2}{V|\mathbf{q}_p|\epsilon_p^b} \sum_a \frac{\mathbf{e}_{\mathbf{q}_p} \cdot \mathbf{Z}_a^b \cdot \mathbf{e}_{\mathbf{q}_p\text{LO}}^a}{\sqrt{2M_a\omega_{\mathbf{q}_p\text{LO}}}}, \quad (6.3)$$

where e is the elementary charge, V is the unit-cell's volume, ϵ_p^b is the in-plane dielectric constant of the bulk (15.37 in MoS₂), and $\mathbf{e}_{\mathbf{q}_p} = \mathbf{q}_p/|\mathbf{q}_p|$. The pre-factor of $1/|\mathbf{q}_p|$ is essentially constant in the range of momenta considered in this work. A small dependency on norm and direction of $\mathbf{q}_p$ appears as the phonon modes deviate from the strictly longitudinal modes. This model is sufficient to reproduce the small-momentum limit of the Fröhlich interaction, as shown in Fig. 6.2 where the plain line is the above model.

Two-dimensional monolayer

Our objective is to derive the Fröhlich interaction in the system of Fig. 6.3. We consider LO phonons in a 2D material of thickness t . Its dielectric tensor $\mathcal{E}^m$ has the form of Eq. 6.2, with in-plane and out-of-plane dielectric constants ϵ_p^m and ϵ_z^m , respectively. Above and below are two semi-infinite spaces with isotropic dielectric properties represented by the dielectric constants ϵ_2 and ϵ_1 , respectively.

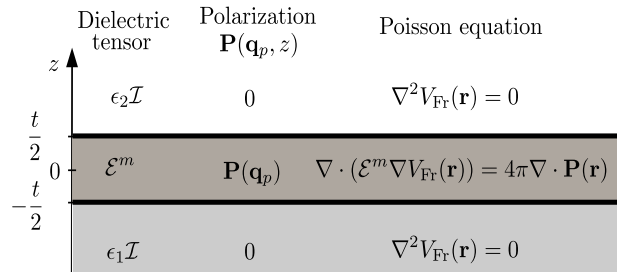


Figure 6.3: Model of the Fröhlich interaction in a polar 2D material of thickness t . LO phonons generate a periodic polarization density $\mathbf{P}(\mathbf{r}_p, z) = \mathbf{P}(\mathbf{q}_p, z)e^{i\mathbf{q}_p \cdot \mathbf{r}_p}$ inside the 2D material. The dielectric properties of the 2D material are represented by the dielectric tensor $\mathcal{E}^m$ with in-plane and out-of-plane dielectric constants ϵ_p^m and ϵ_z^m , respectively. Above and below are two half spaces in which the polarization is zero and the dielectric constants are ϵ_2 and ϵ_1 respectively. The symbol $\mathcal{I}$ denotes the identity matrix. The two thick horizontal black lines represent surface charges at the interfaces of the 2D material due to the abrupt variations in the polarization density. We write the Poisson equation defining the Fröhlich potential V_{Fr} in each region.

The origin of the polar-optical coupling is the polarization density $\mathbf{P}(\mathbf{r}_p, z)$ generated by the atomic displacement pattern associated to a LO phonon of in-plane momentum $\mathbf{q}_p$

$$\mathbf{P}(\mathbf{r}_p, z) = \frac{e^2}{A} \sum_a \frac{\mathbf{Z}_a^m \cdot \mathbf{e}_{\mathbf{q}_p\text{LO}}^a}{\sqrt{2M_a\omega_{\mathbf{q}_p\text{LO}}}} f(z) e^{i\mathbf{q}_p \cdot \mathbf{r}_p}, \quad (6.4)$$

where A is the area of the unit-cell and $f(z)$ is the out-of-plane profile of the polarization (normalized to unity). Such a polarization density induces a potential $V_{\text{Fr}}(\mathbf{r}_p, z) = V_{\text{Fr}}(\mathbf{q}_p, z)e^{i\mathbf{q}_p \cdot \mathbf{r}_p}$ with the same periodicity. The associated EPC can then be written as

$$g_{\text{Fr}}^{2\text{D}}(\mathbf{q}_p) = \int V_{\text{Fr}}(\mathbf{q}_p, z)n_{\text{el}}(z)dz, \quad (6.5)$$

where $n_{\text{el}}(z)$ is the plane-averaged electronic density. By using this expression, we neglect the details of the wave-functions and the associated band-dependency. In the out-of-plane direction, we will consider the electronic density and the polarization to be uniform over the thickness t of the material

$$f(z) = n_{\text{el}}(z) = \frac{\theta(t/2 - |z|)}{t}, \quad (6.6)$$

where θ is the Heavyside function. This approximation should be satisfactory in the long wavelength limit, since $V_{\text{Fr}}(\mathbf{q}_p, z)$ varies mildly in the out-of-plane direction.

The potential V_{Fr} must fulfil the Poisson equation

$$\nabla \cdot (\mathcal{E}(z)\nabla V_{\text{Fr}}(\mathbf{r})) = 4\pi\nabla \cdot \mathbf{P}(\mathbf{r}), \quad (6.7)$$

where $\mathcal{E}(z)$ is a position dependent dielectric tensor. The central objects of the problem are the phonon-induced polarization density and the dielectric tensor. As one travels along the out-of-plane direction, both those quantities change. Inside the 2D material, $\mathcal{E}(z) = \mathcal{E}^m$ and the polarization density is finite and oscillating in the plane. Outside the 2D material, $\mathcal{E}(z) = \epsilon_1\mathcal{I}$ or $\epsilon_2\mathcal{I}$ (where $\mathcal{I}$ is the identity matrix) and the polarization density is zero. Other requirements on the potential are that the associated in-plane electric field $\mathbf{E}^{\parallel}(\mathbf{r})$ and out-of-plane electric displacement $\mathbf{D}^{\perp}(\mathbf{r})$ should be continuous.

The detailed derivation of the solution to this model can be found in App. 6.1.8. To allow for a more direct interpretation of the final solution in Eq. 6.36, we seek a more transparent form. By Taylor expansion of the denominator at the linear order in $|\mathbf{q}_p|$, the full expression of Eq. 6.36 can be recast in the form

$$\begin{aligned} |g_{\text{Fr}}^{2\text{D}}(\mathbf{q}_p)| &= \frac{C_{\mathcal{Z}}}{\epsilon_{\text{eff}}(|\mathbf{q}_p|)} \\ \epsilon_{\text{eff}}(|\mathbf{q}_p|) &\approx \epsilon_{\text{eff}}^0 + r_{\text{eff}}|\mathbf{q}_p|, \end{aligned} \quad (6.8)$$

where the expressions of the parameters are given in table 1. The above form is found to reproduce Eq. 6.36 very accurately. Only when $\epsilon_z^m \approx \epsilon_1$ or ϵ_2 should one retain Eq. 6.36 rather than use Eq. 6.8. More quantitative results, depending on the nature of the monolayer, will be given in Sec. 6.1.5. For now, let us make some qualitative remarks valid as long as the material is a stronger dielectric as the environment, which is the case of the monolayer TMDs discussed in this work, in vacuum or on SiO_2 . The bare magnitude of the polar-optical coupling is given by $C_{\mathcal{Z}}$. The origin of the sharp decrease at finite $\mathbf{q}_p$ is a screening effect specific to 2D materials. It can be associated with the formation of surface charges due to the change in dielectric properties at the interfaces between the 2D material and its environment. The screening is characterized by the parameter r_{eff} which depends on the dielectric properties of the material as well as its thickness. Homogeneous to a distance, it can be interpreted as an effective thickness marking the crossover between two screening regimes. For $|\mathbf{q}_p| \ll r_{\text{eff}}^{-1}\epsilon_{\text{eff}}^0$, the coupling is screened by ϵ_{eff}^0 , which depends mainly on the dielectric properties of the environment. For $|\mathbf{q}_p| \gg r_{\text{eff}}^{-1}\epsilon_{\text{eff}}^0$, the field lines are confined to the material, and the coupling is screened by the material. Materials

Table 1: Full expressions of the parameters involved in the model of the 2D Fröhlich interaction, Eq. 6.8. See Fig. 6.3 and Eq. 6.2 for the definitions of the various parameters in the model. Note that for the isolated TMDs considered in our *ab initio* calculations, we have $\epsilon_1 = \epsilon_2 = \epsilon_{12} = 1$, $\epsilon_z^m \gg 1$, and $\epsilon_p^m \gg 1$, which leads to $F \approx 1$, $\epsilon_{\text{eff}}^0 \approx 1$, and $r_{\text{eff}} \approx \frac{\epsilon_p^m t}{2}$.

$$C_Z = \frac{2\pi e^2}{A} \sum_a \frac{\mathbf{e}_{\mathbf{q}p} \cdot \mathbf{Z}_a^m \cdot \mathbf{e}_{\mathbf{q}p\text{LO}}^a}{\sqrt{2M_a \omega_{\mathbf{q}p\text{LO}}}}$$

$$\epsilon_{\text{eff}}^0 = \epsilon_{12} \frac{\epsilon_z^m \bar{\epsilon}}{\epsilon_z^m \bar{\epsilon} + \epsilon_{12}(\epsilon_z^m - \bar{\epsilon})}$$

$$r_{\text{eff}} = \frac{(\epsilon_{\text{eff}}^0)^2}{\epsilon_{12}} \left(\frac{\epsilon_{12}}{3\epsilon_z^m} + \frac{\epsilon_p^m}{2\epsilon_{12}} F \right) \times t$$

$$F = 1 + \frac{\epsilon_1 \epsilon_2}{\bar{\epsilon}^2} + \frac{\epsilon_{12}}{\bar{\epsilon}} - \frac{\epsilon_{12}^2}{\bar{\epsilon} \epsilon_z^m} - \frac{\epsilon_{12}^2}{\bar{\epsilon}^2} - \frac{\epsilon_{12}}{\epsilon_z^m}$$

$$\epsilon_{12} = \frac{\epsilon_1 + \epsilon_2}{2} \quad \bar{\epsilon} = \sqrt{\epsilon_z^m \epsilon_p^m}$$

with large dielectric constants (with respect to the environment) will tend to focus the field lines more strongly, which results in a larger effective thickness r_{eff} and a sharper decrease in the Fröhlich interaction at finite momenta (note that the slope of the coupling at Γ is proportional to $-r_{\text{eff}}$).

We have derived the general expression for an anisotropic slab and different dielectric media above and below. It can be applied to any polar material. To be quantitatively predictive, we need to evaluate the parameters involved. We now detail how to evaluate those parameters with *ab initio* calculations.

6.1.4 *ab initio* Parameters

Here again, MoS₂ will be used as an example to illustrate the method. The final parameters of interest will then be given for the other TMDs. The parameters of the model are the Born effective charges, dielectric tensors and phonon eigenvectors. The dynamical matrix and the corresponding phonon eigenvectors are available from the electron-phonon calculations. The QE code computes clamped-ions dielectric tensors and Born effective charges by means of linear response calculations with respect to an electric field perturbation[9]. The Born effective charges are related to the derivative of the forces on the atoms with respect to the applied electric field. Since our implementation of the 2D Coulomb cutoff includes the computation of forces, the Born effective charges can be computed in the 2D framework for the monolayers. Note, however, that equivalent results can be obtained with the standard code. Indeed, Born effective charges converge relatively fast towards their 2D values with respect to the distance between periodic images. The dielectric constant, on the other hand, is computed as a macroscopic quantity defined over a three-dimensional supercell. As such, the computation of the dielectric tensor of the bulk $\mathcal{E}^b$ is straightforward and reported in Table 2 for MoS₂. The computation of an equivalent quantity relevant for 2D materials, however, raises issues beyond periodic images interactions [30, 31]. As of yet, we did not implement the modifications necessary to compute dielectric tensors in a 2D framework. In the following, the dielectric tensors of the monolayers will be evaluated using the standard QE code, with an effort to extract relevant 2D quantities

from 3D calculations.

The constant C_Z corresponds to the magnitude of the *bare* Fröhlich interaction. It depends on the Born effective charges and the phonon displacements. The components of the tensors $\mathcal{Z}_a^m$ (computed with 2D Coulomb cutoff) and $\mathcal{Z}_a^b$ (computed without cutoff) for MoS₂ are given in table 2. The components of $\mathcal{Z}_a^m$ for other monolayer TMDs are reported in Table 3. The bare coupling C_Z varies with the direction and modulus of $\mathbf{q}_p$ via the phonon eigenvectors. It reaches a maximum in the $\mathbf{q}_p \rightarrow \Gamma$ limit, where the LO eigenvectors correspond to purely longitudinal modes. It moderately decreases with increasing momenta ($\approx -10\%$ at $|\mathbf{q}_p| \approx 15\%$ of $|\Gamma - \mathbf{K}|$). Since the momentum behaviour of the Fröhlich interaction is largely dominated by the screening factor $\frac{1}{\epsilon_{\text{eff}}(\mathbf{q}_p)}$, we can neglect the variations associated to the phonon eigenvectors and use the $\mathbf{q}_p \rightarrow \Gamma$ value of the bare coupling. Those values are reported in Table 4, in the column named " C_Z (*ab initio*)".

Table 2: Dielectric constants and effective charges of bulk and monolayer MoS₂ as obtained in DFT. In the case of the monolayer, we report the dielectric constant in the case of an isotropic model. The full range of possible values for the in-plane and out-of-plane dielectric constants is given in Fig. 6.5.

Bulk		Monolayer	
Symbol	Value	Symbol	Value
ϵ_p^b	15.37	$\epsilon_p^m = \epsilon_{\text{iso}}^m$	15.5
ϵ_z^b	6.57	$\epsilon_z^m = \epsilon_{\text{iso}}^m$	15.5
$Z_{\text{Mo},p}^b$	-0.9413	$Z_{\text{Mo},p}^m$	-1.0051
$Z_{\text{Mo},z}^b$	-0.5918	$Z_{\text{Mo},z}^m$	-0.0919
$Z_{\text{S},p}^b$	0.4668	$Z_{\text{S},p}^m$	0.4525
$Z_{\text{S},z}^b$	0.2921	$Z_{\text{S},z}^m$	0.0411

Table 3: Effective charges of monolayer TMDs, as computed in QE via the response to an external electric field. $M \equiv \text{Mo, W}$. $X \equiv \text{S, Se, Te}$.

Monolayer	$Z_{M,p}^m$	$Z_{M,z}^m$	$Z_{X,p}^m$	$Z_{X,z}^m$
MoS ₂	-1.00	-0.09	0.45	0.04
MoSe ₂	-1.78	-0.13	0.73	0.04
MoTe ₂	-3.14	-0.15	1.36	0.04
WS ₂	-0.49	-0.07	0.20	0.02
WSe ₂	-1.17	-0.12	0.43	0.03

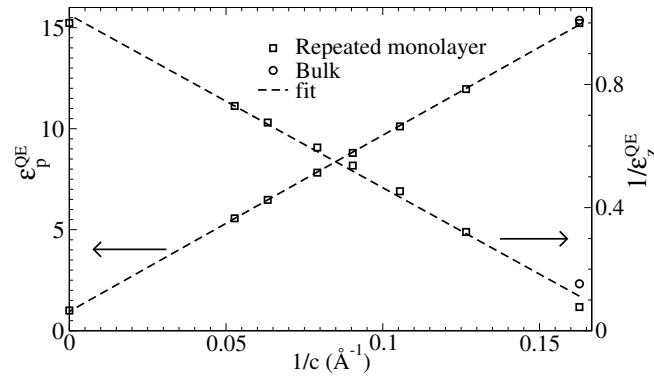


Figure 6.4: The QE quantities ϵ_p^{QE} and $1/\epsilon_z^{QE}$ as functions of the inverse interlayer distance $1/c$, in MoS₂. In each plot, we add the data point corresponding to the bulk.

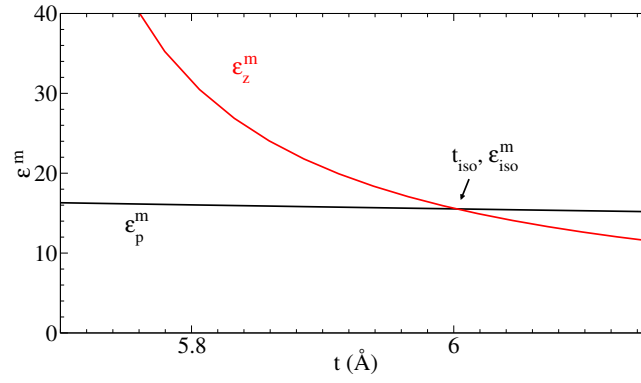


Figure 6.5: Values of ϵ_p^m and ϵ_z^m that would be consistent with direct *ab initio* computation of the supercell's dielectric constants ϵ_p^{QE} and ϵ_z^{QE} , as functions of the corresponding thickness of the monolayer. We indicate the point corresponding to an isotropic system.

We now evaluate the dielectric properties of the monolayer using the standard (3D) QE code. We simulate a system made of repeated monolayers separated by a varying distance c , with vacuum in between. The clamped-ions dielectric tensor of this system, as computed within QE, is written as

$$\mathcal{E}^{\text{QE}} = \begin{pmatrix} \epsilon_p^{\text{QE}} & 0 & 0 \\ 0 & \epsilon_p^{\text{QE}} & 0 \\ 0 & 0 & \epsilon_z^{\text{QE}} \end{pmatrix}. \quad (6.9)$$

In this picture, the dielectric tensor of the bulk simply corresponds to $\mathcal{E}^{\text{QE}}$ with a fixed interlayer distance c (neglecting the small effects of an alternating stacking). To relate $\mathcal{E}^{\text{QE}}$ to the dielectric tensor of the monolayer $\mathcal{E}^m$, we use effective medium theory and introduce the thickness of the monolayer as a parameter. We then have the following relations[32]:

$$\begin{aligned} \epsilon_p^{\text{QE}} &= 1 + (\epsilon_p^m - 1)t/c \\ \frac{1}{\epsilon_z^{\text{QE}}} &= 1 - \frac{(\epsilon_z^m - 1)}{\epsilon_z^m}t/c. \end{aligned} \quad (6.10)$$

Note that in the limit of infinite interlayer distance, this dielectric tensor does not tend toward $\mathcal{E}^m$. Instead, it tends towards the dielectric tensor of vacuum.

In Fig. 6.4, we plot the ϵ_p^{QE} and $1/\epsilon_z^{\text{QE}}$ as functions of $1/c$. Fitting this data, we find slopes $s_1 = 87.2 \text{ \AA}$ and $s_2 = 5.62 \text{ \AA}$ respectively. We then write ϵ_p^m and ϵ_z^m as functions of t according to

$$\begin{aligned} \epsilon_p^m &= 1 + \frac{s_1}{t} \\ \epsilon_z^m &= \frac{t}{t - s_2}. \end{aligned} \quad (6.11)$$

In principle, every set of values $\{\epsilon_p^m, \epsilon_z^m, t\}$ that satisfies the above equations can fit our DFT results. We can assume that $t > s_2$, as we would have $\epsilon_z^m < 0$ otherwise. We can also assume that $t < c_{\text{bulk}} \approx 6.15 \text{ \AA}$, the distance between two monolayers in the bulk. In the lower panel of Fig. 6.4, we plot $\epsilon_p^m, \epsilon_z^m$ as functions of t in this reasonable range of values for the thickness. Fig. 6.4 should thus be understood as a set of possible values for $\epsilon_p^m, \epsilon_z^m$ and the corresponding thickness. Note that $t \approx 6 \text{ \AA}$ is consistent with the width of the equilibrium electronic density found in DFT. One can see that while ϵ_p^m is almost constant in Fig. 6.4, the variation of ϵ_z^m is more pronounced. Similar results are obtained for MoSe_2 , MoTe_2 , WS_2 , and WSe_2 . As far as the above *ab initio* study is concerned, we are thus left with a free parameter to model

the dielectric properties of the 2D materials, that is, a choice to make for the set of values $\{\epsilon_p^m, \epsilon_z^m, t\}$. For all TMDs, there is a reasonable value of $t = t_{\text{iso}}$ leading to an isotropic model with $\epsilon_{\text{iso}}^m = \epsilon_p^m = \epsilon_z^m$. As shown in the next section, this isotropic model is a choice that leads to simple yet accurate results for the Fröhlich interaction.

6.1.5 Effective isotropic model

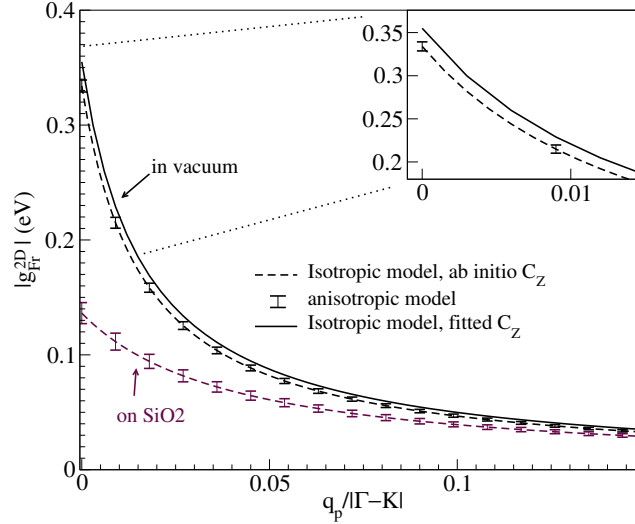


Figure 6.6: Dashed lines are obtained by using the isotropic model ($\epsilon_{\text{iso}}^m = \epsilon_p^m = \epsilon_z^m$, $t = t_{\text{iso}}$) and C_Z from *ab initio* Born effective charges. The errors bars show the deviation from the isotropic model obtained by using an anisotropic model with values of $\epsilon_p^m, \epsilon_z^m$ and t in the range of Fig 6.5. The plain line corresponds to the isotropic model (for MoS₂ in vacuum) with fitted C_Z . This coincides with the direct DFPT calculations of EPC, at least at small momenta (see Figs. 6.2 and ??). The inset is a zoom on the small momenta limit of the models. It shows that a fitted C_Z is necessary, as an anisotropic model would not be enough to fit the direct DFPT calculations of EPC. The SiO₂ substrate increases the screening of the Fröhlich interaction strongly at small momenta.

We now establish a simple effective model to reproduce the small-momentum limit of our direct DFPT calculations of the coupling to LO phonons. We first discuss the effects of selecting different set of values for ϵ_p^m , ϵ_z^m , and t . This depends on the dielectric environment, namely on the average dielectric constant $\epsilon_{12} = \frac{\epsilon_1 + \epsilon_2}{2}$. Our DFPT calculations are performed in vacuum, with $\epsilon_{12} = 1$. Whatever thickness we choose in Fig. 6.5, we have $\epsilon_p^m \gg \epsilon_{12}$ and $\epsilon_z^m \gg \epsilon_{12}$. In that case, the anisotropic model is very close to the isotropic one. This is shown numerically in Fig. 6.6. In dashed lines is the isotropic model, for which we use $\epsilon_{\text{iso}}^m = \epsilon_p^m = \epsilon_z^m$ and $t = t_{\text{iso}}$. The error bars represent the deviation of the full anisotropic model when using other values of $\epsilon_p^m, \epsilon_z^m$, and t within those represented in Fig. 6.5.

Table 4: Comparison of relevant quantities involved in the Fröhlich interaction for the monolayer TMDs MoS₂, MoSe₂, MoTe₂, WS₂, and WSe₂. a_0 is the lattice parameter. We report here the dielectric constants associated to the simplest isotropic model, that is $\epsilon_{\text{iso}}^m = \epsilon_p^m = \epsilon_z^m$ and $t = t_{\text{iso}}$. Note that we use the fact that $r_{\text{eff}} \approx \epsilon_{\text{iso}}^m t_{\text{iso}}/2$. For the bare Fröhlich interaction C_Z , we report both the fitted value (from fit) used in the plots to reproduce the DFPT data and the value found by computing effective charges and phonons eigenvectors (*ab initio*).

Monolayer	a_0 (Å)	t_{iso} (Å)	ϵ_{iso}^m	r_{eff} (Å)	C_Z (eV) (from fit)	C_Z (eV) (<i>ab initio</i>)	ω_{LO} (cm ⁻¹)	ω_{A_1} (cm ⁻¹)
MoS ₂	3.18	6.00	15.5	46.5	0.355	0.334	373.7	396.9
MoSe ₂	3.32	5.94	17.9	53.2	0.521	0.502	277.5	235.4
MoTe ₂	3.56	6.65	20.9	69.5	0.819	0.819	223.6	162.9
WS ₂	3.18	5.52	15.2	42.0	0.165	0.140	345.9	407.4
WSe ₂	3.31	5.97	16.3	48.7	0.323	0.276	239.4	242.1

For most monolayers, using the bare Fröhlich interaction C_Z calculated via the *ab initio* effective charges leads to a slight mismatch with respect the direct DFPT calculations of EPC. The effect of anisotropy in vacuum is too small to explain this mismatch, as seen in Fig. 6.6. To reach better agreement, the parameter C_Z must be adjusted. The fitted values of C_Z for all monolayers are reported in Table 4. Note that *ab initio* and fitted values stay relatively close, meaning that a simple calculation of the effective charges can still lead to a good approximation of the bare Fröhlich interaction. However, the mismatch is clear enough to point to some possible issues in the computation of the effective charges. This imprecision on the computation of C_Z also implies that we cannot resolve the very small effect of anisotropy.

Overall, an isotropic model with dielectric constant $\epsilon_{\text{iso}}^m = \epsilon_p^m = \epsilon_z^m$ and a fitted C_Z (plain lines in Figs 6.2 and ?? of the Appendix) is the best choice to reproduce our DFPT results. Within the assumption that $\epsilon_{\text{iso}}^m \gg \epsilon_{12}$, further simplification and greater clarity can be achieved in the model. Indeed, the parameters of table 1 can be approximated by

$$\epsilon_{\text{eff}}^0 \approx \epsilon_{12} = \frac{\epsilon_1 + \epsilon_2}{2} \quad (6.12)$$

$$r_{\text{eff}} \approx \frac{\epsilon_{\text{iso}}^m}{2} t_{\text{iso}}. \quad (6.13)$$

This simple form allows us to gain physical insight on the screening. In the limit $r_{\text{eff}}|\mathbf{q}_p| \gg \epsilon_{12}$, that is $|\mathbf{q}_p| \gg \frac{2\epsilon_{12}}{\epsilon_{\text{iso}}^m t_{\text{iso}}}$, we have $g_{\text{Fr}}^{2\text{D}}(|\mathbf{q}_p|) \approx g_{\text{Fr}}^{3\text{D}}(|\mathbf{q}_p|)$. Indeed, the factor 1/2 in r_{eff} enables to recover the prefactor of the 3D Coulomb interaction ($2\pi e^2 \rightarrow 4\pi e^2$), while $At \approx V$, and $\epsilon_{\text{iso}}^m = \epsilon_p^m \approx \epsilon_p^b$. In that case, the wavelength of the perturbation associated to the LO phonon is small and the associated field lines stay inside the monolayer. The interaction is then screened by the monolayer. In the $r_{\text{eff}}|\mathbf{q}_p| \ll \epsilon_{12}$ limit, that is $|\mathbf{q}_p| \ll \frac{2\epsilon_{12}}{\epsilon_{\text{iso}}^m t_{\text{iso}}}$, we have $g_{\text{Fr}}^{2\text{D}}(|\mathbf{q}_p|) \approx \frac{C_Z}{\epsilon_{12}}$, which corresponds to the interaction being screened solely by the environment. In vacuum, the crossover between those two regimes happens for $|\mathbf{q}_p|$ around $\frac{2}{\epsilon_{\text{iso}}^m t_{\text{iso}}} \approx 0.02 \text{ \AA}^{-1} \approx 0.015|\mathbf{\Gamma} - \mathbf{K}|$, that is, very close to the $\mathbf{\Gamma}$ point. This is due to the large dielectric constant of the monolayer compared to the environment.

An important benefit of the model is the possibility to evaluate the effects of the dielectric environment[33]. In Fig. 6.6, we present results for the more experimentally relevant case of MoS₂ ion SiO₂, for which $\epsilon_{12} = \frac{1+3.9}{2} = 2.45$. The coupling is shown to be strongly decreased overall. The validity of the approximations $\epsilon_p^m \gg \epsilon_{12}$ and $\epsilon_z^m \gg \epsilon_{12}$ is less clear, and the deviation from the isotropic model in Fig. 6.5 is more discernible. However, for the purpose of estimating the effect of a SiO₂ substrate, and given the simplicity of the above parameters, it is still convenient to use the effective isotropic model.

The relevant parameters, including the thickness t_{iso} and isotropic dielectric constant ϵ_{iso}^m , are reported in Table 4 for all monolayers. In the case of MoS₂, we find that the value of

the coupling at Γ in vacuum, i.e. the bare interaction C_Z , is three times larger than the one predicted in a previous *ab initio* study[20]. The bare interaction C_Z and effective screening length r_{eff} increase with the atomic number of the chalcogen while they decrease with the atomic number of the transition metal.

6.1.6 Transport

To provide a more practical sense of the implications of this work, we compute the following inverse relaxation times for an excited electron or hole scattered by LO or A_1 phonons

$$\frac{1}{\tau_\nu(\varepsilon_{\mathbf{k}})} = \frac{2\pi}{\hbar} \sum_{\mathbf{q}_p} |g_\nu(\mathbf{q}_p)|^2 \times \delta(\varepsilon_{\mathbf{k}+\mathbf{q}_p} - \varepsilon_{\mathbf{k}} \mp \hbar\omega_{\mathbf{q}_p,\nu}) \left\{ \begin{matrix} N_{\nu,\mathbf{q}_p} \\ N_{\nu,\mathbf{q}_p} + 1 \end{matrix} \right\}, \quad (6.14)$$

where $\nu \equiv \text{LO or } A_1$, $N_{\nu,\mathbf{q}_p}$ is the Bose-Einstein distribution for phonon occupation at room temperature and $\varepsilon_{\mathbf{k}}$ is the eigenvalue energy of electronic state $|\mathbf{k}\rangle$, measured from the bottom (top) of the conduction (valence) band. The "-" (respectively "+") sign in the Dirac delta function δ is associated to $N_{\nu,\mathbf{q}_p}$ ($N_{\nu,\mathbf{q}_p} + 1$) and corresponds to phonon absorption (emission). The two contributions are then summed. In Fig. ??, we plot the inverse relaxation times for each of the three bands (K cond, K val, and Γ val) and for each of the MoS_2 , MoSe_2 , MoTe_2 , WS_2 , and WSe_2 monolayers. To compute those quantities, we need EPC matrix elements on a fine grid of momenta $\mathbf{q}_p$. We use the analytical model when possible and linearly extrapolate the DFPT couplings otherwise. More precisely, in the limit of small momenta, the coupling to LO phonons follows our analytical model of the Fröhlich interaction and does not depend on the angle of momentum $\mathbf{q}_p$ or the band. We then use the analytical model $|g_{\text{Fr}}^{2\text{D}}(\mathbf{q}_p)|$. At larger momenta, the coupling depends on the band via the wave functions. We then extrapolate the *ab initio* coupling $|g_{\text{LO}}(\mathbf{q}_p)|$. A few other *ab initio* calculations were performed for momenta up to $|\mathbf{q}_p^{\text{max}}| \approx 0.3|\Gamma - \mathbf{K}|$. A mild angular dependency is possible for the *ab initio* matrix elements $|g_{\text{LO}}(\mathbf{q}_p)|$ and $|g_{A_1}(\mathbf{q}_p)|$. We neglect this angular dependency. The integral of Eq. 6.14 depends on the coupling and the effective masses of the corresponding band. We use effective masses from Ref. [34], reported in table 5. We probe electronic states with electronic momenta $|\mathbf{k}| < |\mathbf{q}_p^{\text{max}}|/2$. This implies that the range of carrier energies we consider depends on the effective masses. Note that only for MoS_2 is it clear that the valence band at Γ should be considered. For the others, this band is lower in energy. For more informations about the band structures of these materials, see Ref. [28].

Table 5: Effective masses are estimated using the results of Ref. [34].

Monolayer	m^*/m_0 K cond	m^*/m_0 K val	m^*/m_0 Γ val
MoS_2	0.45	0.57	2.52
MoSe_2	0.54	0.65	3.70
MoTe_2	0.56	0.72	20.0
WS_2	0.31	0.42	2.17
WSe_2	0.34	0.45	2.79

Fig. ?? shows that optical phonons are capable of relaxing excited carriers on a timescale inferior to the picosecond at room temperature. The strength of the Fröhlich interaction depends on the material considered, mainly via the variations of Born effective charges. However, this is far from being the only aspect to account for when studying relaxation times. Fig. ?? shows a great disparity of the results depending on the phonon mode, the band, and the material.

The analytical model of the Fröhlich interaction is a good estimate of the DFPT calculations only for the valence band at $\mathbf{K}$. The relaxation times depend strongly on the band-specific, large-momentum values of the coupling with LO phonons. This is due to the fact that at the minimum carrier energy ($\varepsilon_{\mathbf{k}} = \hbar\omega_{LO}$), the integral of Eq. 6.14 already involves relatively large phonon momenta $|\mathbf{q}_p|$. The strength of the coupling with A_1 phonons and thus the relative importance of the scattering by LO and A_1 phonons also depends strongly on the bands. Very few comments apply globally. LO phonons seem to dominate optical-phonon scattering around $\mathbf{K}$, for all monolayers except WS_2 . A_1 phonons seem to dominate in the valence band around $\mathbf{\Gamma}$ for all monolayers except MoSe_2 . Although the analytical model with *ab initio* parameters is useful for suspended samples in the small momentum limit to interpret the phenomenon, interpolate the coupling or to estimate the effect of the dielectric environment, direct DFPT calculations of EPC for each band is essential. The great disparity in the relaxation times and the number of phenomenon affecting it highlight the need for direct *ab initio* simulations of electron-phonon interactions in a two-dimensional framework. Furthermore, some additional effects should be included for a quantitative comparison with experiment. This work is a study of the coupling with optical phonons at small-momenta, and should provide useful guidelines to interpret experimental transport data. However, in a full quantitative study of transport properties, one might need to account for spin-orbit coupling, doping effects, the scattering of electrons in the Q band, the scattering between different bands... Those issues can be treated in the framework of QE with 2D Coulomb cutoff.

6.1.7 Conclusion

We have implemented the truncation of the Coulomb interaction in the plane-wave and phonon codes of the Quantum ESPRESSO package.

This method enables us to simulate the small-momentum limit of the Fröhlich interaction in a 2D framework, for monolayer TMDs MoS_2 , MoSe_2 , MoTe_2 , WS_2 , and WSe_2 .

We show that this limit is three times larger than previously assumed in the case of MoS_2 in vacuum.

We develop analytical models for the Fröhlich interaction in 2D materials, along with *ab initio* methods to evaluate the parameters involved.

A simple isotropic model is found to reproduce the small-momentum limit of our DFPT calculations.

We provide the parameters of this model for the various TMDs studied.

We show that screening is paramount to evaluate the strength of the Fröhlich interaction.

In particular the dielectric environment of the 2D material has a strong influence on the small-momentum limit of the interaction.

Namely, the interaction is reduced by a factor $\frac{\epsilon_1 + \epsilon_2}{2}$ with respect to vacuum, where ϵ_1 and ϵ_2 are the dielectric constant of the environment on each side the monolayer.

We consider intraband scattering within the valence and conduction bands around $\mathbf{K}$, and within the valence band around $\mathbf{\Gamma}$.

Above a certain value of the momentum ($\approx 10\%$ of $|\mathbf{\Gamma} - \mathbf{K}|$), the band-dependant form of the electronic wave functions plays a role in the Fröhlich interaction and DFPT calculations are necessary to evaluate deviations from the analytical model.

Finally, we evaluate the inverse relaxation times associated to the scattering of photo-excited carriers by LO and A_1 phonons.

Those modes are shown to be capable of relaxing carriers on timescales smaller than the picosecond.

The efficiency of carrier relaxation by optical phonons in TMDs is found to depend on many parameters.

In addition to the strength of the Fröhlich interaction depending on the monolayer, the large momentum, band-specific coupling affects the relaxation times.

Depending on the material and the band, the relaxation time associated to the A_1 mode can also be quite large.

It is not correct to neglect scattering by either LO or A_1 phonons globally.

Overall, the complexity and disparity highlighted in this work points to the necessity of relying on direct *ab initio* calculations of electron-phonon interactions in a 2D framework.

6.1.8 Analytical model of the 2D Fröhlich interaction

We solve here the model described in the main text, Sec. 6.1.3. The dielectric properties of the system are

$$\mathcal{E}(z) = \begin{cases} \epsilon_1 \mathcal{I} & \text{if } z < -t/2 \\ \mathcal{E}^m & \text{if } |z| < t/2 \\ \epsilon_2 \mathcal{I} & \text{if } z > t/2 \end{cases} . \quad (6.15)$$

The potential V_{Fr} must solve the Poisson equation

$$\begin{cases} \nabla \cdot (\mathcal{E}^m \nabla V_{\text{Fr}}(\mathbf{r}_p, z)) = 4\pi \nabla \cdot \mathbf{P}(\mathbf{r}_p, z) & \text{if } |z| < t/2 \\ \nabla^2 V_{\text{Fr}}(\mathbf{r}_p, z) = 0 & \text{if } |z| > t/2 \end{cases} . \quad (6.16)$$

The associated parallel electric field and orthogonal electric displacement

$$\mathbf{E}^{\parallel}(\mathbf{r}_p, z) = -\frac{\partial V_{\text{Fr}}(\mathbf{r}_p, z)}{\partial \mathbf{r}_p}, \quad (6.17)$$

$$\mathbf{D}^{\perp}(\mathbf{r}_p, z) = \begin{cases} -\epsilon_1 \frac{\partial V_{\text{Fr}}(\mathbf{r}_p, z)}{\partial z} & \text{if } z < -t/2 \\ -\epsilon_z^m \frac{\partial V_{\text{Fr}}(\mathbf{r}_p, z)}{\partial z} & \text{if } |z| < t/2 \\ -\epsilon_2 \frac{\partial V_{\text{Fr}}(\mathbf{r}_p, z)}{\partial z} & \text{if } z > t/2 \end{cases}, \quad (6.18)$$

must be continuous.

The general solution to the differential equation of Eq. 6.16 is the sum of the solution to the homogeneous equation and a particular solution

$$V_{\text{Fr}}(\mathbf{q}_p, z) = V_h(\mathbf{q}_p, z) + V_p(\mathbf{q}_p, z). \quad (6.19)$$

The homogeneous equation is

$$\begin{cases} \nabla \cdot (\mathcal{E}^m \nabla V_h(\mathbf{r}_p, z)) = 0 & \text{if } |z| < t/2 \\ \nabla^2 V_h(\mathbf{r}_p, z) = 0 & \text{if } |z| > t/2 \end{cases}, \quad (6.20)$$

and the particular solution solves Eq. 6.16. To find a particular solution, we first solve Eq. 6.16 inside the anisotropic material:

$$\nabla \cdot (\mathcal{E}^m \nabla V_p(\mathbf{r})) = 4\pi e^2 \frac{i|\mathbf{q}_p|}{A} \times \quad (6.21)$$

$$\sum_a \frac{\mathbf{e}_{\mathbf{q}_p} \cdot \mathbf{Z}_a^m \cdot \mathbf{e}_{\mathbf{q}_p}^a}{\sqrt{2M_a \omega_{\mathbf{q}_p \text{LO}}}} f(z) e^{i\mathbf{q}_p \cdot \mathbf{r}_p} \quad (6.22)$$

$$V_p(\mathbf{q}_p, q_z) = \frac{-2iC_Z |\mathbf{q}_p|}{\epsilon_p^m |\mathbf{q}_p|^2 + \epsilon_z^m q_z^2} f(q_z) \quad (6.23)$$

$$V_p(\mathbf{q}_p, z) = \frac{-iC_Z}{\sqrt{\epsilon_p^m \epsilon_z^m}} \int_{-\infty}^{+\infty} e^{-\tilde{\mathbf{q}}_p |z' - z|} f(z') dz' \quad (6.24)$$

with $\tilde{\mathbf{q}}_p = \sqrt{\frac{\epsilon_p^m}{\epsilon_z^m}} \mathbf{q}$, and C_Z is defined in table 1. Using $f(z') = \frac{\theta(t/2 - |z'|)}{t}$ we get for $z \in [-t/2; t/2]$

$$V_p(\mathbf{q}_p, z) = \frac{-iC_Z}{\sqrt{\epsilon_p^m \epsilon_z^m}} \frac{2}{|\tilde{\mathbf{q}}_p|t} \left(1 - e^{-|\tilde{\mathbf{q}}_p|t/2} \cosh(|\tilde{\mathbf{q}}_p|z)\right), \quad (6.25)$$

where $\cosh$ is the hyperbolic cosine function. We need to extend this particular solution outside the material. We do not require the particular solution to carry any physical meaning outside the material. It only needs to fulfil

$$\nabla^2 V_p(\mathbf{r}_p, z) = 0 \quad \text{if } |z| > t/2. \quad (6.26)$$

We simply choose the solution of the above equation such that the corresponding out-of-plane electric field is continuous at the interfaces. This solution exist, and since we will only need its values at the interfaces, it is not necessary to specify it further.

Let us proceed to the homogeneous solution. Knowing that $V_h(\mathbf{r}) = V_h(\mathbf{q}_p, z)e^{i\mathbf{q}_p \cdot \mathbf{r}_p}$, the homogeneous equation Eq. 6.20 reduces to

$$\begin{cases} \frac{\partial^2 V_h(\mathbf{q}_p, z)}{\partial z^2} = \frac{\epsilon_p^m}{\epsilon_z^m} |\mathbf{q}_p|^2 V_h(\mathbf{q}_p, z) & \text{if } |z| < t/2 \\ \frac{\partial^2 V_h(\mathbf{q}_p, z)}{\partial z^2} = |\mathbf{q}_p|^2 V_h(\mathbf{q}_p, z) & \text{if } |z| > t/2 \end{cases}. \quad (6.27)$$

Adding the condition that the potential must vanish for $|z| \rightarrow \infty$, the solution to the homogeneous equation Eq. 6.20 has the form:

$$V_h(\mathbf{q}_p, z) = \begin{cases} c_3 e^{-|\mathbf{q}_p|z} & \text{if } z > t/2 \\ c_1 e^{|\tilde{\mathbf{q}}_p|z} + c_2 e^{-|\tilde{\mathbf{q}}_p|z} & \text{if } |z| < t/2 \\ c_4 e^{|\mathbf{q}_p|z} & \text{if } z < -t/2 \end{cases} \quad (6.28)$$

with $\tilde{\mathbf{q}}_p = \sqrt{\frac{\epsilon_p^m}{\epsilon_z^m}} \mathbf{q}$. Note that the homogeneous solution has the form of a potential generated by 2 surface charges at the interfaces of the monolayer. The continuity of the potential gives

$$c_3 e^{-|\mathbf{q}_p|t/2} = c_1 e^{|\tilde{\mathbf{q}}_p|t/2} + c_2 e^{-|\tilde{\mathbf{q}}_p|t/2}, \quad (6.29)$$

$$c_4 e^{-|\mathbf{q}_p|t/2} = c_1 e^{-|\tilde{\mathbf{q}}_p|t/2} + c_2 e^{|\tilde{\mathbf{q}}_p|t/2}. \quad (6.30)$$

The continuity of the parallel electric field is fulfilled by construction. We use the continuity of the out-of-plane electric displacement Eq. 6.18 to obtain

$$\begin{cases} \frac{C_Z}{\sqrt{\epsilon_p^m \epsilon_z^m}} (\epsilon_z^m - \epsilon_1) \frac{1 - e^{-|\tilde{\mathbf{q}}_p|t}}{|\mathbf{q}_p|t} = (\epsilon_1 + \sqrt{\epsilon_p^m \epsilon_z^m}) c_1 e^{|\tilde{\mathbf{q}}_p|t/2} + (\epsilon_1 - \sqrt{\epsilon_p^m \epsilon_z^m}) c_2 e^{-|\tilde{\mathbf{q}}_p|t/2} \\ \frac{C_Z}{\sqrt{\epsilon_p^m \epsilon_z^m}} (\epsilon_z^m - \epsilon_2) \frac{1 - e^{-|\tilde{\mathbf{q}}_p|t}}{|\mathbf{q}_p|t} = (\epsilon_2 - \sqrt{\epsilon_p^m \epsilon_z^m}) c_1 e^{-|\tilde{\mathbf{q}}_p|t/2} + (\epsilon_2 + \sqrt{\epsilon_p^m \epsilon_z^m}) c_2 e^{|\tilde{\mathbf{q}}_p|t/2} \end{cases}. \quad (6.31)$$

By defining the following dielectric mismatches

$$\begin{aligned} \alpha_1 &= \frac{\epsilon_z^m - \epsilon_1}{\sqrt{\epsilon_p^m \epsilon_z^m} + \epsilon_1} & \bar{\alpha}_2 &= \frac{\sqrt{\epsilon_p^m \epsilon_z^m} - \epsilon_2}{\sqrt{\epsilon_p^m \epsilon_z^m} + \epsilon_2} \\ \alpha_2 &= \frac{\epsilon_z^m - \epsilon_2}{\sqrt{\epsilon_p^m \epsilon_z^m} + \epsilon_2} & \bar{\alpha}_1 &= \frac{\sqrt{\epsilon_p^m \epsilon_z^m} - \epsilon_1}{\sqrt{\epsilon_p^m \epsilon_z^m} + \epsilon_1}, \end{aligned} \quad (6.32)$$

we finally have

$$c_1 = \frac{C_Z}{\sqrt{\epsilon_p^m \epsilon_z^m}} \frac{1 - e^{-|\tilde{\mathbf{q}}_p|t}}{|\mathbf{q}_p|t} \frac{\alpha_1 + \bar{\alpha}_1 \alpha_2 e^{-|\tilde{\mathbf{q}}_p|t}}{1 - \bar{\alpha}_1 \bar{\alpha}_2 e^{-2|\tilde{\mathbf{q}}_p|t}} e^{-|\tilde{\mathbf{q}}_p|t/2} \quad (6.33)$$

$$c_2 = \frac{C_Z}{\sqrt{\epsilon_p^m \epsilon_z^m}} \frac{1 - e^{-|\tilde{\mathbf{q}}_p|t}}{|\mathbf{q}_p|t} \frac{\alpha_2 + \bar{\alpha}_2 \alpha_1 e^{-|\tilde{\mathbf{q}}_p|t}}{1 - \bar{\alpha}_1 \bar{\alpha}_2 e^{-2|\tilde{\mathbf{q}}_p|t}} e^{-|\tilde{\mathbf{q}}_p|t/2}. \quad (6.34)$$

The Fröhlich interaction is thus

$$g_{\text{Fr}}^{2\text{D}}(\mathbf{q}_p) = \frac{1}{t} \int_{-t/2}^{t/2} (V_p(\mathbf{q}_p, z) + V_h(\mathbf{q}_p, z)) dz \quad (6.35)$$

$$g_{\text{Fr}}^{2\text{D}}(\mathbf{q}_p) = \frac{C_Z}{\sqrt{\epsilon_p^m \epsilon_z^m}} \left[\frac{2}{|\tilde{\mathbf{q}}_p|t} \left(1 + \frac{e^{-|\tilde{\mathbf{q}}_p|t} - 1}{|\tilde{\mathbf{q}}_p|t} \right) + \frac{(1 - e^{-|\tilde{\mathbf{q}}_p|t})^2}{|\mathbf{q}_p|t|\tilde{\mathbf{q}}_p|t} \frac{\alpha_1 + \alpha_2 + (\bar{\alpha}_1\alpha_2 + \bar{\alpha}_2\alpha_1)e^{-|\tilde{\mathbf{q}}_p|t}}{1 - \bar{\alpha}_1\bar{\alpha}_2e^{-2|\tilde{\mathbf{q}}_p|t}} \right]. \quad (6.36)$$

The isotropic solution is ($\epsilon_p^m = \epsilon_z^m = \epsilon_{\text{iso}}^m$):

$$g_{\text{Fr}}^{2\text{D}}(\mathbf{q}_p) = \frac{C_Z}{\epsilon_{\text{iso}}^m} \left[\frac{2}{|\mathbf{q}_p|t} \left(1 + \frac{e^{-|\mathbf{q}_p|t} - 1}{|\mathbf{q}_p|t} \right) + \frac{(1 - e^{-|\mathbf{q}_p|t})^2}{(|\mathbf{q}_p|t)^2} \frac{\alpha_1 + \alpha_2 + 2\alpha_1\alpha_2e^{-|\mathbf{q}_p|t}}{1 - \alpha_1\alpha_2e^{-2|\mathbf{q}_p|t}} \right] \quad (6.37)$$

6.1.9 Coupling with optical phonons in TMDs

In Fig. ?? we plot the small-momentum coupling to the A_1 and LO modes in monolayer TMDs MoS_2 , MoSe_2 , MoTe_2 , WS_2 , and WSe_2 . Note that that WSe_2 is similar to MoS_2 . WS_2 shows significantly smaller Fröhlich interaction. MoSe_2 and MoTe_2 are similar to each other, with large Fröhlich interaction and some different trends in the A_1 mode. Note also that the analytical model coincides relatively well with the DFPT results for the valence band at $\mathbf{K}$ in every material.

6.2 My Discussion

6.2.1 My Conclusion

6.2.2 Most Important General Questions

6.2.3 My Questions about Their Methods, Statements and Results

6.2.4 Questions about Assumed Knowledge

6.2.5 Things That I Maybe Understood Wrongly

6.2.6 Potential Future Research Directions

7 Non-equilibrium quantum domain reconfiguration dynamics in a two-dimensional electronic crystal: experiments and quantum simulations by Vodeb, Diego, Vaskivskyi, Logaric, Gerasimenko, Kabanov, Lipovsek, Topic, Mihailovic (2021)

Relaxation dynamics of complex many-body quantum systems brought out of equilibrium and subsequently trapped into metastable states is a very active field of research from both the theoretical and experimental point of view with implications in a wide array of topics from

macroscopic quantum tunnelling and nucleosynthesis to non-equilibrium superconductivity and new energy-efficient memory devices. (nothing is useful in this sentence)

Understanding the dynamics of such systems is crucial for exploring fundamental aspects of many-body non-equilibrium quantum physics. (no, it is not crucial)

In this work we investigate quantum domain reconfiguration dynamics in the electronic superlattice (= lattice of conducting electrons which sit on top of the atomic lattice) of a quantum material where classical dynamics is topologically constrained (topologically constrained??) (they paraphrase the title) .

The crossover from temperature to quantum fluctuation dominated dynamics in the context of environmental noise (context of environmental noise??) is investigated by directly observing charge reconfiguration with time-resolved scanning tunneling microscopy. (is that theory from LS applicable here??? is it connected to domains?) (so they see how much charges hop and deduce whether charge calculations were quantum or thermal)

(where is this crossover in the article??? I missed it)

The process is modelled using a programmable superconducting quantum simulator (a strange special device) in which qubit interconnections correspond directly to the microscopic interactions between electrons in the quantum material (this is what always happens in such simulators) .

Crucially, the dynamics of both the experiment on the quantum material and the simulation is driven by spectrally similar pink noise (pink noise??) .

We find that the simulations reproduce the emergent time evolution and temperature dependence of the experimentally observed electronic domain dynamics remarkably well.

The combined experiment and simulations lead to a better understanding of noise-driven quantum dynamics in open quantum systems. (why are they noise driven? what did we understand now better???)

From a practical viewpoint, the results are important for understanding the origin of the retention time in non-volatile memory devices such as those based on 1T-TaS₂. (retention time in non-volatile memory devices????? read about it)

7.1 Article

7.1.1 Conclusion

(we have learned nothing new about physical properties of the TaS₂, right? or what have we learned after such a simulation???)

The motivation for the present quantum treatment arose from the fact that temperature-independent electronic domain relaxation in 1 T – TaS₂ at low temperatures cannot be explained by classical processes (which classical processes??? which have been tried to explain it?) because their relaxation is topologically inhibited ⁴² (topologically inhibited??) .

Yet we find that the phenomenological parameters extracted from the T-dependence of the relaxation rate and the crossover to T-dependent dynamics are inconsistent with conventional quantum decay (what is the conventional quantum decay???) . (why are they inconsistent? which parameters have been extracted?)

Introducing a new approach for modelling the domain dynamics we use a microscopic model implemented on a superconducting qubit processor, directly mapping the electron-electron interactions onto the PQA inter-qubit connections. (what is new here?)

In the crucial next step which we demonstrate here is to treat the noise from the surroundings as coupled two-level systems (HOs) (see discussion, what is about modeling the noise?) with the ubiquitous $1/\nu$ frequency dependence (dependence of what?) that has been shown

experimentally to be present in both 1 T – TaS₂⁴⁶ and the PQA⁴⁷. (so, treat and investigate what?)

The emergent many-body dynamics and associated domain reconfigurations are thus simulated solely on the basis of microscopic interactions with a single adjustable parameter r tuning the 'quantum-ness' of the system. (this was said before, except the onfo about r) (what is the r ???)

The simulations clearly display the crossover from T -activated dynamics to T -independent domain melting that is experimentally observed in the STM measurements, giving direct insight into how the phenomenological relaxation rates emerge from microscopic interactions. (make sure that I understand it from the article)

The present calculations demonstrate the usefulness of simulations on a noisy quantum processor for modelling emergent non-equilibrium many-body dynamics. (which useful conclusion did they give?)

With appropriate mapping, such an approach can be applied to other non-equilibrium open quantum systems that are subject to external sources of incoherent noise - including quantum materials such as the quantum paraelectric SrTiO₃⁶⁶(what about this material, read???) , various hydrogen-bonded systems⁶⁷(what about this material, read???) , in the folding of proteins through a similarly multidimensional, topologically defined energy landscape⁶⁸(what about this material, read???) , or tunneling between false vacuum states that emerge from elementary interactions^{69–71} (it is another not related field of science) .

Apart from fundamental interest, modeling quantum reconfiguration dynamics is important for low-temperature memory devices⁴¹ (read, why?) , in which quantum domain melting processes functionally limit the long-term data retention⁵¹ (read, why?) .

7.1.2 Introduction

(SUMMARY: there were many other simulations and experiments, but now they want to do the domain reconfiguration. they don't explain, why they want this?)

Many-body systems emerging through symmetry-breaking phase transitions often end up in inhomogeneous intermediate states before reaching a homogeneous ground state. (like type II SC do)

In the aftermath of second-order transitions, such as the superconducting transition in type-2 superconductors, fluctuations in the phase of the order parameter force causally unconnected (causally unconnected??? we are not doing special relativity here, why is it here??) regions to evolve independently, forming mesoscopic vortex structures^{1–3} (I think, vortices are not because of fluctuations of phases, it is a strange statement which is better to forget then to check) .

In the aftermath of first-order phase transitions, the classical dynamics involves nucleation of the new phase, followed by coalescence⁴ and "ripening"⁵ (classical dynamics involves nucleation, coalescence, ripening????? never heard of) .

Topological and jamming transitions present more complex non-equilibrium dynamics that recently became topics of wider interest^{6,7} (topological and jamming transitions???) .

In classical systems (which??) , the kinetics is primarily diffusion-driven (diffusion-driven??) , while metastability arises from symmetry or topological constraints (metastability arises from symmetry or topological constraints?????) .

In quantum systems⁸(which??) , particularly at low temperatures we may expect to observe either coherent quantum dynamics for perfectly isolated systems, or incoherent macroscopic tunneling (IMT)(read about IMT) aided by noise-assisted processes (noise-assisted processes??) causing transitions between different mesoscopic state configurations⁹.

The challenge is to quantitatively measure state reconfigurations of a many-body system in order to identify mesoscopic tunneling processes (which can be there mesoscopic tunneling processes which will be identified?) between different domain configurations, and then compare such data with model simulations of the dynamics.

Because such processes are quite common, and have important potential applications¹⁰ (which potential applications?), the ability to faithfully simulate their dynamics on a quantum level would lead to significant progress in understanding metastable states in quantum materials and non-equilibrium quantum devices (they repeat what was written before).

In electronic crystals, the ordering of domains (areas where electrons are ordered in a particular way) and discommensurations(discommensurations?) are traditionally modelled classically by an anisotropic Ising model with competing interactions¹¹ (check how they are modeled?) or by continuum models^{12,13}, but these models give little insight into how inhomogeneities evolve in the quantum regime (what is “quantum regime”??) . (what exactly they don’t tell?)

Ab-initio methods can give detailed electronic band structure information of individual domain walls¹⁴ (learn ab-initio methods!) , but cannot be used to simulate the emergent many-body collective dynamics (why? which collective dynamics?) .

Non-equilibrium dynamics pose an especially difficult challenge to faithful classical simulation¹⁵, where an exponentially large Hilbert space dimension is required (why exponentially large Hilbert space? write formulas somewhere where I try to simulate it classically?) .

Brute force state vector simulations can barely exceed 50 qubits even on the best high-performance computer clusters currently available¹⁶ (interesting, read this paper) .

On the other hand, quantum Monte Carlo calculations with added noise are not developed for direct probing of non-equilibrium dynamics, and it is still an open question whether, and how they could be applied at all. (why? what is the limit of applicability of QMC?)

Quantum simulations of ground state properties (which simulations of ground state?) in many body systems, as well as metastable decay (which metastable decay?) of complex systems using ultracold atomic lattices have recently been demonstrated^{17,18}, and a lot of recent attention has focused on noisy intermediate scale quantum (NISQ) processors (what is NISQ?) . (nothing is informative in this sentence)

But extension to real-world non-equilibrium systems requiring thousands of qubits in 2D, such as is addressed here, is particularly challenging because it requires extreme, currently unavailable computational resources, as well as presently still unachievable control of decoherence. (what exactly is needed to do such simulations?)

Macroscopic quantum motion of domain walls in the presence of noise has attracted a lot of attention since the 1980s (what have been done for 40 years?) .

Typically, spin tunnelling in a ferromagnets^{19,20} (spin tunnelling in a ferromagnets?) is considered, which may be formulated in terms of domain wall tunnelling^{21,22} (domain wall tunnelling?) .

Research of this type includes magnetotransport measurements on thin ferromagnetic wires²³ (magnetotransport measurements?) , and magnetization experiments on single particles^{24,25}, nanomagnet ensembles^{26–28} and rare-earth multilayers²⁹. (some experiments are there, it is irrelevant)

A different method involves investigating macroscopic disordered ferromagnets^{30–33}. (also, it is irrelevant)

Here we report for the first time a study of quantum noise driven domain wall dynamics of strongly correlated electrons. (wasn’t it studied before at all???)

Our experimental system is the prototype quasi-two-dimensional (2D) strongly correlated transition metal dichalcogenide material 1TTaS₂³⁴ : It is chosen because it displays prototypical electronic crystal ordering behavior³⁵ (which prototypical behavior?) .

As a result of the strong electron-phonon interaction in this material, the electronic kinetic energy K is exponentially reduced ³⁶, and Coulomb energy V becomes dominant ³⁷. (isn't it because of electron-electron interaction?)

The essential physics in this regime thus comes from the formation of mutually repulsive heavily dressed quasiparticles - polarons ³⁵, with a variety of polaron-ordered states and metastable domain structures ^{35,38,39}. (this is typically said about this material)

In response to external perturbation 1T-TaS₂ exhibits fundamentally interesting and practically useful switching behavior ^{10,35,40–42} between different metastable states associated with different configurations of domains of the low-temperature electronic superlattice.

At low temperatures, the temporal reconfigurations can be effectively investigated by scanning tunneling microscopy (STM).

The classical many-body relaxation dynamics of such domain states is topologically inhibited ^{43,44} (topologically inhibited???) , effectively creating an energy barrier for the transition between different domain configurations (dynamics creates the energy barrier???) .

In such a system where the dynamics of classical processes is topologically inhibited, quantum dynamics is necessary for metastable state relaxation, especially at low temperatures. (they again just repeat what was said before)

Understanding these processes is directly relevant for controlling functional properties, and in particular data retention in non-volatile configuration memory devices ^{10,45}. (they again just repeat what was said before)

Using a new approach to modeling emergent non-equilibrium behavior, we investigate the electronic domain dynamics in 1 T – TaS₂, with a parallel simulation using a superconducting quantum simulator. (they again just repeat what was said before)

The decoherence of domains in the simulation - just as in 1 T – TaS₂ - is governed by $1/\nu$ pink noise ^{46,47}, so the simulations can be thought to utilize the principles of simulating nature with nature, as originally proposed by Feynman ⁴⁸ (they again just repeat what was said before, what is the pink noise wasn't explained before and not explained here) .

Here we find that the quantum simulator describes the natural noise-driven processes remarkably well. (what is the criterion? if it was so, wouldn't we need the kinetic term?)

The reproduction of the emergent metastable decay behavior that is observed in the experiments is particularly striking (nothing is informative here) .

The results lead to valuable insights into how microscopic many-body interactions between electrons on a superlattice conspire to display metastable quantum domain relaxation dynamics observed in the experiments on 1T-TaS₂ (nothing is informative here) .

7.1.3 Results

(SUMMARY: ?)

Domain Reconfiguration Measurements in 1T-TaS₂

(SUMMARY: there are reconfigurations of domains, there are t and R parameters and the tip does not influence the dynamics nearly at all)

(we start with CCDW phase, then we insert new electrons. this is why the system goes to the CCDW phase finally (this reconfiguration brings us to the CCDW state))

In our experiments, a metastable domain state in the $\sqrt{13} \times \sqrt{13}$ electronic superlattice of 1 T – TaS₂ is set up by electrical pulse charge injection through an STM tip ^{43,49,50} (Fig. 1c). (learn about the electrical pulse charge injection)

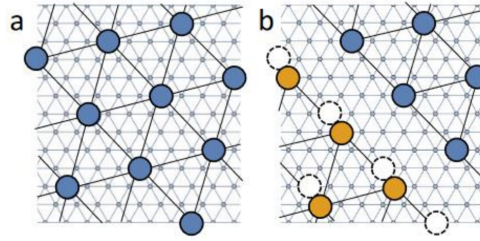


Figure 7.1: Figure 1. a) The crystal lattice showing Ta atoms (small circles) (why there are no S atoms?) .

Occupied electron sites (blue and orange circles) a) in the ground state, and b) near a domain wall.

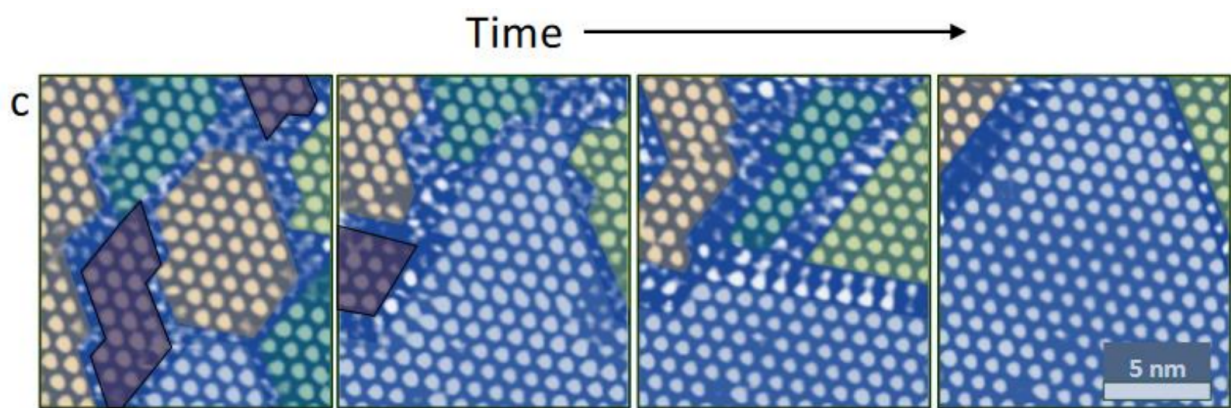


Figure 7.2: Figure 1. c) A series of STM measurements at regular time intervals showing domain reconfiguration. Domains are colored to signify a displacement relative to the main commensurate lattice (light blue). (STM parameters: -0.8 V, 50 pA). (so what happens here? relaxation or some special dynamics???)

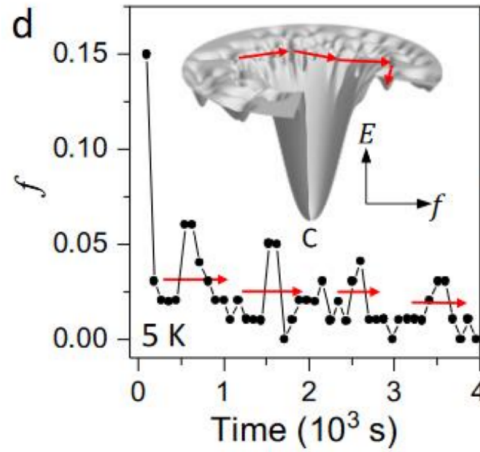


Figure 7.3: Figure 1. d) The fraction of electrons moved $f(t)$ as a function of time measured within the same area at **5K**. The jumps correspond to large (observable) configurational changes (and what changed?) .

The inset shows a schematic of the configurational free energy E as a function of configurational coordinate (Hamming distance) f . (why f denotes two things??? how did this plot was obtained???)

The excited states within each well represent states which conserve f (see text).

(the following sentences are clear) As the domain structure evolves in time, its configuration is recorded periodically by STM at different temperatures. A relaxation sequence at 5 K is shown in Fig.1c. The tip is retracted and set to zero bias between measurements to avoid reconfiguration by spurious signals from the tip. This measurement results in classical sequential "snapshots" of the domain configurations at different temperatures (see SI for experimental details).

The reconfigurations between sequential images are quantified by measuring the Hamming distance (Hamming distance is a metric used to measure the difference between two equal-length sequences or strings. It is calculated by counting the number of positions at which the corresponding symbols or bits are different. It represents the minimum number of single-character or single-bit substitutions required to change one string into the other) (why Hamming distance is here???) , defined here as the number of altered occupied polaron positions between frames (Fig.1c), and expressed as the fraction of polarons moved $f = \Delta N/N$, where N is the total number of polarons per frame (Fig.1d).

Characteristically, jumps of f appear in time (Fig.1d), reflecting the discrete nature of the domain reconfiguration process ⁵¹ (discrete nature??? so at one time a lot of polarons jump, at another nearly no one jumps?) .

When f is averaged over a large number of scans on different areas of the sample an approximately exponential decay of is observed (Fig. 1e).

The classical power law time dependencies $f(t) \sim r(t)^2 \sim t^{-1}$ or $t^{-2/3}$, that would be characteristic of nucleation and coalescence processes ⁴ respectively at higher temperatures ⁵² (check, why there are such dependences???) , cannot be made to fit the 5 K domain relaxation data (Fig.1e).

Considering the difference of the processes involved, this is not surprising.

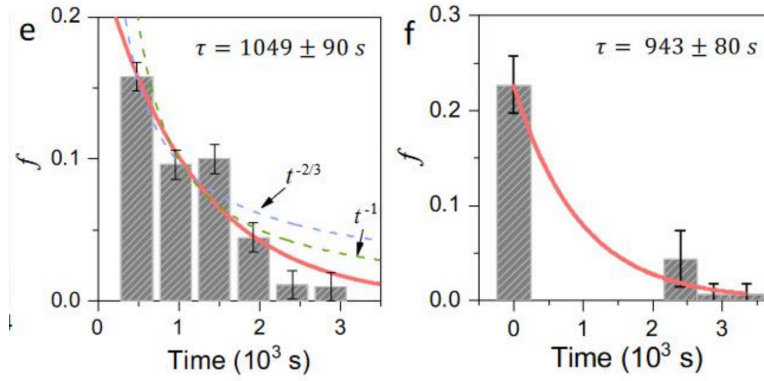


Figure 7.4: Figure 1. e) (the main takeaway is that tip does not influence at all, since the τ is the same within the errors) $f(t)$ averaged over different areas of the sample, with periodic STM scans. Exponential and power law fits to the data are shown (solid and dashed lines respectively). Error bars represent counting errors. f) Same as e), except with a 32-minute gap (meaning that the tip goes with the 32 minute delay each time comparing to e)) in scanning the first point. (why there are no f for many 10^3 seconds??? looks very strange???) The exponential fit is the red line. (on how many particles and experiments it was averaged??)

A crucial test of the experiments is to see if, and how, the STM tip influences the reconfiguration process. (is STM the source of a noise???)

Comparing $f(t)$ obtained by tip scanning at regular intervals (Fig.1e), with $f(t)$ measured under identical experimental conditions, but with a retracted tip over a longer time interval, we see in Fig.1f that the two relaxation times are very similar: $\tau = 1040 \pm 90$ s and 945 ± 80 s respectively, implying that within experimental error the influence of the STM tip is negligible. (this is the main reason that noise is not coming from the tip. it is not clear where the noise is coming from finally, maybe from quantum or temperature fluctuations?)

A number of other tests that support this conclusion are given in the supplement, including a detailed calculation of Joule heating by the STM tip current. (read the SI, which tests?)

We have thus established that the noise in 1T-TaS₂ does not originate from the STM tip, but has a different non-thermal origin. (why non-thermal origin?)

Other possible excitation sources are acoustic phonons, quantum fluctuations in two-level systems (TLSs) in the sample, the substrate and at the interface, as well as spurious external electro-magnetic fields brought by the grounded sample contact. (have these effects been researched???)

Importantly (why is it important?) for our purposes, in 1 T – TaS₂ the noise has been experimentally shown to have a $\sim 1/\nu$, frequency dependence.⁴⁶ (check this paper, why? if it was known, why do they test the origin of the noise?)

The dependence of the reconfiguration rate $R(T) = \frac{1}{\Delta t} \int_0^{t_{\text{exp}}} f(t) dt$, where Δt is the time interval between subsequent image samplings and t_{exp} the duration of the experiment at temperature T , on sample temperature in 1 T – TaS₂ is shown in Fig. 1 g for $\Delta t \cong 480$ s.

(why at all we are interested exactly in the $R(t)$???????????????????? why is it so with such times in its def.?)

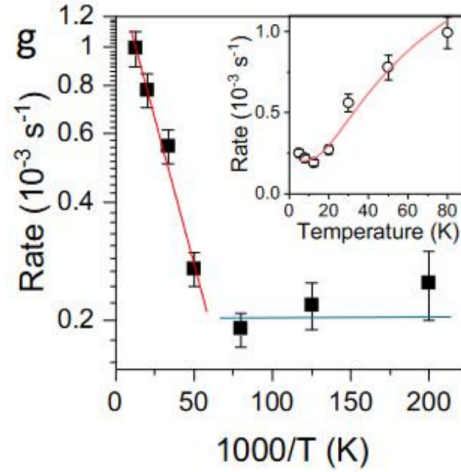


Figure 7.5: Figure 1. g) The temperature dependence of R averaged over a large number of decays on a logarithmic scale with the inset showing a linear scale.

$R(T)$ exhibits a distinct crossover from T -independent to T -dependent behavior at a temperature $T_0 \approx 20$ K.

The data can be fit well to: $R(T) = R_q + R_0 \exp(-E_M/k_B T)$, where $R_q \simeq 8 \pm 1 \times 10^{-4} \text{ s}^{-1}$ is the T -independent tunneling rate, and the second term describes T -activated hopping across a barrier. (is there a physical reason for this formula?) (why the notation for E_M is such???) is it connected to $H_M = -\sum_{\langle ij \rangle} t_{ij} c_i^\dagger c_j + \sum_{\langle ij \rangle} V(i, j) q_i q_j - \mu \sum_i q_i$???)

The value $E_M = 6 \pm 3 \text{ meV}$ obtained from the fit to the data in Fig. 1g is not far from the activation energy $E_A = 10 \sim 20 \text{ meV}$ obtained from previous macroscopic resistance relaxation measurements of bulk samples⁵¹, providing an important experimental consistency check.

Since by STM we observe "snapshots", which are effectively separated by large time windows, we assume that reconfigurations correspond to single escape events from a local minimum in a multidimensional free energy landscape of dimension $D = 2^N$ (since we have an N qubit system), where N is the number of atomic sites, shown schematically in 1 D as a function f is in the insert to Fig.1d (how was it obtained? I don't see a connection to this model).

Different minima in $E(f)$ correspond to different configurational states, while the excited states within the wells correspond to configuration processes which conserve f , such as translations. (why translations?)

Quantum decay rate

(SUMMARY: Caldeira-Legget theory is not applicable for this material because some E_M is too little)

First we check whether existing analytical theory of noise mediated quantum dynamics in the presence of a thermal bath can explain the crossover in $R(T)$. (what exactly to explain???)

The canonical Kramers-Caldeira-Legget (KCL) quantum decay rate (QDR) theory^{53,54} assumes a system moving through a cubic potential in a 1D configurational landscape (Fig. 2b) and does indeed predict an $R(T)$ crossover. (what does it predict???)

Here, we approximate the movement of polarons in 1 T-TaS₂ through its multidimensional energy landscape with a series of local 1D paths, each representing a single reconfiguration event (see insert to Fig. 1d).

According to KCL, polarons in 1T-TaS₂ are initially trapped in the metastable minimum of the cubic potential separated by a barrier from a lower energy state, which can be overcome

by either noise mediated incoherent quantum tunneling at low T or thermal activation at high T .

The crossover occurs at temperature T_0 within a range ΔT .

If we take the experimental values $E_M, T_0 = 20$ K and $\Delta T = 10$ K, obtained from Fig. 1 g (how to obtain them???) and plug them into KCL theory in order to characterize an average reconfiguration event, it predicts $\frac{E_M}{\hbar\omega_0} \simeq 0.4 \sim 1.4$, where $\hbar\omega_0$ is the kinetic energy scale of polarons in 1 T – TaS₂.

This is in direct contradiction with the underlying assumptions of KCL theory ($\frac{E_M}{\hbar\omega_0} \gg 1$). (why does it require such values???)

Therefore, the assumptions of the KCL theory are fundamentally incompatible with the observed behavior in 1T-TaS₂.

An extension of the KCL theory into the multidimensional case as well as $E_M \sim \hbar\omega_0$ is required, which unfortunately currently does not exist. (what is known about extensions of CL theory?)

Quantum simulation of domain reconfiguration dynamics

(SUMMARY: we map the model to the PQA and get the plots of change of dynamics)

An alternative to analytical theory is simulation of the system microscopically, and examine the emergent behavior in comparison with experiments of the dynamics of domains in 1 T – TaS₂. (KL model was also microscopical, so what is the difference now?)

(behavior in GB English is behaviour, before there was "tunnelling", so the use the GB English. not important. seems that another author was writing this part of an article)

We start with a single Ta band (Ta band?? which bands are there??) of tight-binding electrons⁵⁵ coupled to phonons via the Fröhlich interaction (Fröhlich interaction is always used, all other interactions fit to the Fröhlich model), interacting via a long-range Coulomb repulsion $V_c(i, j)$.

In the limit of strong electron-phonon interaction, such a model exhibits repulsive polarons as slow quasiparticles with an exponentially suppressed tunneling matrix element t_{ij} ³⁶. (why do we have a strong electron-phonon interaction? what is the criterion or the value of it?)

Here we focus on charge ordering of such polarons and neglect the spin degree of freedom (does the spin degree of freedom play any role?), attributing to each atomic site a binary variable $q_i \in \{0, 1\}$ (a qubit), which represents the polaron occupancy of site i on a triangular lattice (of superlattice of electrons, which is fixed) (right???) and assume only nearest neighbor repulsion $V(i, j)$.

The Hamiltonian is then

$$H_M = - \sum_{\langle ij \rangle} t_{ij} c_i^\dagger c_j + \sum_{\langle ij \rangle} V(i, j) q_i q_j - \mu \sum_i q_i,$$

(why there is the minus before the kinetic term???) ($V(i, j) = V_0 \exp(-r_{i,j}/l_s)/r_{i,j}, l_s$ from SI) with $c_i^\dagger c_i = q_i$, and chemical potential is μ , which is chosen such that the ground state at $t_{ij} = 0$ is a triangular polaronic superlattice where each polaron can occupy one of 3 atomic lattice sites (Fig. 2a). (why at all μ is in the H???? shouldn't it be in the grand potential of the grand canonical ensemble???) (if there are some particles that go away from the system, should we decrease the μ ???) (I have never understood how the change in μ can change the GS... how should we change μ to get another GS?)

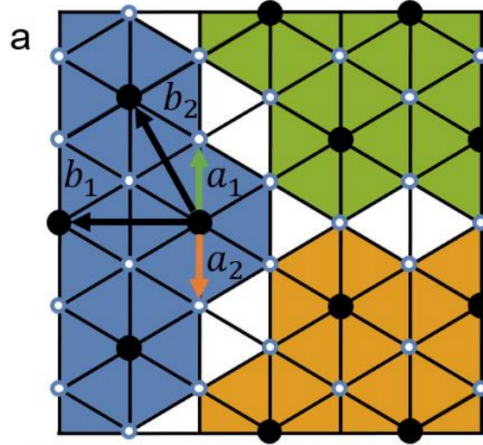


Figure 7.6: Figure 2. a) The three possible ground states of the NN repulsion we deployed on the quantum annealer. They are a $1/3$ polaronic lattice with primitive vectors $\mathbf{b}_1$ and $\mathbf{b}_2$, shifted by two possible atomic lattice vectors $\mathbf{a}_1$ and $\mathbf{a}_2$. The different superlattices are colored for clarity. (we fix empty and filled points, we do the translations. only these three options are possible here)



Figure 7.7: Figure 2. c) An example of a relaxation sequence with parameters $t_a = 5\mu s$, $r = 9$ and $T_{eff} = 1.33$ (are these parameters the best ones? why??) . (why at all there can be an empty hole? isn't it energetically more favorable to fill all the positions?)

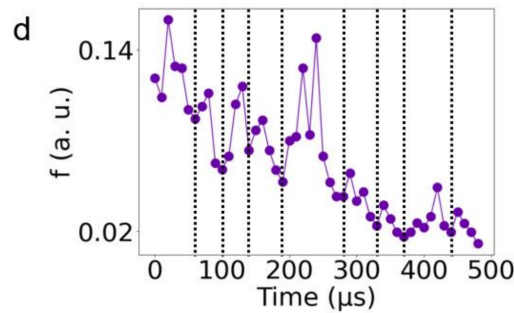


Figure 7.8: Figure 2. d) (looks very not like in the fig. 1, it is ok????? there were no peak in the measurements) The Hamming distance $f(t)$ sampled from the quantum annealer for the sequence shown in c). This can be compared with experimental data in Fig. 1d). Black dashed lines show the intermediate metastable states that emerge during the relaxation process.

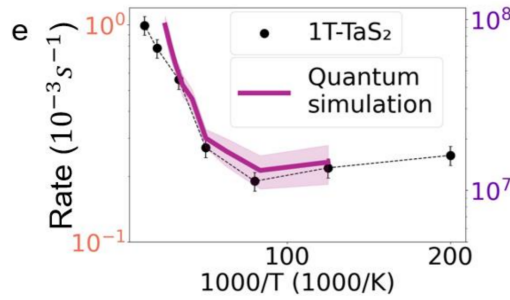


Figure 7.9: Figure 2. e) $R(T)$ extracted from the PQA with parameters $t_a = 5\mu s$ and $r = 15$, and 1 T – TaS₂. The temperature scale for the PQA was chosen to be $T = T_{\text{eff}} \cdot 4K$, for demonstration purposes (why $T = T_{\text{eff}} \cdot 4K$?). See SI for actual parameter estimation. (why do we have such a different scales of the measurement and simulation????) (we have a strange scale on the horizontal axes, there is no sense to multiply by 1000 and then have a scale of 100-s) (why the simulation line ends so early???) (is the signal really T-independent??? looks like maybe it can have a slight dependence)

Quantum dynamics calculations of sufficient system sizes required to capture reconfiguration dynamics of hundreds of polarons in the experiment are presently unrealistic on a classical digital computer. (typical statement)

(here, it can be said "there are some analytical methods, which will boil down anyway to some computation on a classical computer, so let's just skip them, anyway we'll use a PQA method below")

We thus explore the alternative possibility of using a programmable quantum annealer D wave Advantage 6.1 (PQA) to model the dynamics, which has already been shown to exhibit multiqubit tunnelling in the presence of a thermal noise^{56–59}. (read these articles about multiqubit tunnelling (?? what is it??), they look very relevant!!!)

Importantly, the superconducting qubit TLS dynamics of the PQA is mediated by coupling to TLSs in the environment (????????????? what at all is meant here? mediated by coupling to TLSs in the environment??? which TLSs????) which has a very similar $1/\nu$ frequency dependence of the noise as 1 T – TaS₂^{46,47}. (A more detailed comparison of noise characteristics is made in the SI. (read it, I don't understand noises!!))

The PQA is designed for simulations that are extensions of the transverse field Ising model (TFIM) with adjustable temperature: (how does this formula relate to the previous H ???? maybe the SI has such mapping?)

$$H_{PQA}/k_B T = \left(- \sum_i \sigma_i^x / 2 + r[s(t)] \left(\sum_{\langle ij \rangle} V(i, j) q_i q_j - \mu \sum_i q_i \right) \right) / T_{eff}[s(t)]$$

(so the kinetic term is taken into account, right???? the mapping is unclear, but they say that they take $r_s = 58$, which means that still it there, but small, right???) where $\sigma_i^z = 2q_i - 1$, where $\sigma_i^{x,z}$ are Pauli matrices operating on q_i and $s(t)$ is a custom time dependent function ranging from 0 to 1, conventionally called the annealing schedule in the simulation. (what is known about T_{eff} why is it so and why at all here we write it with "eff"??)

The TFIM model was originally introduced to describe collective motion between of protons in microscopic hydrogen bonded double well potentials⁶⁰. (I thought that it was introduced to describe magnets, interesting, read it later, it is not relevant here anyway)

It is known that solutions of the TFIM in 1D can be used to model domain walls propagating as free particles (domain walls propagating as free particles?? how is it??) in the background of strong interactions with an associated false vacuum state (background of strong interactions???)

that describes the transitions between different domain configurations ⁶¹. (it is a confusing and anyway irrelevant sentence. false vacuum decay is not related to the problem which is addressed here)

It has also been shown recently ⁶² that with a 2D TFIM with strong nearest neighbor interactions, domain walls behave as free fermions with conventional hopping $\sum_{\langle ij \rangle} c_i^\dagger c_j + h.c.$ in the limit of strong interactions ($r \gg 1$) (interesting, look later), which is closely analogous to domain walls between polaronic lattices (isn't it exactly what happens here??).

Through $s(t)$ we are able to control the two tunable parameters in our simulation: the effective dimensionless temperature $T_{\text{eff}}[s(t)]$ and the ratio between the potential and kinetic energy, $r[s(t)]$ ⁶³. (and how are they dependent on s ???? what is this s , I forgot???)

We map μ onto individual qubits biases (individual qubits biases??) and $V(i, j)$ to couplers between qubits, with a 4/3 ratio of physical to logical qubits (Fig. 2b) (why 4/3?) . (what happens in Fig. 2b??? I don't understand it at all???)

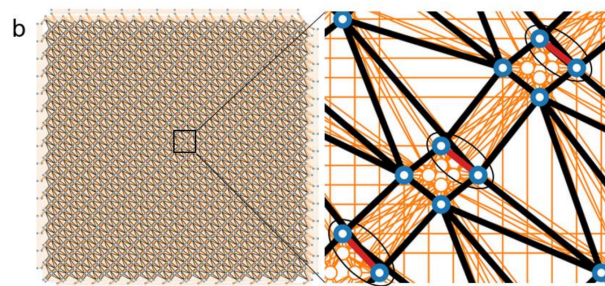


Figure 7.10: Figure 2. b) (I don't understand this figure at all!!!) Embedding of the triangular lattice used in our simulations on the PQA with the inset showing the detailed connections between qubits. The white dots encircled with blue represent individual atomic sites (also in c)), black lines are connections between qubits we used for the nearest neighbor repulsion, red lines are physical connections used for creating logical qubits (also encircled in black) on a triangular lattice and the orange lines are the unused physical connections on the processor.

In this way, the TFIM makes it possible to describe the tunneling dynamics between different 2D domain states of 1T-TaS₂. (why wouldn't we just set the atomic lattice to the sites of TFIM???)

(so how to incode the polaronic configuration in TFIM?)

The calculation should be considered as a salient model which ignores coupling to phonons, as well as long-range interactions, but given that the classical charged lattice gas modelling describes low-temperature ordering in 1 T – TaS₂³⁸ (no, CLG does not reproduce the plot from the experiment, it has a lot of extra peaks. there is no comparison from the experiment to that phase diagram. I don't understand this statement), the use of the TFIM in the limit of strong interaction may be justified for weak quantum tunneling effects at low T . (how the CLG model is connected at all to the TFIM???)

(what exactly it does not include??? there are different models, so it is hard to day what exactly is included in TFIM, it is just a model with some parameters)

The simulation does not explicitly address the sources of environmental noise ⁶⁴ (environmental noise???? is it a pink noise??? I still don't understand the sources of noise, I need to read cited papers), but it is assumed to have $1/\nu$ frequency dependence (why it is assumed so???) , similar as in 1 T – TaS₂⁴⁶ (why does it have such a noise?) , based on previous measurements of the PQA⁴⁷.

(More discussions on the application of the TFIM model on the D-Wave Advantage quantum annealer is given in the SI). (check it!)

(how to encode the state into the quantum computer??? maybe it is written in the SM, but I don't know it at all now)

We emulate the STM measuring process by initializing the system of qubits (polarons) into a domain state (as a product state in the qubit q_i basis) similar to the initially observed states in 1T-TaS₂.

The domain walls separate the 3 possible ground states (still a question, what is different about them???) .

(For simplicity, in the simulation we have used 3 rather than 13 possible degenerate ground states, as in 1 T – TaS₂). (why there can be other 13 GS??? I understand the 3 ones, but other 10 come from where???)

The PQA allows us to adiabatically tune $r[s(t)]$ and $T_{eff}[s(t)]$ via $s(t)$ in order to bring them to the range of values for which we want to observe dynamics. (it was written before)

After we let the system of qubits evolve for a preset amount of time, we perform a measurement and observe the polaronic configuration that the qubits have evolved into.

Then, we use the measured configuration as the new initial product state, thereby faithfully emulating the iterative STM measurement. (do they say that there is no influence from the tip?)

From the point of view of Hamiltonians, we start with $H_{PQA}(t = 0) (/k_B T) = \left(-\sum_i \sigma_i^x + r[1] \left(\sum_{\langle ij \rangle} V(i, j) q_i q_j - \mu \sum_i q_i \right) \right) / T_{eff}[1]$, where $r[1] \approx 10^{10}$, and initialize the qubits into the initial domain state in the qubit computational basis, then adiabatically tune to $H_{PQA}(t = \frac{t_a}{2}) (/k_B T) = \left(-\sum_i \sigma_i^x / 2 + r \left[s \left(\frac{t_a}{2} \right) \right] \left(\sum_{\langle ij \rangle} V(i, j) q_i q_j - \mu \sum_i q_i \right) \right) / T_{eff} \left[s \left(\frac{t_a}{2} \right) \right]$ (what is the t_a ???) and let the system evolve in time, and finally adiabatically tune back to $H_{PQA}(t = t_a) = H_{PQA}(t = 0)$, which constitutes a measurement (why does it constitute measurement? why do we put it back???) . (this method of changing r_s is only technical, for their quantum computations, it has no physics, it is just for preparing the state and exists only because we can't initialize immediately the needed Hamiltonian)

(is the t_a a computational time??? how does it relate to the real time??? real time is in half an hour, but t_a should be way smaller, no???)

(WHY AT ALL WE CHANGE TIME BY CHANGING THE t_a ???? sounds so strange....)

The annealing time t_a is of the order of $10\mu s$ and the energy scale of H_{PQA} is a few GHz .

We focus on values $r \left[s \left(\frac{t_a}{2} \right) \right] \gg 1$, where the kinetic energy of domain walls is small (below it is written $r_s = 58$) compared to the interaction energy and study the behavior of domain wall dynamics at different T_{eff} .

Details on the methodology are given in the SI. (check it)

We observe translations and melting of the domain walls towards one of the 3 uniform ground states from the initial domain wall state, just as it occurs in 1 T – TaS₂ (Fig. 1c and Fig. 2c). (how to know, which the GS is preferred? should they have the same energy be def. of GS?)

The characteristics of the domain melting processes captured by the fraction of moved polarons $f(t)$ in 1TTaS₂ (Fig. 1d) also experiences intermediate saturations and jumps in the PQA (Fig. 2d). (but this plot looks very different comparing to f from fig. 1. is the model still applicable???)

Most importantly, both systems exhibit a crossover in the relaxation rate $R(T_{eff})$ from T -dependent activation processes at high T to T -independent noise mediated quantum tunnelling events at low T (Fig. 1g and Fig. 2e). (how does fig. 2 d) is connected to fig. 2. e)? connection

of R and t ? yes, d) has time, e) has temperature, but still???) (it is about that plato on the plot of R)

$R(T_{\text{eff}})$ saturates to a T -independent non-zero rate due to slow system dynamics (why due to slow system dynamics?) compared to the sampling time, which is the rate at which we measure with the STM tip in 1T-TaS2 or the rate of qubit measurements in the PQA.

If the system is given enough time to fully relax to the uniform ground state, then the dynamics eventually stops. (this is obvious, the dynamics eventually stops)

In order to reproduce the experimental timescale of the dynamics (~ 1000 s), we need to set $r \approx 58$. (how can we see it? why exactly 58?????)

As an indirect comparison, the usual criterion for Wigner crystallization in 2D $r_s = \frac{e^2 m^*}{\hbar^2 \sqrt{n}} = 31 \sim 38$ see the articles^{34,65} (check that it is so), justifying the use of a dominant interaction term with small kinetic energy in the calculations.

(why the Wigner crystallization is relevant for this material?)

7.1.4 Discussion

(SUMMARY: there are some parameters involved, noise affects tunneling, and we can get the polaronic bandwidth w from the rate of tunneling? But I don't understand statements from this section!!!!)

(what finally conclusion about noise is here????????? many statements, but I see nothing clear and encoded in the model which we are dealing with)

Let us interpret the physical processes involved in noise mediated quantum tunnelling.

1T-TaS2 and the PQA are both described by a Hamiltonian H_S , coupled via H_I to an external thermal bath B with a $1/\nu$ noise spectrum (why $1/\nu$ noise spectrum?) at temperature T , where the total Hamiltonian is $H = H_S + H_I + H_B$.

We can represent an arbitrary bath described by a spectral function $\mathfrak{J}(\omega) = \frac{\pi}{2} \sum_{\alpha} (C_{\alpha}^2 / m_{\alpha} \omega_{\alpha}) \delta(\omega - \omega_{\alpha})$ with a system of decoupled harmonic oscillators (HOs) with mass m_{α} , frequencies ω_{α} , and couplings C_{α} in H_I ⁹. (learn the CL model, I don't understand it, but it is referenced to it here)

Temperature effects are taken into account by populating each HO with a Bose-Einstein distribution with temperature T , meaning that at low T HOs effectively reduce to TLSs. (formula for it?)

In the limit of $H_I \rightarrow 0$ we would only observe pure tunnelling events from an initial classical polaronic configuration (meaning, we will observe reconfigurations) into other configurations, determined by their overlap with instantaneous eigenstates (overlap with instantaneous eigenstates?) during the adiabatic evolution, as well as the shape of the annealing schedule. (why reconfiguration is determined by the annealing schedule??? is it also physical process? is it that change of r , which we should make relevant physically?)

By bringing the initial classical configuration adiabatically into a superposition state of multiple configurations (how to we bring to a state of multiple configurations???) and then back, we introduce a probability of tunnelling to other configurations involved in the superpositions. (write formulas for it!! how is it? is it about the change of r_s again?)

We found that the kinetic energy contribution is very small compared to the interaction ($r \approx 58$), which means that pure tunnelling events would be highly constrained in the energy difference between the initial and final configuration. (wasn't it known before?)

In fact, the energy difference (energy difference of what?) tends to 0 in the limit of $r \rightarrow \infty$, meaning that we would have no configurational changes at $T = 0$ and zero noise.

Now we discuss the effect of noise and temperature on quantum tunnelling.

The number of HOs (of the bath around the system) , populated at temperature T , required to describe a particular spectral function (for example, which? we have only one general formula for spectral function. why is it at all important?) is much larger than the number of polarons, meaning that they effectively serve as an infinite energy reservoir for the polarons and are constantly bringing them into thermal equilibrium with respect to T . (this is obvious, no?)

Noise is represented by the influence of HOs on the energy spectrum of H_S , which is a static energy shift of energy levels ⁶⁴ (why static energy shift?? write formulas for the noise) .

The simplest example is when both H_B and H_S are two-level systems.

The two levels of H_S represent two polaronic eigenstates and the two levels of H_B are the first two HO levels. (write formulas for it, idk what is meant here?)

Each polaronic state is split by $\hbar\omega_\alpha$ into two levels by adding the HO degree of freedom, meaning that a properly chosen ω_α can bring two polaronic states to the same energy, thereby making quantum tunnelling between them possible. (I understand the statement, but why is it so, that noise does this??)

This is what we mean by noise mediated macroscopic quantum tunnelling.

We introduce the $1/v$ noise spectrum by increasing the number of HOs and choosing appropriate C_α, m_α and ω_α . (and which they should be?) (how exactly they introduce the $1/v$ noise????)

The polaronic state energy level then becomes an energy band with width W , given by an integral over the noise spectrum, as shown in Fig. 2f. (how to get the W ? is it the same as the band from other effects from Alexandrov, Mott?)

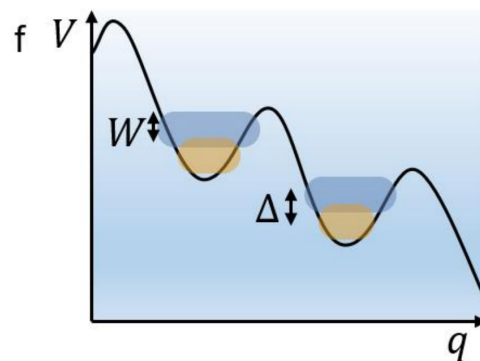


Figure 7.11: f) (how to get this plot???) The washboard potential of the PQA flux qubit with 2-level system spacing Δ (why the spacing is here???) coupled to the external bath with an integral over noise W . (do not confuse f here from the well-used f in the text)

If energy bands overlap, then a transition between the bath degrees of freedom (transition between the bath degrees of freedom?) can already induce a polaronic configurational change.

If they do not overlap, the energy gap is still reduced by W , increasing the probability for a transition. (it is not exactly correct statement. system can be at the higher excited state, so it is more probable for it to jump) (if we have W , does it mean that the system will be at the top of the band??? will it affect the tunnelling probability at all?)

Both represent incoherent macroscopic tunneling (IMT) processes. (how the coherent tunnelling could look like?)

(here we have both words "tunneling" and "tunnelling")

Quantum simulation gives us some other unique insights into the emergent tunneling phenomenon. (which insights? I don't understand them from below)

The dynamics of the two systems (which two systems?) is governed by an anharmonic metastable state potential (anharmonic metastable state potential?) in terms of the configurational coordinate (configurational coordinate?), measured by f , for 1 T – TaS₂ and the PQA respectively.

While the washboard potential and two-level system dynamics of flux qubits in the PQA emerge from the device concept (why the washboard potential emerge from the device concept???) , the energy landscape of the metastable state of 1T-TaS₂ is determined by the topology (determined by the topology???) and the microscopic details of the domain structure arising from discommensurations (which microscopic details??) ¹⁴.

The extracted parameters from the simulations describing the emergent processes are the barrier energy E_B (height) and the barrier width w (little w is the same as W , it is a typo) which describe the rate of tunneling between domain configurations.

(and what is the value of these parameters??? these are just fits in our model)

In 1TTaS₂, the thermal activation energy E_B is determined directly from the T -dependence of the rate in Fig. 1c or resistivity relaxation to be $E_M \simeq 10 \sim 20\text{meV}$. (resistivity relaxation?)

On the other hand, w is related to f , where both are measured in terms of the configurational coordinate (this was written before, it is still unclear what is meant here?) , which is set by the state of N Bloch spheres representing qubits, parametrized by $2N$ spherical angles (yes, if we map all the states to the qubits, then we have an N dim block sphere, so what? how does it relate to the configurational coordinate?) .

The plot of $f(t)$ in Fig. 1d thus reflects the tunnel barrier width for each measured reconfiguration step. (and how to find this barrier from that plot?)

7.2 SM

(SUMMARY: there are 32 pages of the SM!!! I am not sure that reading it is really needed... I'll read only some relevant parts in it. I am not motivated to read 32 pages.)

7.2.1 1 SM Notes 1

SM: 1.1 The experimental setup, domain creation by laser or charge injection through tip

(SUMMARY: it is important for experimentalists, I skipped it)

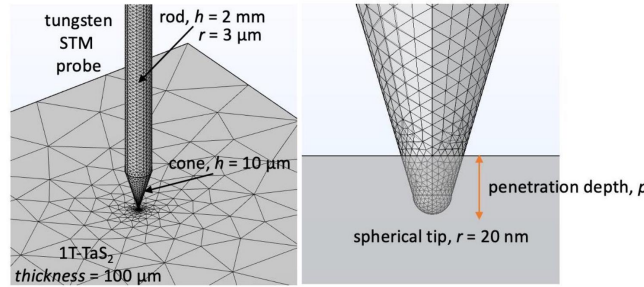
Domains may be created at 4 K either by exposure to a laser pulse ¹, or by an electrical pulse from an STM tip ^{2–4}, or by a current pulse passed through a set of electrodes on the surface ^{4,5}. (as was written in the intro)

In this work the domain state was created by using an electrical pulse from the STM tip on a freshly cleaved 1T-TaS₂ sample in UHV. The tip is initially retracted at 50 nm from the sample's surface, then approached with a bias voltage of 5V and a tunneling current of 10-50 nA. Alternatively, the tip can be approached to the surface with a voltage bias of 0.05 V and a tunneling current of 1 – 3nA, then a 4V electrical pulse of 100 ms duration is applied. The two described procedures generate a domain state area of around 10^4 nm^2 . The properties of the resulting domain formation ^{2,3,6–8}, ordering ⁹ and resistance relaxation as a function of temperature and on different substrates have been reported in detail elsewhere ⁵.

SM: 1.2 Calculation of the STM tip and sample temperature during transformation and scanning

(SUMMARY: it is important for experimentalists, I skipped it)

Thermal simulations were performed by solving partial differential equations governing heat conduction using the finite element method (FEM). The thermal model was coupled to the electromagnetic model which calculated the resistive losses (Joule heating) in the contact region: $\rho C_p \frac{\partial T}{\partial t} - \nabla \cdot (k \nabla T) = Q_e$ where $Q_e = \sigma |\nabla V|^2$. The density ρ , heat capacity C_p ¹⁰ thermal conductivity k ¹¹, and electrical conductivity σ of all the materials were taken from literature and/or calibrated by experiment¹. The exact geometry of the W tip, tip mount, tip mount heat sink, 1T-TaS₂ crystal sample and sample holder mount in the STM UHV chamber were reproduced in the model calculations. The 1T-TaS₂ sample (100 μm thick) is glued to the conducting (Mo) sample holder substrate, which is clamped to the cryostat vessel at base temperature (4.5 K) with conducting silver paste. The calculation of temperature of the W tip and 1T-TaS₂ sample for different tunneling currents and tip penetration depths is performed using the COMSOL package. The geometric elements at the tip-sample contact used in the calculation are shown in SM Fig. 1.



SM Figure 1 | Specification of the geometry in the COMSOL calculations. The tip material is tungsten (W). The base temperature in the calculation is 4.5 K.

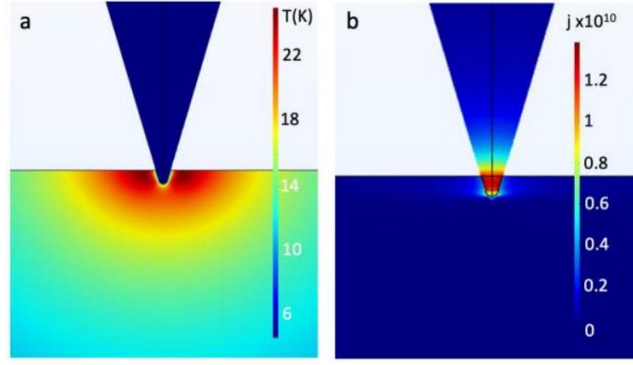
The calculations take into account the temperature of the sample and the tip when a current is passing between the tip and the substrate. The model calculation also takes into account:

- the temperature dependence of thermal conductivity, and the specific heat capacity of both 1T-TaS₂ and tip material (W)
- the temperature-dependence and anisotropy of electrical conductivity of both materials. For 1T-TaS₂, the different electrical conductivities of the C and the H phase are taken into account.
- thermal clamping of the tungsten rod at a distance 2 mm to the STM tip mount
- the heat sink of the piezoelectric STM actuator which is in wide-area thermal contact with the tip mount is at base temperature, connected to the cryostat cold finger by multiple copper braids.

The thermal contact between the sample and the sample holder is assumed to be ideal. The calculations are shown in SM Fig. 3 for various penetration depths p . As expected, the behavior beyond a few nm is not very dependent on p .

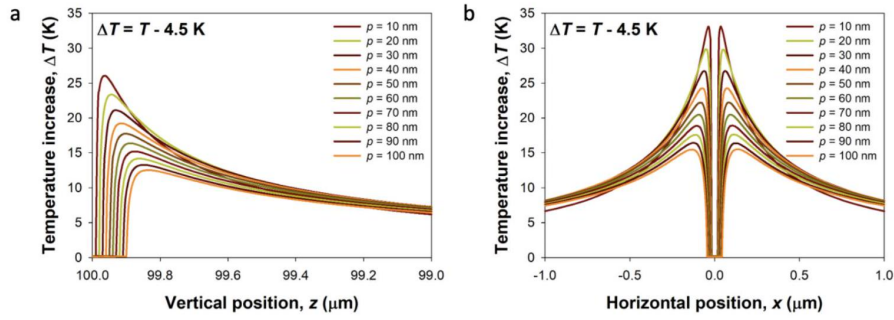
1.2.1 Thermal behavior of the sample during the creation of the domain state by a single electrical pulse

(SUMMARY: it is important for experimentalists, I skipped it)



SM Figure 2 | Temperature (a) and current density (b) maps for the strong pulse used to create the domain state. The starting state parameters correspond to the high-resistivity C state. The domain state is examined at ~ 50 nm from the center. The current density is in units of Amperes /m³.

A calculation of the tip and sample temperatures in the contact area during single pulse excitation is shown in SM Fig. 2. The maximum temperature at the center reaches ~ 30 K. The temperature drops rapidly away from the contact point. The thermal perturbation is therefore too small to heat the sample through the nearest phase transition to the trigonal (T) or nearly-commensurate (NC) phase. We can safely conclude that the main effect is in response to charge injection, and not thermal.

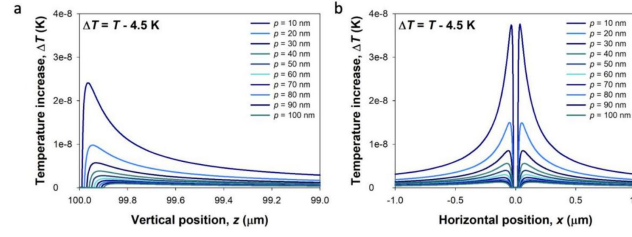


SM Figure 3 | Vertical (a), and lateral (b), temperature profiles within the 1T-TaS₂ sample for different STM tip penetration depths p (see SM Figs. 1,2) resulting from the pulse causing the transformation to the domain state (5 V, 50nA). A steady state is assumed, so these are maximum attainable temperatures during the passing of the applied current.

1.2.2 Heating of the sample by the tip current during relaxation measurements.

(SUMMARY: it is important for experimentalists, I skipped it)

The temperature calculated for the current and voltage parameters used in the relaxation measurements shown in Fig. 1 of the main text are shown in SM Fig. 4. The maximum calculated temperature rise is < 0.000001 K. We conclude that the temperature rise due to the STM tip currents used in relaxation measurements can be neglected.



SM Figure 4 | Vertical (a), and lateral (b), temperature profiles within the 1T-TaS sample for different STM tip penetration depths p (see SM Figs. 1, 2) during relaxation measurements using the parameters presented in Fig. 1 of the main text. The maximum temperature rise is < 0.000001 K. The sample and tip mount base temperatures are both 4.5 K.

SM: 1.3 Detection of domain reconfiguration

(SUMMARY: it is important, I'll read later it)

STM measures the local density of states (LDOS) at the point of tunnelling from the STM tip into the sample. In the local state approximation, appropriate for the Wigner crystal state, for state E_i the LDOS is given by ¹², $\rho_{\text{local}}(E, r) \propto \sum_{i=1}^N |\psi_i(E_i, r)|^2 \delta(E - E_i)$. Integrating $\rho_{\text{local}}(E, r)$ over energy in the interval $\pm \Delta/2$, where Δ is the full bandwidth of state E_i , we obtain a real-space electron density $\rho(r)$ for state E_i . The total charge ρ in state E_i is given by the integral over a contour S around a localized state $\int_S \rho(r) dr = \rho$. If charge is localised, maxima in STM images can be interpreted as an electron count, which can be used to quantify the domain wall reconfiguration. By measuring $\rho(r)$ patterns as a function of time, one obtains a quantitative measure of charge reconfiguration in each frame. We note that this does not imply any single particle motion between frames, but measures the number of sites involved in the domain reconfiguration in a given time interval. Furthermore, the absolute number density is not of interest, only the changes with time. The criterion for domain wall characterization is thus somewhat arbitrary. To obtain an accurate rate it is important that the counting is performed consistently.

In these measurements, the border between the ground state and the domain state is first found. SM Fig. 5 shows an example of such an STM image. An area is typically chosen for analysis with as few imperfections and structural defects (such as the bright yellow spots in SM Fig. 5) as possible. A series of N images of the same area ($40 \times 40 \text{ nm}^2$) are taken at regular intervals to record the relaxation of the domain structure (SM Fig. 6). Tipscanning parameters are $-0.8V$ for voltage bias, $50pA$ for tunneling current and 84 nm/s is the tip speed. The tip scans each line from left to right along the x -axis and then moves to the upper line (y -axis). 8 minutes are required to scan the entire area under these conditions. Images within the same series are rigidly translated referring to a fixed point common to each image (e.g. a stationary polaron) and then uneven borders are cut. This corrects possible shifts of the tipsample relative position. To compare two consecutive images (i and $i + 1$; with $i = 1, \dots, N$), we detect the polarons' centers in each image (shown by red dots in SM Fig. 7) by using a blob detection algorithm in Python environment. Then the centers' patterns are juxtaposed (SM Fig. 8a) to count the number of polarons which have moved.

The allowed displacement of the electrons is defined by the internal structure of 1T-TaS₂ polarons, each of which involves thirteen Ta atoms arranged in the shape of a David's star, with 6 Ta atoms on the vertexes, 6 at the corners, and one in the center (SM Fig. 8b). Due to the periodicity of the system, there are only two non-trivial ways to move a polaron, i.e. move the central atom to a corner or to a vertex of the David's star. This corresponds to a minimum polaron's movement of $\sim 0.33 \text{ nm}$. Thus, to determine if a certain polaron moved between two images, we take its coordinates in the two images and we evaluate if they differ by more

than 0.33 nm. In the affirmative case, the polaron is considered as moved. SM Fig. 8c shows one possible arrangement of the possible polaron positions at the domain wall enumerated by Ma et al ². The movement of a domain is associated with an energy cost ΔE . To first order, $\Delta E \sim N$, where N is the number of polarons involved in the reconfiguration.

The fraction (f) of moved polarons is calculated as the number of moved polarons divided by the total number of polarons:

$$f(i, i+1) = \frac{[\text{number of moved polarons between images } (i) \text{ and } (i+1)]}{[\text{total number of polarons in image } (i)]}. \quad (1)$$

We estimated the error of f as given mainly by polarons which are detected only in one of the two compared images (this usually occurs on the border of the images or inside the domain walls). Its value is calculated as the relative difference between the total detected polarons in the two images:

$$\delta f(i, i+1) = \frac{[|\text{total polarons in } (i) - \text{total polarons in } (i+1)|]}{[\text{total polarons in } (i)]}. \quad (2)$$

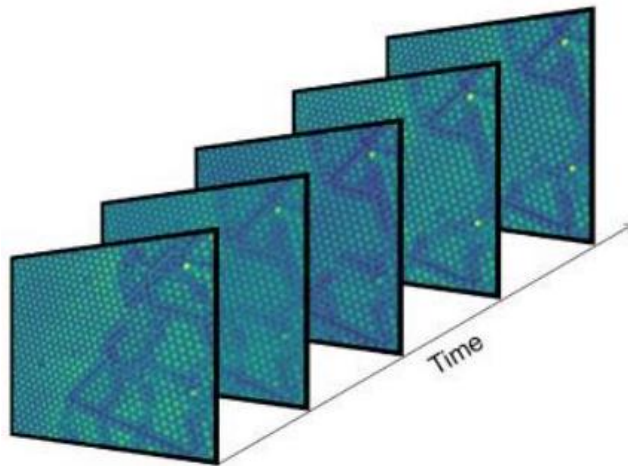
The described procedure is repeated for each pairs of consecutive images in a certain series. Finally, summing all the calculated fractions and dividing by the time (T) needed to scan the N images of the series ($T = N \times 8 \text{ min.}$), we obtain the rate R of movements in the series:

$$R = \frac{\sum_{i=1 \dots N-1} f(i, i+1)}{T} \quad (3)$$

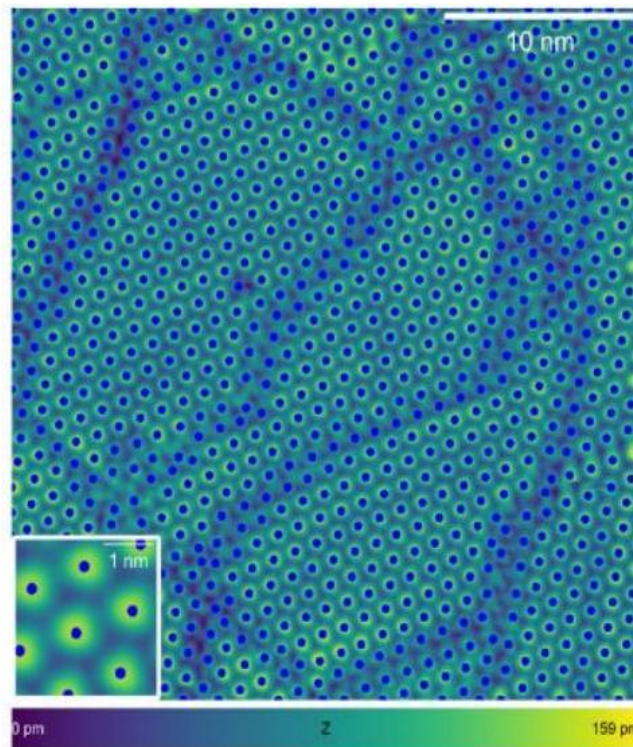
$$\delta R = \frac{\sum_{i=1 \dots N-1} \delta f(i, i+1)}{T}$$

With this definition, R is always ≤ 1 . This is due to the fact that if a polaron moves two (or more) times between two images, it would still be detected as a single event (or 0, if the polaron returns to its starting site). Note that the absolute value of N is of no significance, while the accuracy of the rate measurement is ensured by the use of a consistent algorithm throughout the analysis.

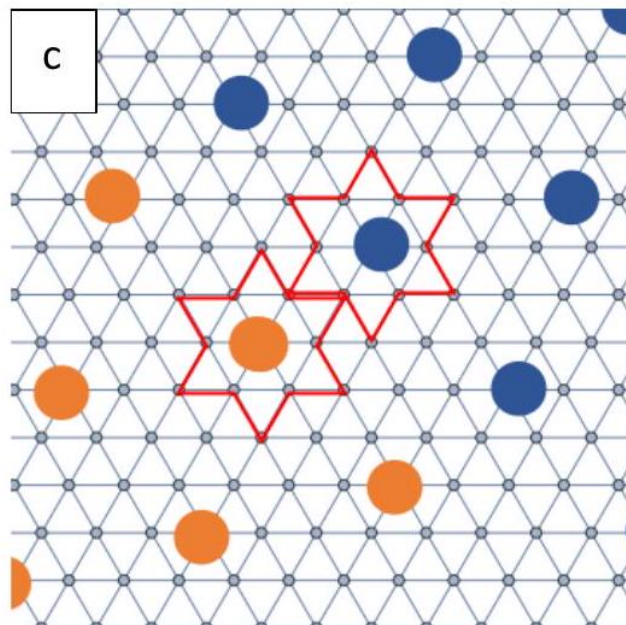
SM Figure 5 | An STM image of the border between the ground state (down/left) and the domain state (up/right) in 1T-TaS₂



SM Figure 6 | Scheme of a series taken while relaxation of the domain state occurs. Each image shows the same area. Images are separated by 8 minutes.



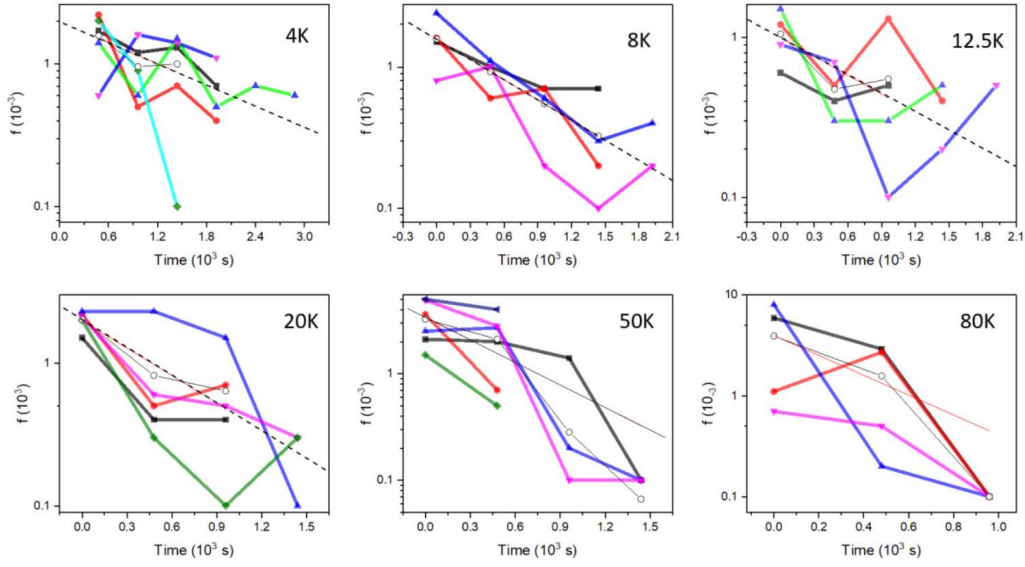
SM Figure 7 | Patterns of polarons in two consecutive images of the same area. The patterns are superimposed to the STM images. In the bottom-left corner of both images the pattern is enlarged.



SM Figure 8 | a, Juxtaposition of polarons' centres of images in SM Fig. 7 When the polaron didn't move, the red dot covers the blue dot, otherwise both dots are visible. b, The possible 6 nearest and 6 nextnearest neighbour Ta positions to which an electron can move in a domain reconfiguration. c, An example of a domain wall ^{2,9}, showing explicitly the positions of the polarons at the junction of two domains.

SM: 1.4 Temperature dependence of domain reconfiguration rate

(SUMMARY: it is important, I'll read later it)



SM Figure 9 | Reconfiguration f of the domain state at 6 different temperatures T . (what is the dependence on the time of measurements?)

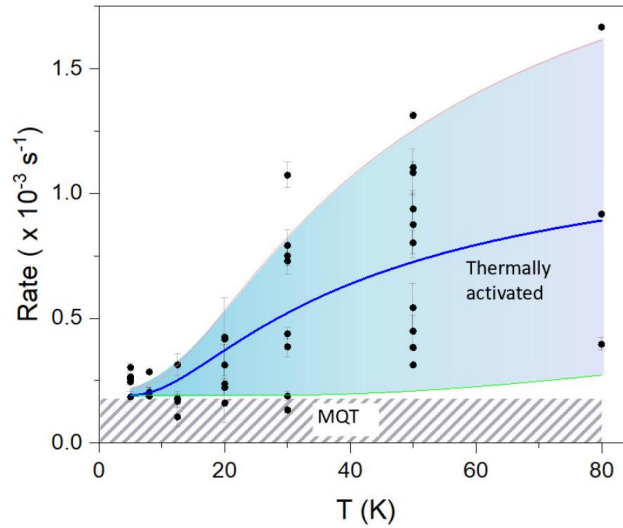


Figure 7.14: SM Figure 10 | Reconfiguration rate $R(T)$ as a function of temperature with error bars representing counting errors of polaronic reconfiguration events. Experimental runs presented in SM Fig. 9 are shown separately. The fits are described in the text.

SM Fig. 9 shows the raw data on relaxation at different temperatures. The scatter of the data is a result of the fact that domain reconfiguration process is measured on a relatively small area which is comparable to the domain size. Measurement of a larger area would require faster scanning, which in turn would sacrifice resolution of the measurement of polaron motion. The presented measurements are a compromise that optimizes the resolution and measurement area.

SM Fig. 10 shows the data of relaxation as a function of temperature for all measurements individually. Note that the scatter of the data is very small at low temperature, but increases with temperature. As discussed in the main text, the temperature-activated domain relaxation processes have a range of different E_B , reflecting the wide spread of relaxation rates, as defined

by the changing energy landscape each time the configuration changes^{2,3}. The average rate is presented in Fig. 1 of the main paper. The boundaries of the blue shaded area represent fits to the phenomenological model¹³ given in the main text, where $R(T) = R_q + R_0 \exp\left(-\frac{E_B}{k_B T}\right)$ with values of $E_B = 40$ K (top curve) and $E_B = 200$ K (bottom curve) with $R_0 = 0.0023\text{s}^{-1}$ and 0.001s^{-1} respectively. The blue curve is the fit to the average of all the data shown in the main text, giving $E_B = 36$ K, with $R_0 = 0.0011\text{s}^{-1}$. Note that the lowtemperature value for the quantum rate $R_q = 1.9 \times 10^{-4}\text{s}^{-1}$ is the same in all three fits. The patterned area represents the base quantum rate, which is temperature independent.

SM: 1.5 Tip current and voltage dependence of domain reconfiguration: measurement details

(SUMMARY: this is again only for people who want to do experiments about it)

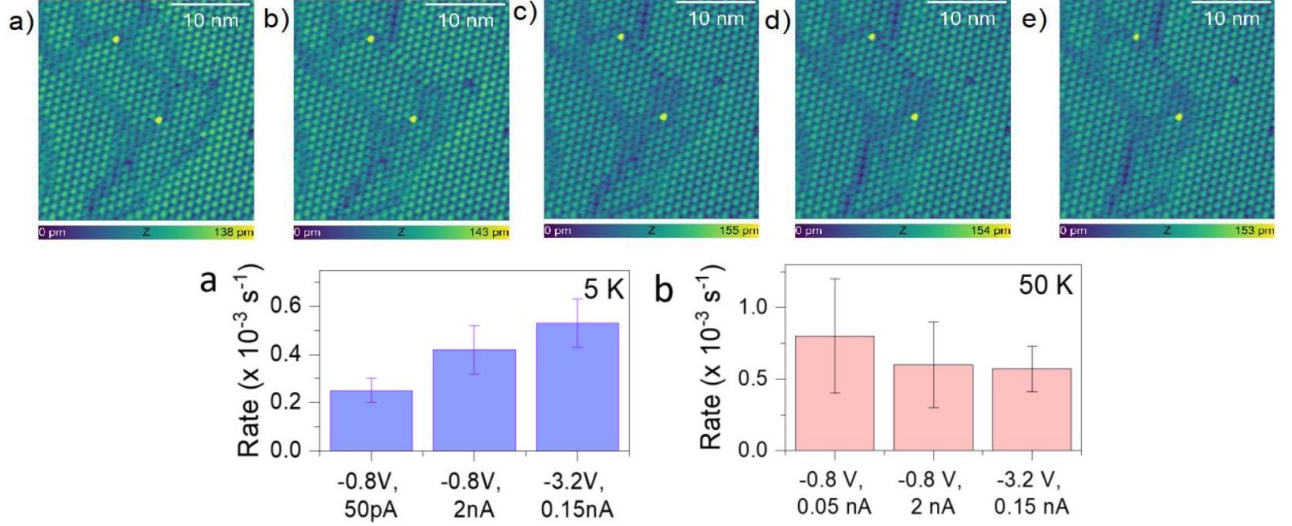
The thermal calculation in section 1.2 has shown that during scanning the effect of Joule heating on the sample is negligible. However, the small tunneling currents may transfer sufficient charge to modify the charge configuration state according to the established mechanisms^{1,14,15}. To determine this empirically and determine the role of the tip in the relaxation process, we performed systematic measurements with different scanning parameters (I and V) both at 5 K and 50 K.

Exploring first the effect of STM bias voltage and tip-tunnelling current on R , we find that increasing either the tip current, or the tip-to-sample voltage at 5 K results in a slight increase on the relaxation rate (SM Fig. 12a). SM Fig. 11 shows an example of relaxation series at 5 K for 40-fold increased tunneling current 2nA and -0.8 V, compared with 50pA and -0.8 V for the sequences presented in Fig. 1 of the main text. The 40-fold increase in tip current (from 50pA to 2nA) increases R rather modestly, from $\sim 2.5 \times 10^{-4}\text{s}^{-1}$ to $\sim 4.2 \times 10^{-4}\text{s}^{-1}$ (a factor of ~ 1.7). Similarly, quadrupling the tip voltage from -0.8 V to -3.2 V and simultaneously increasing the current three-fold from 50pA to 150pA results in a similarly modest change of R from $\sim 2.5 \times 10^{-4}\text{s}^{-1}$ to $\sim 5.5 \times 10^{-4}\text{s}^{-1}$ (a factor of 2.2). SM Fig. 12 shows the comparison between the range of all rates measured for normal scanning parameters (50pA and -0.8 V) and the average rates for two combinations of different parameters (2nA and -0.8 V ; 150pA and -3.2 V). Thus, the application of huge increases in current or voltage apparently causes very small changes in R at 5 K.

At 50 K, the effect of changing the scanning parameters over the same range becomes undetectable. SM Fig. 12b shows that relaxation rates at 50 K for different parameters (150pA and -3.2 V ; 2.0nA and -0.8 V) are compatible with the rate at normal scanning parameters (50pA and -0.8 V) presented in Fig. 1 of the main text. This confirms that the tip-induced relaxation is small in comparison with intrinsic quantum and thermally activated relaxation rates R_q and R_0 respectively.

A possibility exists that external electrical noise influences R . The electrical noise floor within the UHV LT STM is many orders of magnitude below the value required to change the rate, as discussed above, so it is unlikely to cause enhanced relaxation. Cosmic rays are known to cause perturbations in quantum electrical devices, such as detectors and quantum processors (see main text), and they are also likely to trigger domain reconfiguration by locally depositing energy. However, this would be visible in the STM scans in the form of spikes. These are not very common on our apparatus, and cannot be correlated with relaxation, so at present cannot be identified as an external stimulus that drives relaxation.

The presented data lend support to the arguments presented in the main text (and in the next section, 1.6) based on tunnelling arising from retracted-tip measurements (Fig. 1f). We emphasize that for the purpose of this study it is not important to eliminate completely external relaxation triggers, but only to ascertain that a finite intrinsic rate of domain reconfiguration is present. From our experiments presented above we can safely conclude that while the tip field or current and other external processes may enhance relaxation, a significant part of R_q arises from quantum processes that are intrinsic, and independent of external stimuli.



SM Figure 12 | a, Relaxation rates for different parameters at 5 K. The first bar contains all measured rates for normal scanning parameters (50pA and $-0.8V$). Second and third bars are the average rates and relative errors for different parameters (2nA and $-0.8V$; 150pA and $-3.2V$). b, Relaxation rates for different parameters at 50 K. The first bar contains all measured rates for normal scanning parameters (50pA and $-0.8V$). Second and third bars are the average rates and relative errors for different parameters (2nA and $-0.8V$; 150pA and $-3.2V$).

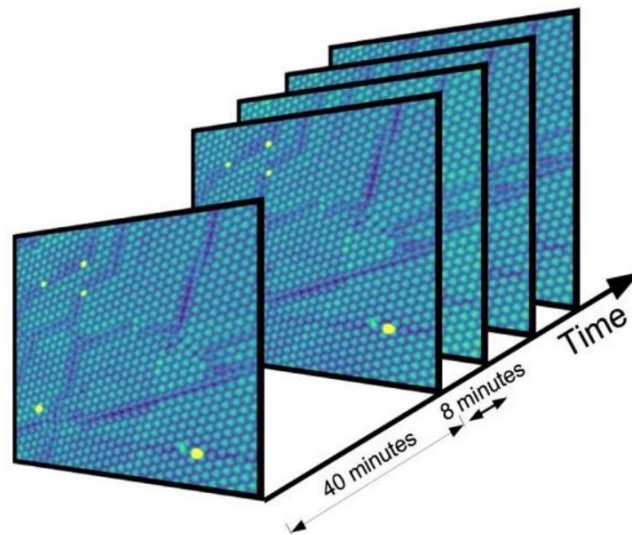
SM: 1.6 The experiments measuring 'light' and 'dark' relaxation by STM

(SUMMARY: this might be also relevant...)

A series with a long pause between images (dark series) were measured at 5 K to further investigate the role of the tip in the relaxation process.

The procedure consists of scanning a first image ($i = 1$) (which requires 8 minutes), then retract the tip several nm away from the surface, wait 32 minutes ("dark relaxation") and finally start scanning a normal "light" series with 8 minutes of scanning time between images ($i = 2, \dots, N$).

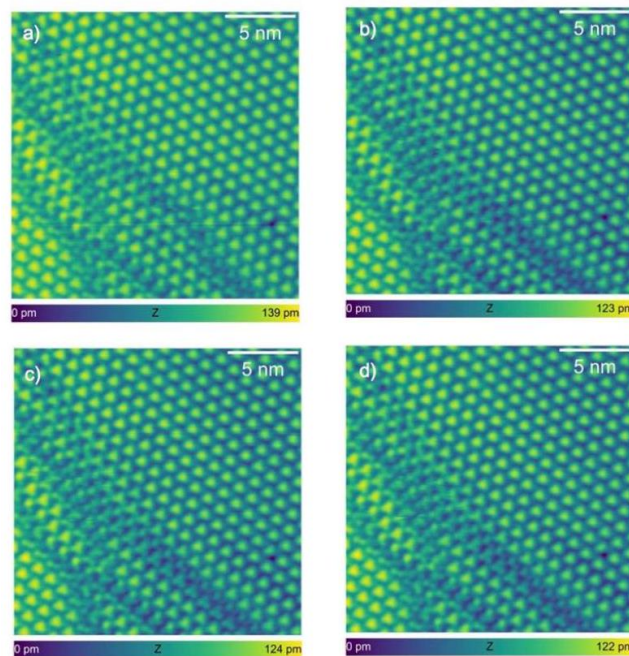
SM Fig. 13 shows the scheme of the dark relaxation series.



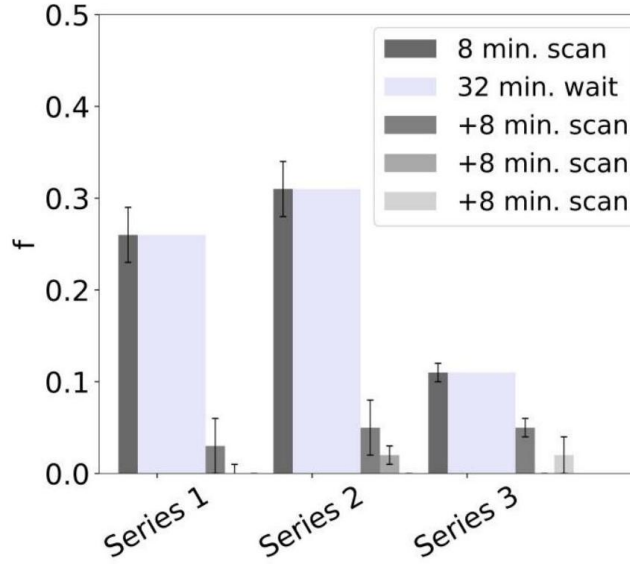
SM Figure 13 | Scheme of a "dark" relaxation series.

The fraction f of the moved polarons between consecutive images is then calculated as discussed in section 1.3 for all pairs of consecutive images.

SM Fig. 14a shows an example of a dark series with its relative centers' patterns, while the results for three different dark series are summarized in SM Fig. 14b. As can be seen from the pattern and from the plot, the fraction of moved polarons is consistently larger than the fraction between all other pairs of images. This suggests that the system relaxes to a new configuration during the first 8 + 32 minutes (with no tip scanning) and then doesn't change significantly thereafter.



SM Figure 14 | Dark series and relative centers' pattern. Left panel: a, initial image at time = 0 (blue in the pattern), b, after 8 minutes of scanning + 32 minutes of not scanning (orange in the pattern), c, subsequent 8 minutes of scanning (green in the pattern) d, subsequent 8 minutes of scanning (red in the pattern). The right panel shows all four patterns superimposed.



SM Figure 15 | Histogram of dark relaxation series with error bars representing counting errors in measuring polaronic reconfiguration events.

The average fraction of moved polaron during the dark relaxation (8 minutes of scanning S + 32 minutes of not scanning NS) was then compared with the average fraction of moved polarons between images with light relaxation (8 minutes of scanning S) taken in this work (and discussed in section 1.3) at the same scanning conditions (5 K, $-0.8V$ for tip-sample voltage bias, $50pA$ for tunneling current). A histogram showing the polaron fraction moved in a number of repeated measurements is shown in SM Fig. 15.

In order to estimate the tip-induced effects on the obtained results, the average fraction of moved polarons during dark relaxation was compared to the one measured during regular observation. The comparison shows that: (why there is such a formula???)

$$\frac{f_{ave}(8S + 4 * 8S) - f_{ave}(8S + 32NS)}{f_{ave}(8S + 32NS)} \ll 1. \quad (4)$$

This suggests that the fraction of polaron moved during the 8+32 minutes of dark relaxation can mostly be attributed to non-tip-induced processes. We conclude that domain reconfiguration takes place at a similar rate in the absence of tip scanning as with tip scanning. The tip thus has a relatively minor effect.

A fit to the 'dark' reconfiguration rate is shown in Fig. If of the main text, on the same timeline as for 'light' measurements where a scan takes place continuously. The rates are comparable.

7.2.2 2 SM Notes 2

The low-temperature charge ordering in 1 T – TaS₂ is considered to be in the lattice Wigner crystal (WC) limit, which occurs when the electronic Coulomb energy significantly exceeds their kinetic energy¹⁶. The criterion for Wigner crystallization is defined in terms of the dimensionless Wigner-Seitz radius $r_s = V/T$, where V is the Coulomb energy and T is the kinetic energy. For a 2D electron system, $r_s = e^2m/(\hbar^2n^{1/2})$, where n is the electron density, e is elementary charge, and m is the effective mass of electron. In 1T-TaS₂, r_s is enhanced by the small carrier concentration (one electron per 13 unit cells - see Fig. 1a) and due to strong coupling to the lattice, polaronic effects renormalize the electronic bands, resulting in an increase of the effective mass. Altogether, this leads to a large expected r_s , and WC physics¹⁶. Doping, external charge

injection^{4,5,7,8} or optical perturbation^{1,5} introduces additional charges in the WC, which leads to a complex phase diagram with the formation of domains, discommensurations⁵ and charge fractionalization^{14,16} (Fig. 1b). The resulting domain wall structure allows multiple possible configurations, arising from different relative domain positions, each of which is a well-defined macroscopic quantum state in the occupation number basis, separated from each other by a potential energy barrier. Such DWs arising from electron "overcrowding" have been observed experimentally by STM in numerous transition metal dichalcogenides¹⁶. 1T-TaS is of particular interest because the domain reconfiguration dynamics can be tuned by temperature⁵ such that at sufficiently low temperatures, the domain reconfigurations are slow enough to be recorded by scanning tunneling microscopy (STM).

SM: 2.1 Details of the theoretical model

(SUMMARY: this looks like something which I know, but I'll read later)

In this chapter we introduce our theoretical model of 1T-TaS₂ already developed and explored in our previous work¹⁶. We present its classical charge ordering aspects and their relevance to the simulation on D-Wave's quantum computer. The Hamiltonian presented in this section is mapped onto the D-Wave Hamiltonian H_{DW} .

At the Fermi level, 1T-TaS₂ exhibits a sparsely populated ($1e^-$ per 13 unit cells) narrow single Ta band. According to¹⁷, chapter 4.2, we choose an appropriate model of an interacting single electron band within the tight-binding approximation

$$H = \sum_{i,j,s,s'} (t_{i,j} - \mu\delta_{i,j}) \delta_{s,s'} c_{i,s}^\dagger c_{j,s'} + \sum_{q,i,s} \omega_q n_{i,s} (u_{i,s}(q) d_q + h.c.) + \frac{1}{2} \sum_{i,j,s,s'} V_c(i,j) n_{i,s} n_{j,s'} + \sum_q \omega_q (d_q^\dagger d_q + 1/2), \quad (5)$$

where $t_{i,j}$ is the hopping integral between lattice sites i and j , μ the chemical potential, $c_{i,s}$ the annihilation operator of an electron at site i with spin s , $n_{i,s} = c_{i,s}^\dagger c_{i,s}$. Electrons interact with each other via Coulomb interaction $V_c(i,j)$, as well as with phononic degrees of freedom, where d_q is the annihilation operator of a phonon with wave vector q and ω_q is its frequency. The electron-phonon interaction is taken to be Fröhlich like and its matrix element is $u_{i,s}(q)$ and $\hbar = 1$. In the strong electron-phonon interaction limit, H can be solved exactly via the Lang Firsov canonical transformation ($\tilde{H} = e^S H e^{-S}$, $S = \sum_{q,i,s} n_{i,s} (u_{i,s}(q) d_q - h.c.)$), where electrons get dressed by a surrounding lattice deformation and therefore become quasi particles dubbed as polarons. After the transformation H becomes

$$\tilde{H} = \sum_{i,j,s,s'} (T_{i,s,j,s'} - \mu\delta_{i,j}) \delta_{s,s'} \tilde{c}_{i,s}^\dagger \tilde{c}_{j,s'} - E_p \sum_{i,s} \tilde{n}_{i,s} + \frac{1}{2} \sum_{i,j,s,s'} v(i,s,j,s') \tilde{n}_{i,s} \tilde{n}_{j,s'} + \sum_q \omega_q (\tilde{d}_q^\dagger \tilde{d}_q + 1/2) \quad (6)$$

where $\tilde{c}_{i,s} = c_{i,s} \exp\left(\sum_q u_{i,s}(q) d_q - h.c.\right)$ is the annihilation operator of a polaron and $\tilde{d}_q = d_q - \sum_{i,s} n_{i,s} u_{i,s}^*(q)$ is the new displaced phonon annihilation operator. The polaronic hopping integral is now $T_{i,s,j,s'} = t_{i,j} \exp\left(\sum_q [u_{i,s}(q) - u_{j,s'}(q)] d_q - h.c.\right)$, the polaron-polaron interaction is $v(i,s,j,s') = V_c(i,j) - 2 \sum_q \omega_q (u_{i,s}(q) u_{j,s'}^*(q))$ and E_p is the polaronic binding energy. In the strong electron-phonon interaction limit, the hopping integral of polarons can be neglected, which makes $\tilde{H}$ diagonal in the polaronic occupation number basis and is therefore

exactly solved. Here, we focus on the configurational ordering of polarons due to the interaction between them. Therefore, we consider them as spinless charged particles on a triangular lattice.

We rewrite $\tilde{H}$ with the classical 2D interaction Hamiltonian

$$H_{\text{int}} = \frac{1}{2} \sum_{i,j}^N V(i,j) q_i q_j - \mu \sum_i^N q_i \quad (7)$$

where $V(i,j) = V_0 \exp(-r_{i,j}/l_s)/r_{i,j}$, l_s is the screening radius, $r_{i,j} = |r_i - r_j|$, r_i is the i -th out of N lattice sites, $q_i \in \{0,1\}$ is the occupation number of lattice site i and the sum runs over all lattice sites. The number of polarons in the system is varied by the chemical potential μ . Polarons are considered as screened point charges that can only reside on Ta sites of the triangular atomic lattice. In this work we considered a triangular lattice with 2008 sites and open boundary conditions, where polarons repel each other via nearest neighbor repulsion. μ was set to a fixed value for which the ground state of H_{int} is a 1/3 polaronic lattice¹⁶.

H_{int} describes the domain structure and salient features of the phase diagram very well^{16,18}, but not quantum dynamics. To introduce quantum tunneling between different configurations of domains we first simplify H_{int} to $H'_{\text{int}} = \sum_{i,j}^N Q_{i,j} q_i q_j$, where $Q_{i,j} = \frac{1}{2} V(i,j) - \mu \delta_{i,j}$. This makes $\tilde{H}$ applicable to the quadratic unconstrained binary optimization formalism implemented on the D-Wave "Advantage" quantum processor, with > 5000 physical qubits. The Hamiltonian that is simulated on the device is the transverse field Ising model (TFIM)

$$H_{DW} = -\frac{A(t)}{2} \sum_i \sigma_i^x + \frac{B(t)}{2} \left(\sum_{i<j} J_{i,j} \sigma_i^z \sigma_j^z + \sum_i h_i \sigma_i^z \right), \quad (8)$$

where $\sigma_i^{x,z}$ are Pauli matrices operating on qubit q_i , $J_{i,j}$ are couplings between qubits q_i and q_j and h_i is the longitudinal external field exerted upon q_i . In order to simulate 1T-TaS₂ with DWave's quantum computer, we map H'_{int} onto H_{DW} by applying the transformation from spin to qubit variables $\sigma_i^z = 2q_i - 1$. Consequently, $h_i = \sum_{j=i}^N Q_{i,j}/2$ and $J_{i,j} = Q_{i,j}/4$, which reduces H'_{int} to the second term of H_{DW} . The σ^x term in H_{DW} describes tunneling between different configurational states and with this additional term our simulated model can also be viewed as an extended two-dimensional TFIM on a triangular lattice. The triangular lattice with 2008 sites combined with the correlated structure of H_{int} requires a specific embedding which uses 2673 qubits subject to the TFIM. Details on the embedding can be found in a subsequent chapter.

In order to make the connection of our model as deployed on D-Wave and a Wigner crystal, we interpret the σ^x term as the kinetic energy of polarons. Using the 2D Jordan Wigner transformation

$$\begin{aligned} \sigma_i^{\pm} &= \sigma_i^x \pm i\sigma_i^y; \sigma_i^- = a_i \exp(i\alpha_i); \sigma_i^+ = a_i^\dagger \exp(-i\alpha_i); \\ \alpha_i &= \pi \left(\sum_{x=1}^{i_x-1} \sum_{y=1}^{N_y} q_{x,y} + \sum_{y=1}^{i_y-1} q_{i_x,y} \right); q_i = q_{i_x,i_y} = a_i^\dagger a_i, \end{aligned} \quad (9)$$

where σ_i^+ is the spin raising, σ_i^- spin lowering operator and a_i the annihilation operator of the spinless polaron or qubit, H_{DW} becomes

$$H'_{DW} = -\frac{A(t)}{4} \sum_i \left(a_i^\dagger e^{-i\alpha_i} + a_i e^{i\alpha_i} \right) + \frac{B(t)}{2} \sum_{i<j} Q_{i,j} q_i q_j \quad (10)$$

In the limit of strong interactions, domain walls dominate the system and the kinetic energy term simplifies into a hopping term for the domain walls $\sum_{\langle ij \rangle} t_{ij} a_i^\dagger a_j + h.c.$ ¹⁹

The Wigner-Seitz radius r_s in our case is therefore related to the ratio between the second and the first term. The kinetic energy has an anomalous form and can be interpreted as the creation or annihilation of a spinless polaron at site i , which depends on the current polaronic configuration. The comparison between the effect of this form of kinetic energy and the conventional hopping form is beyond the scope of this work and remains an interesting question for future studies.

In this paper we use an analogue to the 1/13 electronic lattice which forms in TAS. We use a 1/3 electronic lattice due to the smaller system sizes considered here. We have shown already in ¹⁶ that classically the system behaves very similar to the 1/13 case albeit at a higher polaron density. We assume here that this generalizes also to the quantum version of this model, which is considered in this work.

In order to capture non-equilibrium quantum domain wall reconfiguration dynamics, we require at least a few hundred atomic sites or qubits, which is impossible with state-of-the-art classical simulation methods and hardware ²⁰. Another promising candidate are quantum Monte Carlo simulations with added noise, which are not developed for directly probing non-equilibrium dynamics and it is still an open question whether they could be applied in our case. We also checked whether classical Monte Carlo simulations (next section) in the presence of a thermal bath can predict a crossover in $R(T)$. As expected, thermally activated processes are responsible for the T -dependent reconfiguration rate. However, they cannot explain the T -independent behavior we observe in 1 T – TaS₂ at low T for interaction potentials known from previous literature ^{14,21,22}.

SM: 2.2 Classical Monte Carlo simulations

(SUMMARY: this looks also relevant, idk how it was measured??)

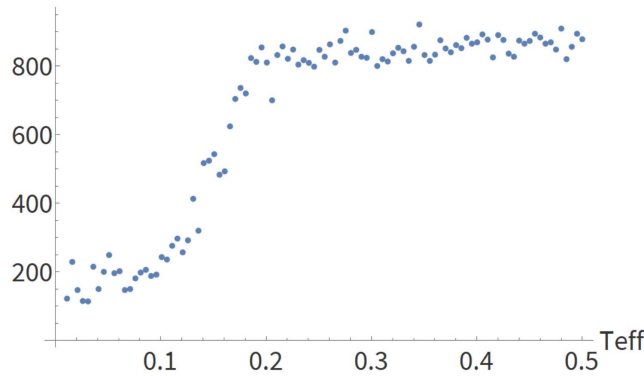
We performed classical Monte Carlo (MC) simulations in the form of simulated annealing, analogous to the quantum annealing performed on the D-Wave Advantage. Our classical simulations consist of Markov chain dynamics with the Hamiltonian $H_{\text{int}} = \frac{1}{2} \sum_{i,j}^N V(i,j) q_i q_j - \mu \sum_i^N q_i$, on a triangular lattice using the standard Metropolis algorithm. The proposed successive state in the chain consists of switching the positions of a particle and a hole on two randomly selected nearest neighboring sites. After this step, we also select a random site and destroy a particle if it's occupied or create one if it's empty. The simulations were performed at a fixed value of $\mu = V_0$ on a triangular lattice with 2008 sites and lattice spacing a , depicted in the section "Applying the model on the D-Wave's machine". The interaction potential $V(i,j)$ is a positive constant V_0 when i and j are nearest neighbors and, in a subsequent case, also nextnearest neighbors. Simulated annealing was performed by decreasing the effective temperature $T_{\text{eff}} = k_B T / V_0$ from 0.5 to 0.001 in a 100 steps with 1000 MC sweeps at each temperature point. Our system exhibits an ordering phase transition from a high-temperature disordered gaseous phase to a crystalline ordered phase at low temperature. SM Fig. 16 shows snapshots of the simulated annealing process at 4 different values of T_{eff} . The left-most image is far above the phase transition, where the polaronic configuration is essentially random. The next two images toward the right are close above and below the phase transition temperature. The right-most image shows the final state, which is a striped ordered state. This is not the ground state of the model, which is a uniform blue lattice. The reason why we don't observe the ground state is due to the fact that the domain walls cost zero energy in terms of interaction.

However, the energy could be lowered still with the addition of more polarons in the domain walls and thereby decreasing the chemical potential term. When the simulation crosses the phase transition, bubbles of the 3 possible ground state lattices begin to form and inevitably produce domain walls. After their formation they are very hard to get rid of from the point of view of simulated annealing, due to their low energy cost. For example, the final state in SM Fig. 16 has an energy per particle (if $V_0 = 1$) -0.7316 compared to the -0.9895 in the case of the same Hamiltonian being applied to the right-most configuration in SM Fig. 18.

Despite our failure of finding the ground state using MC simulations, it is still important to investigate this specific instance of the Hamiltonian and observe if the rate of polaronic movements $R(T_{\text{eff}})$ can explain the experimentally observed rate. SM Fig. 17 shows the average $R(T_{\text{eff}})$ during the MC simulation. There is an apparent phase transition at $T_c \approx 0.19$ when the slope of the rate changes abruptly. Also, the rate saturates above the phase transition due to the system effectively sampling from random polaronic configurations. It saturates at low T_{eff} due to the system's finding a local minimum from where it cannot escape. There are a few similarities and key differences between the MC simulations, D-Wave simulations and the 1T-TaS₂ experiment:

(i) There is a saturation above the phase transition in both the MC and D-Wave simulations due to melting of the ordered phase and thereby sampling from effectively random configurations. There is no such saturation present in 1T-TaS₂ because the crystalline order is never melted there.

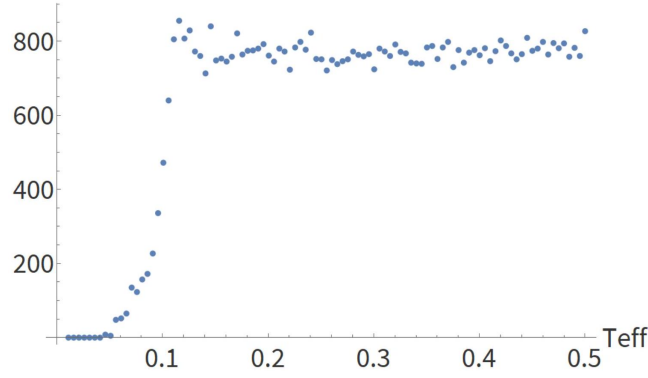
SM Figure 16 | Snapshots of polaronic configurations with nearest neighbor repulsion at different T_{eff} , which increases from right to left as shown on the image.



SM Figure 17 | Average rate of polaronic movements measured during the nearest neighbor repulsion Monte Carlo simulation versus T_{eff} . The phase transition at $T_c \approx 0.19$ is obvious from the sharp change of slope in the rate. There is a saturation of the rate at both high and low T_{eff} .

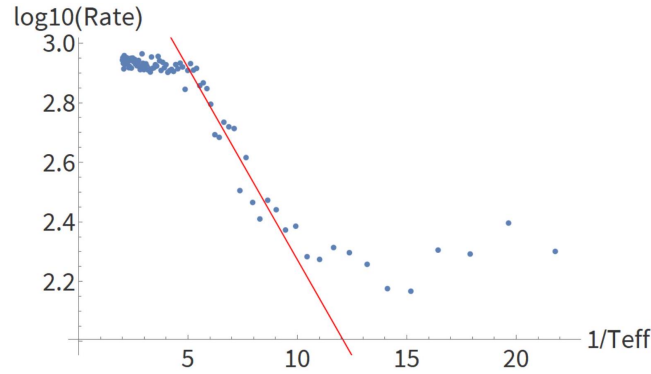
(ii) There is a saturation at low temperatures in all 3 cases, but for very different reasons. In MC simulations it occurs due to the exact zero energy cost of moving a domain wall. This is an artefact of a nearest neighbor repulsion simulation. It is very unlikely that the repulsion in 1TTaS₂ is only nearest neighbor. In fact, previous work has shown that this is not the case^{14,16}. As soon as we turn on next-nearest repulsion with magnitude V_0 , we observe the saturation of the rate to the value 0 as we would expect from classical simulations. SM Figs. 18 and 19 show the polaronic snapshots of such a simulation and its $R(T_{\text{eff}})$, respectively. The saturation in 1T-TaS₂ and D-Wave simulations are of a different origin. They come from incoherent macroscopic quantum tunneling processes, which is discussed in the main text.

SM Figure 18 | Snapshots of polaronic configurations with next-nearest neighbor repulsion at different T_{eff} , which increases from right to left as shown on the image.

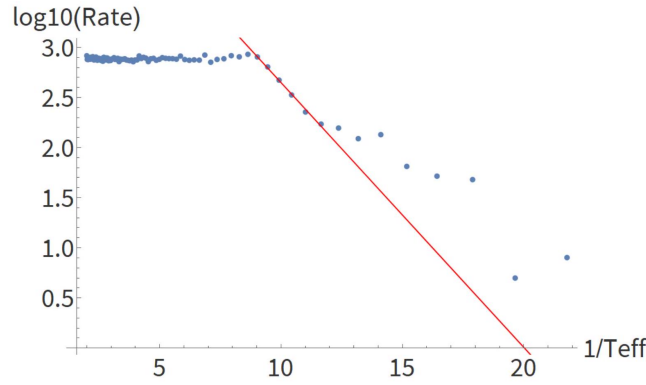


SM Figure 19 | Average rate of polaronic movements measured during the next-nearest neighbor repulsion Monte Carlo simulation versus T_{eff} . The phase transition at $T_c \approx 0.12$ is obvious from the sharp change of slope in the rate. There is a saturation of the rate at both high and low T_{eff} .

(iii) The final difference is in the slope of $R(T)$ below the phase transition. SM Figs. 20 and 21 show the Arrhenius law fit to the average rate in both cases of MC simulations.



SM Figure 20 | Logarithm of the average rate in the nearest neighbor repulsion Monte Carlo simulation versus $1/T_{eff}$. The slope of the red Arrhenius fit shows a dimensionless energy barrier $\frac{E_B^{NN}}{V_0} = 0.3 \pm 0.2$.



SM Figure 21 | Logarithm of the average rate in the next-nearest neighbor repulsion Monte Carlo simulation versus $1/T_{\text{eff}}$. The slope of the red Arrhenius fit shows a dimensionless energy barrier $E_B^{\text{NNN}}/V_0 = 0.6 \pm 0.2$.

The average dimensionless energy barrier is twice as high in the next-nearest neighbor repulsion than in the nearest neighbor case, which is consistent with a stronger repulsion potential. We cannot compare this gap to the experiment because we do not know the energy scale for the

polaronic dynamics a priori. However, we can compare it with D-Wave simulations. We obtain them from plots like the one shown in Fig. 2e shown in main text and SM Fig. 33. The dimensionless gaps are $\delta_{r=1} = 3.5 \pm 0.3$; $\delta_{r=2} = 5.3 \pm 0.9$; $\delta_{r=5} = 7.6 \pm 0.9$; $\delta_{r=10} = 13.8 \pm 0.5$; $\delta_{r=15} = 17.2 \pm 1$, where the subscript denotes the value of r in the simulation. The value increases with r as we would expect when the kinetic energy of polarons is reduced compared to the potential energy. The corresponding MC slope can be found in the region $r < 1$, which is inconsistent from the extrapolated value of $r = 58$ in the main text. Therefore, we cannot compare the results obtained from D-Wave simulations with results from MC simulations, which makes sense as the former is a quantum version of the latter.

In conclusion, we have found that MC simulations are highly inconsistent with experimental observations. The main reason is in the simple fact that a classical rate generally saturates to the value 0 under a certain temperature, and the quantum rate doesn't. We have shown that there is in principle a way for the classical rate to be non-zero for any temperature, but this is only possible in the specific case when the energy cost for movement is exactly 0. This is inconsistent with previous work done on $1\text{ T} - \text{TaS}_2$. We have also shown that the quantum model deployed on D-Wave cannot be reproduced with MC simulations because the phase transition characteristics do not match.

SM: 2.3 WKB Approximation and Macroscopic Quantum Tunneling

(SUMMARY: I still don't understand how WKB is relevant for many body models????? I'll think later. where is this potential there???)

For coherent quantum tunneling, which we do not expect to observe in either system, the WKB rate, for $E_b > k_B T$ is given by:

$$R_q = v \exp\left(-2w\sqrt{2m^*E_b/\hbar^2}\right)$$

where w is the width of the barrier, and m^* is the effective mass of the object. The physical meaning of the attempt frequency v is related to the tunneling of the entire object (domain) of mass m^* from one configuration to another in which all electrons change position by $\sim 0.3\text{ nm}$. v it may be estimated by the energy at which the oscillatory dynamics of a domain patch crosses over from thermally activated to quantum, and the thermal energy becomes comparable to the

energy of a quantum oscillator $k_B T \sim \frac{1}{2} m^* \omega^2 x^2$. The reconfiguration we observe may involve 100 – 1000 polarons, depending on the size of the domains. Taking an individual polaron mass of $m_p \simeq 3m_e$, we may have $m^* \sim 3 \times 10^3 m_e$. For two domains to fuse, the electrons collectively move a distance of approximately elementary crystal one unit cell, $x \simeq 0.3$ nm. At 4K this gives an attempt frequency of $v = \sqrt{\frac{k_B T}{2\pi^2 m^* x^2}} \sim 3 \times 10^{11} s^{-1}$. For comparison, the frequency of oscillation arising from a level spacing E_0 in a system of 1000 electrons trapped within a square well potential $v = \frac{E_0}{\hbar} = \hbar/8mL^2$. For a well width of $L \sim 0.3$ nm, we obtain a similar value of $v \sim 10^{11} s^{-1}$.

With this values of v , assuming a barrier width of 1 nm, and an experimentally determined $E_B = 2\text{meV}$, gives an estimated $R_q \simeq 3 \times 10^{-3} s^{-1}$. The rate estimate is very sensitive to the values in the exponent. However, the reasonable agreement between the experimentally measured $R_q = 2.2 \pm 0.3 \times 10^{-4} s^{-1}$ and the estimated R_q above shows that macroscopic quantum tunnelling between domain configurations is plausible on this timescale for our system with reasonable input parameters. In this estimate we ignore dislocations in the domain structure that topologically hinder relaxation. Such topological defects are an emergent property, which arise from the microscopic interactions that MQT does not describe. We also ignore the effects of pinning of electrons due to crystal lattice imperfections that may reduce the rate of relaxation.

SM: 2.4 Quantum Kramers theory of metastable decay

(SUMMARY: I'll read it later, maybe it is a good theory, but it is not applicable for this material)

A natural model for domain reconfiguration dynamics in 1 T – TaS₂ is a succession of single escapes from local minima in the energy landscape towards the global minimum (ground state), approximated locally by a cubic potential, assuming also some degree of coupling to an external Ohmic bath. Since the experimental $\Gamma(T)$ is averaged over many different escape events at temperature T , we may apply the canonical single particle escape from a cubic potential with Ohmic dissipation in order to estimate its average parameters. This relatively simple model predicts the classical high temperature Arrhenius law as well as the crossover to a temperature independent quantum decay at some crossover temperature T_0 . The former arises from classical thermally activated hopping over the potential barrier E_B and the latter from tunneling events in the presence of dissipation, which exponentially suppresses the tunneling probability. From the experimental crossover temperature $T_0 = 20$ K and crossover temperature range $\Delta T = 10K$, we obtain according to Ref. ²³ the dimensionless Ohmic damping parameter $\alpha = 0.3$ and the ratio of the activation barrier energy over the curvature (energy scale) of the local metastable minimum $\frac{E_B}{\hbar\omega_0} \simeq 0.4 \sim 1.4$, which is inconsistent with the underlying assumption of this model $E_B/\hbar\omega_0 \gg 1$. Therefore, quantum Kramers theory of metastable decay cannot explain the relaxation dynamics observed in 1T-TaS₂.

SM: 2.5 Details on the incoherent macroscopic tunneling of our model

(SUMMARY: this looks like the most relevant part of the SI to understand what is going on?)

Here we make the argument for the mechanism of the decay process in 1 T – TaS₂ being incoherent macroscopic tunneling. We observe in experiment that the system starts off in some non-equilibrium domain state. Afterwards, we observe a reconfiguration event on a timescale of $\sim 10^3 s$, which is separated by a factor of 10^{15} from the timescale obtained from the Arrhenius fit to the experimental rate $\hbar/E_B \sim 1ps$. It follows that the system is stuck in the initial state for a long time before decaying to the next configuration. Therefore, only the local energy levels in the energy spectrum are relevant to the decay, the next level lower in energy from the

initial level being the most important. This is why a local two-level system approximation is appropriate for each observed reconfiguration event. The whole relaxation process can thereby be thought of as a succession of local decays in a two-level system, which is characterized by the tunneling rate $\Gamma_q \sim \Delta^2/W$ (discussed below). This is shown schematically in Fig. 2f. First, we assume a two level system with a bare gap Δ . If we couple such a system to a two-level oscillator bath, the 2 levels will split into 4 and the gap is reduced by $\sim W$. If the number of oscillators tends to ∞ , the 2 levels become bands with width W . In our consideration of both the quantum annealer, as well as 1 T – TaS, we assume a large enough W for the two energy bands to overlap. Therefore, the transitions of the oscillators of the bath are the cause of the incoherent macroscopic tunneling processes we are observing.

Now we investigate the consequences of the conjecture that incoherent macroscopic tunneling is the mechanism responsible for domain reconfiguration dynamics in 1 T – TaS₂, driven by the Hamiltonian $H = H_S + H_I + H_B$, where H_S describes the polaronic system, H_B represents a generic harmonic oscillator bath at temperature T , described by the spectral density $S(\omega)$ and H_I the system-bath interaction. If a two-level system is chosen as an approximation for a single reconfiguration event from a higher to a lower energy level in the full polaronic spectrum, where $H_S = -(\epsilon\sigma^Z + \Delta\sigma^x)/2$, where σ^i are Pauli matrices, ϵ is the bias towards the system being in one of the two levels represented by the 2 values of σ^Z and Δ the matrix element for pure tunneling between the two levels, analytical results are known from literature^{24–28}. According to Amin et al²⁵ we assume $H_I = Q \otimes \sigma^Z$, where Q is described by the bath spectral density $S(\omega) = \int_{-\infty}^{\infty} dt e^{i\omega t} \langle Q(t)Q(0) \rangle$, where $\langle \dots \rangle$ denotes averaging over the bath degrees of freedom, and write their main result $\Gamma_q \sim \Delta^2/W$, where $W^2 = \int \frac{d\omega}{2\pi} S(\omega)$ is the bandwidth of the bath noise. Γ_q is not the exact result of Amin et al; it only represents the scale of the quantum decay rate they obtained for level transitions. If the system is initialized in some nonequilibrium state, the bath will of course drive the system towards its thermal equilibrium at temperature T , but the timescale of these thermally induced transitions is still determined by Γ_q . Transitions occur between different system-bath product states $|S\rangle|B\rangle$ and are characterized by an incoherent tunneling rate $\Gamma_q \sim \Delta^2/W$. For example, in a single transition $|S\rangle$ might stay the same, while $|B\rangle$ undergoes some change, which leads to dephasing or decoherence of the whole system-bath state. This means that it is entirely possible for $|S\rangle$ states to retain coherence and for us to not observe any transitions, even though meanwhile, the bath is dephasing the whole state. On the other hand, $|S\rangle$ might undergo a transition simply due to a transition in $|B\rangle$. This occurs when the two bands corresponding to the two spin states are overlapping, which means that for some energy region, $|S\rangle|B\rangle$ states are separated by the energy gaps between $|B\rangle$ states and not Δ . The rate for such transitions is Γ_q . According to the aforementioned equivalence assumption that 1 T – TaS₂(M) and the quantum annealer (P) are both governed by the same H , and the fact that we are able to reproduce the saturation of $R(T)$ in M with P, meanwhile observing similar reconfiguration processes in P as in M, we argue that the perturbation theory developed for P is also applicable to M.

Now we apply the developed perturbation theory to our experiment and simulations, which takes the system's energy landscape into account through considering the entire energy spectrum system and focusing on the transitions between different energy levels (Fig. 2f). We assume that when the STM tip measures a polaronic configuration, it measures the occupation number $\langle \psi_M | n_i | \psi_M \rangle$ for every atomic site i and is insensitive to the bath degrees of freedom, which represent the noise of the system. The unperturbed Hamiltonian (when the STM tip is present) is therefore the potential energy between polarons, the coupling to the bath, and the bath ($B(s)H_z + H_I + H_B$), because they only contain n_i and bath operators. The unperturbed energy spectrum contains all the possible polaronic configurations ranked by potential energy,

which are broadened into bands by the bath. Of course, a single STM measurement forces the system into one specific polaronic configuration, where the bath degrees of freedom remain unspecified. This means that the whole polaron-bath system can lie anywhere on one of the polaronic energy spectrum bands, where the bath degrees of freedom change across the band, but the polaronic configuration is the same. The perturbation is the kinetic energy of polarons ($A(s)H_x$), which is always present but only contributes significantly when the STM is removed or turned off. Since the time-scale τ_M for relaxation is so large compared to t_M , the probability for transitioning to another configurational state is $\ll 1$, thus justifying the perturbation theory approach.

The gap $\Delta = g(H)E$ is characterized by the overall energy scale of the system E , where $g(H)$ is now the dimensionless gap, which typically depends exponentially on the Hamiltonian parameters^{29,30}. (why this formula is such?)

The energy scale of P, $E_P = 1.6 \pm 0.8 \mu\text{V}$, governing the low temperature relaxation dynamics of system P is set by the magnetic fields operating on the SQUIDS serving as qubits on the QPU³¹, while $E_M = 3 \pm 0.4\text{meV}$ was measured in the STM experiment.

We also know from previous literature^{32,33} that the spectral density of noise in both M and P is well described as $1/\nu$ noise at low frequencies, which we assume is the dominant effect of noise in both cases.

In order to make the connection from the fundamental time-scale to quantum incoherent relaxation, we rewrite $\Gamma_q = \frac{\Delta^2}{W} = g(H)^2 \frac{E}{W} E$ in terms of the energy scale, as well as the measured time-scale $\tau_M \approx 1000s \approx 10^{15}t_0^M$, where $t_0^M = \frac{\hbar}{E_M} \approx 2ps$.

If $\Gamma = 1/\tau$, then $\Gamma_M = 10^{-15}E_M/\hbar \sim 10^{-15}E_M$.

The 15 orders of magnitude difference is therefore explained by the quantity $g(H)^2 \frac{E_M}{W_M} = 10^{-15}$. In order to estimate the ratio $\frac{E_M}{W_M}$ in system M, we turn to the definition $W^2 = \int \frac{d\omega}{2\pi} S(\omega)$ (see²⁷) (why there is such a def.???) and turn to measurements of low-frequency voltage fluctuations³², which suggest that we can approximate the spectral density of the external bath of M with $1/\nu$ behavior as $S_M(\omega) = \frac{2.6 \cdot 10^{-8} e^2 V^2}{\frac{\omega}{2\pi} + 0.34 \text{ Hz}}$.

Integrating in the range of 3 – 100 Hz returns a value of $W_M \approx 0.3\text{meV}$.

Therefore, $\frac{E_M}{W_M} \approx 10$, which leads to $g(H) \sim 10^{-8}$, which in turn leads to a gap $\Delta_M \sim 10\text{peV}$ between different polaronic configurational states.

If we take the value of W_P from literature³³ and calculate $\frac{E_P}{W_P} \approx 10$, we obtain a similar value as $\frac{E_M}{W_M}$.

If we combine the same $1/\nu$ shape of the noise spectrum in both P and M with a similar quantitative value of energy scale to noise bandwidth ratio, we can conclude that the influence of noise is the same in P and M.

7.2.3 3 SM Notes 3

In order to simulate quantum melting of domains we need to first be able to map our model on to an actual D-Wave machine. In this paper we use the newly released Advantage6.1 quantum computer with 5436 physical qubits. In this chapter we present all the necessary steps required for a successful deployment of our model.

SM: 3.1 Applying the model on D-Wave's machine

The Hamiltonian that is simulated by the D-Wave machine takes the form of the transverse field Ising model

$$H_{DW} = -\frac{A(t)}{2} \sum_i \sigma_i^x + \frac{B(t)}{2} \left(\sum_{i < j} J_{i,j} \sigma_i^z \sigma_j^z + \sum_i h_i \sigma_i^z \right), \quad (11)$$

where $\sigma_i^{x,z}$ are Pauli matrices operating on a qubit q_i , $J_{i,j}$ are couplings between qubits q_i and q_j and h_i are the longitudinal external fields at q_i . The maximum value that $A(t)$ and $B(t)$ take is about 10 hGHz³⁴. The parameter t has a range of $[0, t_a]$ and plays the role of time, where t_a is the annealing time with a maximum available value of $2000\mu s$. The forms of $A(s)$ and $B(s)$ will be addressed in the next subsection.

In order to map our model onto $\tilde{H}$, we need to apply the transformation from spin to qubit variables $\sigma_i^z = 2q_i - 1$. We can directly map the simplified version of our model H_{int} onto the second term of H by setting $h_i = \sum_{j=i}^N Q_{i,j}/2$ and $J_{i,j} = Q_{i,j}/4$. Since our model takes place on a two-dimensional lattice, it is therefore equivalent to an extended two-dimensional transverse field Ising model.

The next step in deploying the model is embedding it on the D-Wave machine's architecture. Here we need to assess the connectivity graph between our logical qubits (q_i in H_{int}) G and the actual connectivity graph between physical qubits on the machine G' . If G is not a subgraph of G' then we need to do a process called minor-embedding. We impose additional constraints between certain physical qubits by setting the couplings between them to the maximum possible ferromagnetic value ($J = -1$, for example) and link them in a chain. This setup forces all the physical qubits in a chain to assume the same value. Each chain then represents a single logical qubit. This process allows us to connect a logical qubits to more logical qubits than the connectivity of G' would allow us to if we just used one physical qubit to represent a single logical qubit. In practice due to quench dynamics as well as temperature and other noise effects, chains sometimes break. This means that when physical qubits in a chain are measured, they do not all have the same value. A D-Wave machine outputs information regarding broken chains in the form of the chain break fraction, which is simply the number of broken chains divided by the number of all chains.

In order to embed a triangular lattice with only nearest neighbor interactions onto the D-Wave Advantage processor, we first turn to the notation of physical qubits (PQs) used by Boothby et al³⁵. By taking $M(= 16)$ as the parameter for the actual machine, we can parametrize the coordinates of a qubit on the physical quantum processing unit (QPU) as (u, w, z, k) , where the index of the qubit available to the user is calculated by using $z + (M - 1)(k + 12(w + Mu))$. Dattani et al³⁶ developed a more intuitive qubit coordinate representation defined by $(x_D, y_D, z_D, i_D, j_D, k_D)$ with the mapping

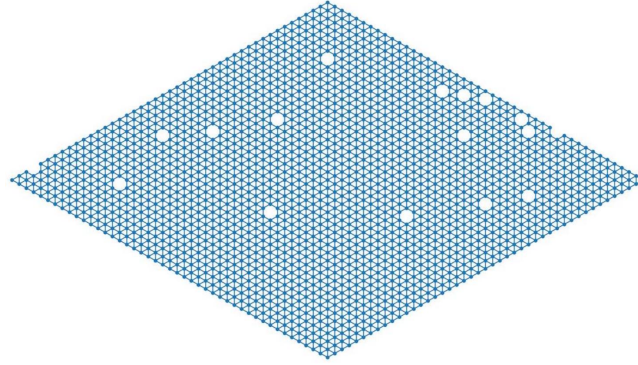
$$(u, w, z, k) = \left(i_D, (1 - i_D) x_D + i_D(M - 1 - y_D), (1 - i_D) \right. \\ \left. (M - 2 - y_D + \delta_{z_D,0}) + i_D(x_D - \delta_{z_D,0}), k_D + 2j_D + 4z_D(1 - 2i_D) + 8i_D \right). \quad (7.1)$$

We obtain a triangular lattice by assigning a logical qubit (LQ) to either 1 or 2 physical qubits according to

$$\begin{aligned} (-3y_D, 3x_D + 3y_D)_{LQ} &= [(x_D, y_D, 0, 0, 0, 0)]_{PQ} \\ (-3y_D + 1, 3x_D + 3y_D)_{LQ} &= [(x_D, y_D, 0, 1, 1, 1)]_{PQ} \\ (-3y_D, 3x_D + 3y_D + 1)_{LQ} &= [(x_D, y_D, 0, 1, 0, 0), (x_D, y_D, 0, 0, 1, 1)]_{PQ} \\ (-3y_D - 1, 3x_D + 3y_D + 2)_{LQ} &= [(x_D, y_D, 1, 0, 0, 0)]_{PQ} \\ (-3y_D, 3x_D + 3y_D + 2)_{LQ} &= [(x_D, y_D, 1, 1, 1, 1)]_{PQ} \\ (-3y_D - 1, 3x_D + 3y_D + 3)_{LQ} &= [(x_D, y_D, 1, 1, 0, 0), (x_D, y_D, 1, 0, 1, 1)]_{PQ} \end{aligned} \quad (12)$$

$$\begin{aligned}
(-3y_D - 2, 3x_D + 3y_D + 4)_{LQ} &= [(x_D, y_D, 2, 0, 0, 0)]_{PQ} \\
(-3y_D - 1, 3x_D + 3y_D + 4)_{LQ} &= [(x_D, y_D, 2, 1, 1, 1)]_{PQ} \\
(-3y_D - 2, 3x_D + 3y_D + 5)_{LQ} &= [(x_D, y_D, 2, 1, 0, 0), (x_D, y_D, 2, 0, 1, 1)]_{PQ},
\end{aligned}$$

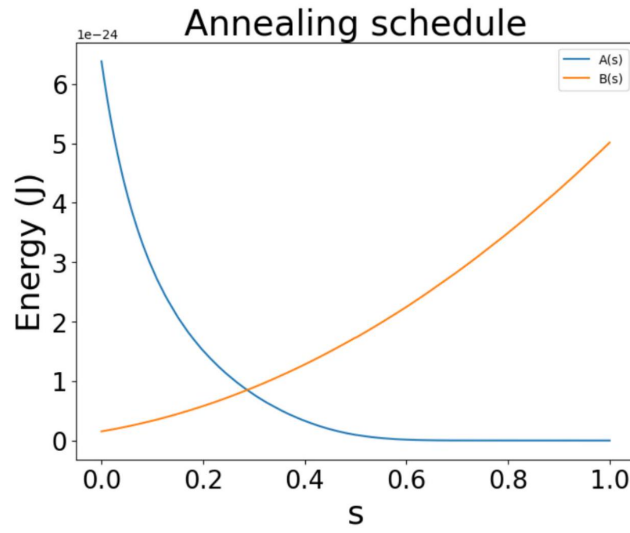
where $x_D \in [0, M - 1]$ and $y_D \in [0, M - 1]$. For the actual Python code, we employed for calculating the embedding, see our GitHub ³⁷. The maximum size of the triangular lattice we are able to currently embed on the actual QPU includes 2008 logical qubits, which consist of 2673 physical qubits. During our calculations on the actual QPU, there were 17 unavailable logical qubits, which reduced our lattice size from 2025 to 2008 sites. SM Fig. 22 shows the triangular lattice used in our calculations.



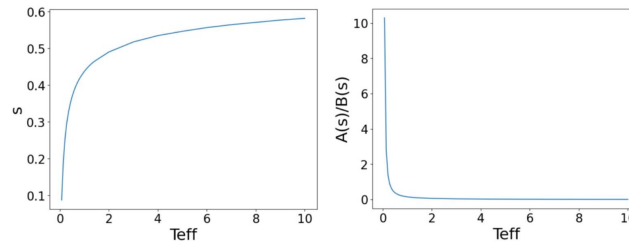
SM Figure 22 | Triangular lattice consisting of 2008 sites with nearest neighbor interactions used in our calculations. (why there are holes here?)

SM: 3.2 Introducing quantum dynamics by reverse annealing

In order to successfully model the experiment presented in this paper we needed to somehow introduce quantum dynamics into the system. We employed a feature provided by D-Wave called reverse annealing, where we can specify the annealing schedule. The time dependent functions $A(s(t))$ and $B(s(t))$ are both specified with a single function $s(t)$. We can then specify up to 12 points $[t, s(t)]$ in the range $[0, t_a] \times [0, 1]$ from which D-Wave's Ocean TM software interpolates a polynomial for $s(t)$. We start off in the classical state ($s(0) = 1$), which is predetermined by us. We then reduce the value of $s(t)$ to $s_{\min}$ and bring it back up to 1 in t_a amount of time. In our simulations, we specified three points for the annealing schedule $(0, 1), (t_a/2, s_{\min}), (t_a, 1)$. The idea behind using this kind of schedule is to bring the system into a quantum superposition of different domain states close enough in energy so that a tunneling event between them becomes possible on the time scale used in our simulations. SM Fig. 23 shows the predetermined annealing schedule used by the D-Wave Advantage6.1 used in our calculations. The temperature of the physical quantum processor was fixed to $T_{DW} = 16 \pm 0.1\text{mK}$. SM Fig. 24 shows the typical range of $s(t), T_{\text{eff}} = k_B T_{DW}/A(s)$ and $A(s)/B(s)$ we used.



SM Figure 23 | Predetermined annealing schedule used in our calculations.

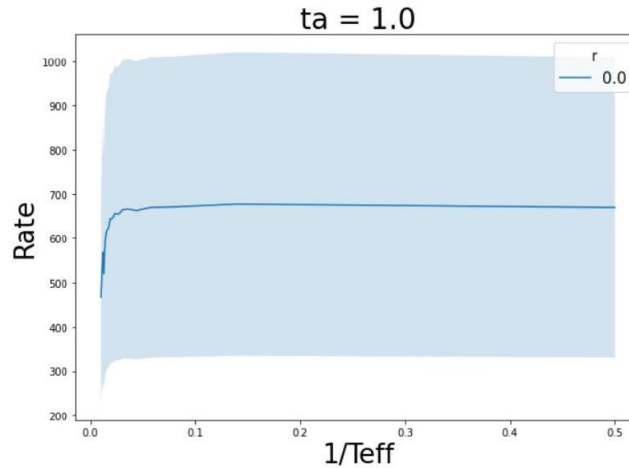


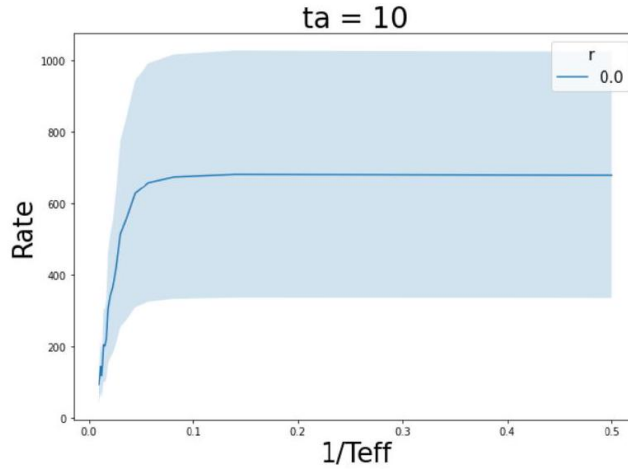
SM Figure 24 | On the left, the dependence $T_{\text{eff}}(s)$ shown in the typical range used in our calculations. On the right, $\frac{1}{r} = A(s)/B(s)$ also shown in the typical range.

7.2.4 4 SM Notes 4

SM: 4.1 Limitations by the annealer on the parameter space

After defining the parameters of our Hamiltonian under study $T_{\text{eff}} = k_B T_{DW}/A(s)$ and $r = JB(s)/A(s)$, we performed two experiments in order to ascertain the limitations on our parameter space. The first was designed in order to find the T_{eff} range in which we can operate. SM Fig. 25 shows the dependence of the rate $R(T_{\text{eff}})$ as defined in the main text.



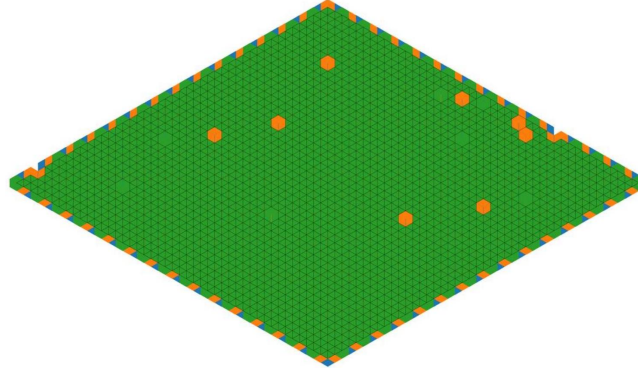


SM Figure 25 | $R(T_{\text{eff}})$ dependence at $r = 0$, where a constant rate is expected shown for different annealing times $t_a = 1, 10\mu$ s. The shaded area shows the standard deviation when averaging over 1000 experiments.

We studied the value of $r = 0$, which is in the limit for which we know exactly what to expect. Since only the kinetic energy term is present with no interaction between polarons, we should effectively sample from random spatial configurations and the rate should therefore be temperature independent. This is exactly the case for $T_{\text{eff}} \in [2, 10]$ as shown in SM Fig. 25. For $T_{\text{eff}} > 10$ there is a sharp drop off of the rate, which is simply due to the fact of s_{min} becoming large enough for $A(s_{\text{min}})$ to be small enough not to be able to drive single qubit dynamics in the system within our measurement time scale. Simulations are therefore useless in this regime. On the other hand, the smallest T_{eff} at a certain value of r is set by the value of s and $J = 1$. In other words, at every $T_{\text{eff}}(s)$ we can tune r from $B(s)/A(s)$ to 0 by tuning J from 1 to 0, which is the allowed range on a D-Wave machine. The smallest possible non-zero r with $J = 1$ is $\frac{B(0)}{A(0)} \approx 0.0241$, which leads to a smallest $T_{\text{eff}}(0) \approx 0.0346$. When s increases from 0 to 1, $A(s \rightarrow 1) \rightarrow 0$, then $r \rightarrow \infty$ and $T_{\text{eff}} \rightarrow \infty$, but we have already found the upper limit of s above. We chose to investigate the range $\frac{B(s)}{A(s)} \in [0.1, 90]$, which leads to a temperature range $[0.14, 10]$ at $r = 0.1$ and $[10, 10]$ at $r = 90$, thereby covering the whole parameter space currently available on the annealer.

SM: 4.2 Phase diagram calculation details

We calculated the phase diagram by sampling $\beta H_S = \frac{1}{T_{\text{eff}}}(-H_x + rH_z)$, where $r = [0.0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1.0, 1.1, 1.2, 1.3, 1.4, 1.5, 1.6, 1.7, 1.8, 1.9, 2.0, 3.0, 4.0, 5.0, 6.0, 7.0, 8.0, 9.0, 10.0, 20.0, 30.0, 40.0, 50.0, 60.0, 70.0, 80.0, 90.0, 100.0]$ and $T_{\text{eff}} = [0.07, 0.14, 0.21, 0.28, 0.35, 0.42, 0.49, 0.56, 0.63, 0.7, 0.77, 0.84, 0.91, 0.98, 1.05, 1.12, 1.19, 1.26, 1.33, 1.4, 2, 3, 4, 5, 6, 7, 8, 9, 10]$. The initial state was a fully occupied lattice, as shown in SM Fig. 26.

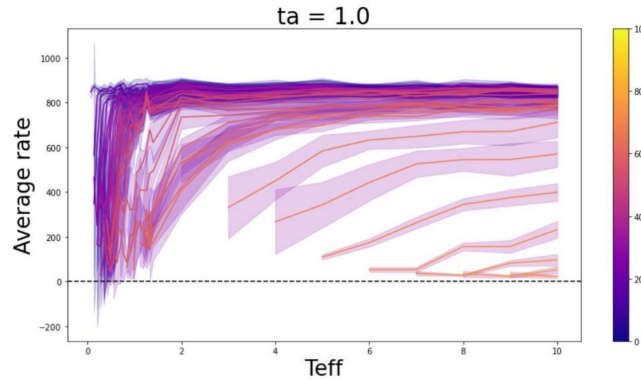


SM Figure 26 | Fully occupied triangular lattice of polarons, used as the initial state for phase diagram calculations.

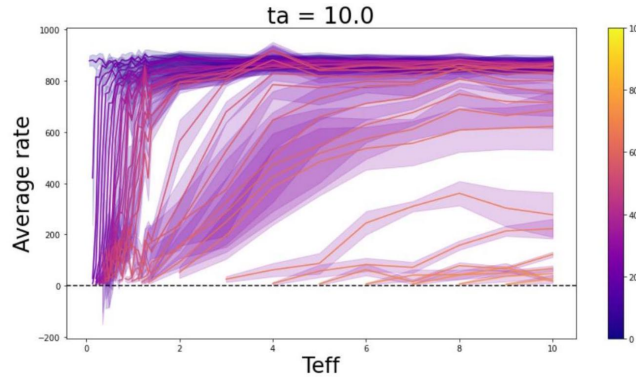
The interaction in QUBO language was set to $Q_{i,j} = 4$ for nearest neighbors and to $Q_{i,i} = -4$ for self-interaction. We then scaled $Q_{i,j}$ appropriately with J . We performed the reverse annealing protocol described previously 50 times, where the input state for the next iteration was the output of the previous. SM Figs. 27 and 28 show the measured average rate of all the iterations for two annealing times $t_a = 1, 10\mu s$.

In both cases we observe the phase transition from low-temperature ordering processes, which reduce the rate close to 0, to high temperature dynamics, where the system effectively samples from random distributions of polarons. This is why the rate saturates to a plateau, which is also the case at $r = 0$, where the system samples from random states at all temperatures. The main difference between $t_a = 1\mu s$ and $t_a = 10\mu s$ dynamics is in the low temperature ordering processes. In the former, the system typically does not order like in the latter case. While it is clear from configuration snapshots that at $t_a = 1\mu s$ the system samples the same kind of low energy states as in the $t_a = 10\mu s$ case, the latter case remains in the ground state or close by in energy. On the other hand, the former case is driven continuously from the ground state into

some excited state with domain walls. We conjecture that due to a fast enough annealing schedule, diabatic processes are responsible for transitions into higher energy states. This is not something we observed in 1T-TaS₂ experiments, which is why we decided not to focus on diabatic processes, but on the stable relaxation toward the ground state. Both plots also nicely show how the transition temperature increases when r increases.



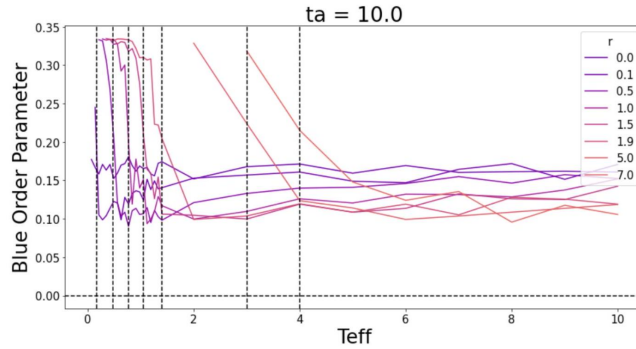
SM Figure 27 | Average rate of polaronic movement versus T_{eff} for $t_a = 1\mu s$. The shaded area shows the standard deviation when averaging over 1000 experiments.



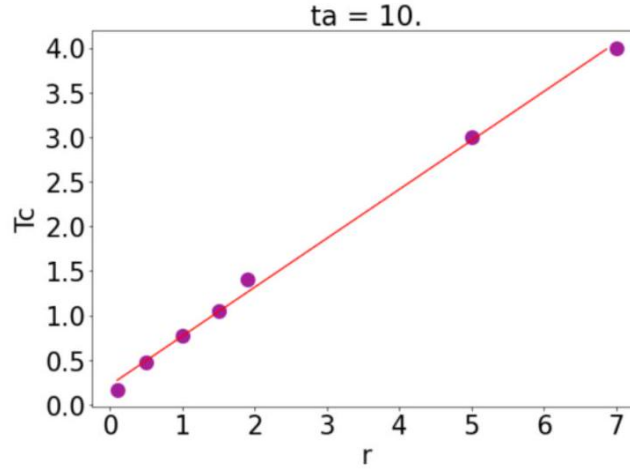
SM Figure 28 | Average rate of polaronic movement versus T_{eff} for $t_a = 10\mu$ s. The shaded area shows the standard deviation when averaging over 1000 experiments.

The transition temperature was measured by using the "blue order parameter", which is defined as the fraction of polarons in the positions of the blue colored $1/3$ triangular lattice as drawn in Fig. 2a of the main text. This turns out to be the ground state for the particular realization of our model on the D-Wave machine, separated by a very small energy difference from the orange and green ground states. For an ideal system, there is no difference between the 3 ground states. Therefore, if the blue order parameter grows to $1/3$, the system is in the ordered phase, and is significantly less in the gaseous phase where these blue lattice sites are occupied randomly.

SM Fig. 29 shows the blue order parameter dependence on T_{eff} , with the vertical dashed lines representing our determined transition temperature for a specific r . The chosen transition temperatures were plotted versus r and a linear fit was done in order to extrapolate the transition temperature at higher values of r as shown in SM Fig. 30. See main text for the discussion.



SM Figure 29 | Blue order parameter versus T_{eff} for $t_a = 10\mu$ s. The legend in the top right corner shows the values of r for which we measured the transition temperature from the low temperature ordered phase, to the high temperature gaseous phase. The vertical dashed lines show our choice of the transition temperatures by hand. The horizontal dashed black line is a guide to the eye for the value 0 of the blue order parameter.



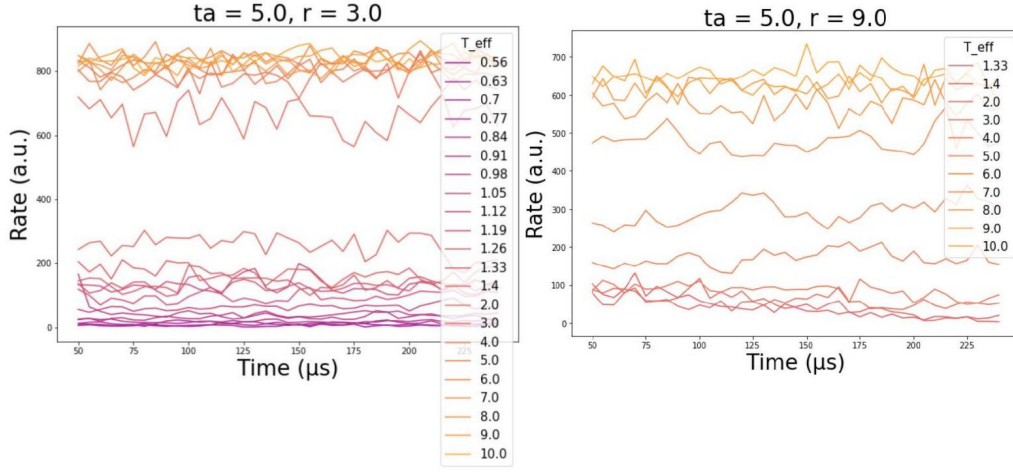
SM Figure 30 | Transition temperature T_c dependence on r and a linear fit to the data $T_c = 0.55r + 0.22(1 \pm 5\%)$.

SM: 4.3 Relaxation measurements

In order to simulate the experiment on D-Wave's quantum computer, we first initialized a triangular lattice with 2008 sites in a domain state of a $1/3$ filled polaronic lattice shown in Fig. 2c (leftmost) and then performed a series of 50 reverse anneals. The initial domain state was obtained by a single reverse anneal from a fully occupied classical state at a high value of r . The output of the measured state after one reverse anneal was used as the input for the next. This procedure serves as an analogue to the actual real-world experiment in 1T-TaS₂. The initial polaronic configuration is also in a domain state of a $1/3$ filled polaronic lattice. We have

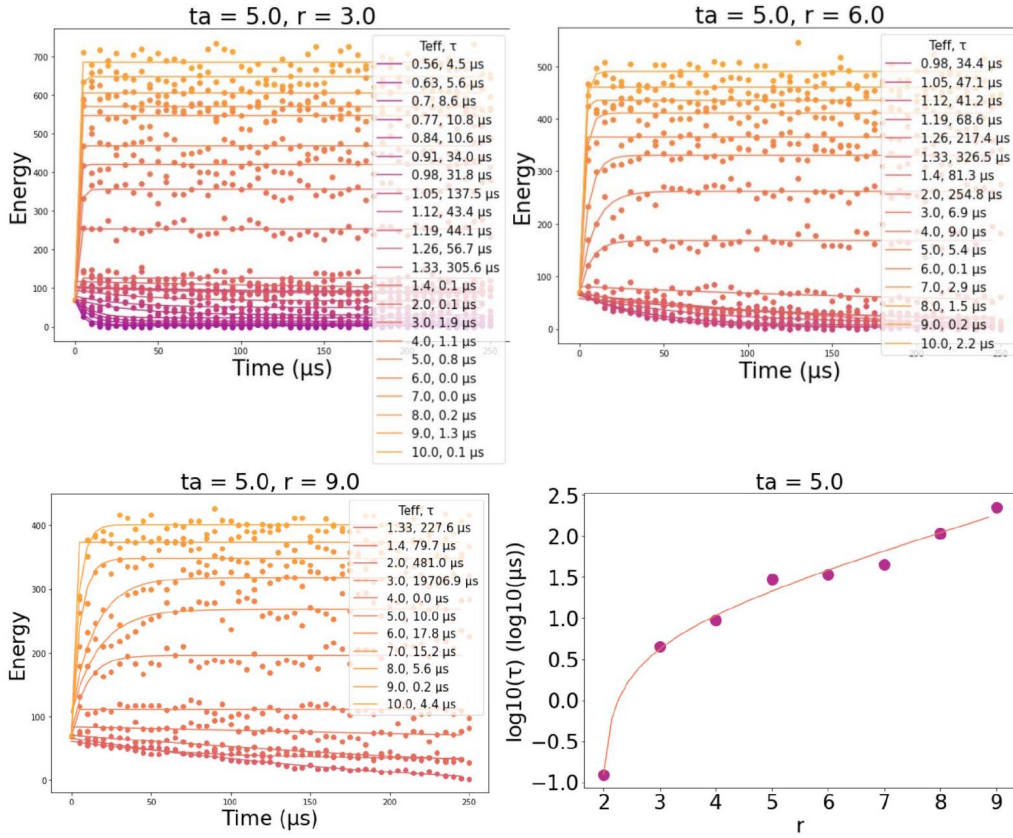
shown already in Ref. ¹⁶ that the behavior of polaronic lattices with different fillings is qualitatively the same. The initial domain state is then scanned with a scanning tunneling microscope (STM) sequentially in time and a relaxation to the $1/3$ ground state is observed after some time. The reverse annealing process on the D-Wave machine as performed in our case simulates what happens between two sequential scans. We therefore assume that the STM scan acts as a quantum measurement on a quantum state and collapses the wave function into a state in the classical number operator basis (n_i).

However, the true Hamiltonian of the system is quantum in the sense that a state in the number operator basis is not its eigenstate. In our simulations on D-Wave's machine the true quantum Hamiltonian is limited to the two-dimensional extended transverse field Ising model due to the physical architecture of the machine as described before. H_{int} , which represents charged classical polarons in our model of 1T-TaS₂, can be mapped from the number operator (n_i) basis to the spin basis (σ_i^Z). The transverse field term (σ_i^X) therefore introduces non-trivial quantum effects such as tunneling between different configurations of qubits (polarons). However, we would like to point out that the transverse field in our case serves only as a means of introducing non-trivial quantum dynamics and we conjecture that the system would behave similarly with other forms of non-commuting terms added to H_{int} . Investigating this conjecture is out of the scope of this paper. SM Fig. 31 shows typical rate dependence on time, which is just the index of the reverse annealing iterations multiplied by the t_a is which it was performed.



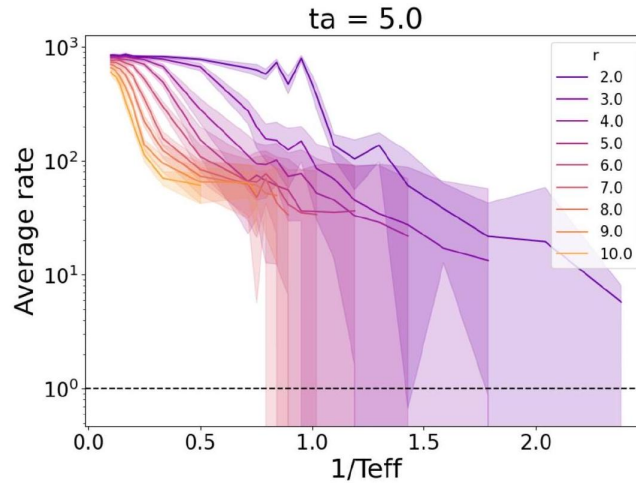
SM Figure 31 | Rate as measured after every reverse annealing iteration vs time in the case of $r = 3$ (left) and $r = 9$ (right). Both datasets were obtained with $t_a = 5\mu s$.

There is a clear distinction between the low-temperature ordering dynamics and hightemperature random reconfigurations. It is also clear how the rate saturates to 0 at the lowest temperatures, because the system has reached the ground state as well as in the case of the highest temperatures, because the rate between two random configurations is on average the same. The $r = 9$ case shows a much slower rate relaxation as the $r = 3$ case at low T_{eff} , meaning that the system requires more reverse annealing iterations and hence more time in order to reach the ground state. This is due to the sufficiently large gap between states during the reverse annealing process, which suppresses the rate. This suppression of relaxation can best be seen in SM Fig. 32, which shows the energy measured at the end of each reverse anneal versus time as well as the exponential fits made to it and the extracted relaxation times dependence on r . The dependence is $\tau(r) = A * \exp\left(\frac{r}{r_0}\right) + B$, where $A = 2.6 \pm 1.2$, $B = 6.6 \pm 2.2$ and $r_0 = 2.1 \pm 0.3$.

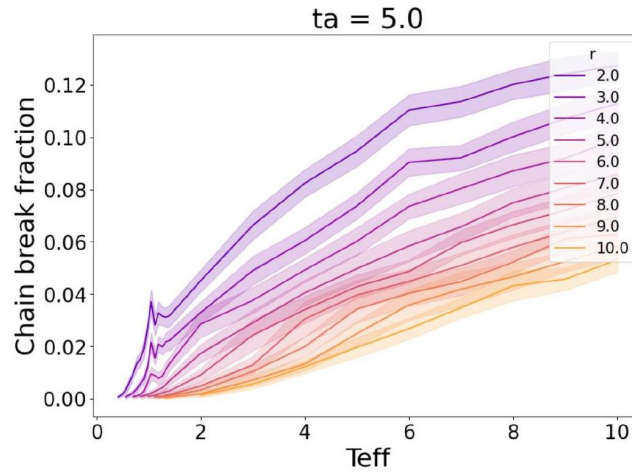


SM Figure 32 | Energy measured after every reverse annealing iteration vs time in the case of $r = 3$, $r = 6$ and $r = 9$. All datasets were obtained with $t_a = 5\mu$ s. The bottom right plot shows the $\tau(r)$ dependence, extracted from exponential fits in the other 3 plots in the figure, and its exponential fit (given in corresponding text).

The average rates at values of r other than the one presented in the main text are shown in SM Fig. 33. At high T_{eff} , all rates saturate to the same value, determined by the average rate between two random configurations. At higher values of r , the rate saturates at low T_{eff} due to the system not yet reaching the ground state within the time window of our simulation. However, for lower values of r , the average rate tends more towards 0, which is inconsistent with our experimental observations. We emphasize here that if the time window of our simulation, or in the actual experiment would be long enough so that the system reaches the ground state, then the average rate would always be 0. The reason why it is not 0 in any case is simply due to the fact that the system has not yet reached the ground state. This is the reason we chose the value of $r \geq 9$ in the main text, as it most closely resembles the experimental plot of $R(T)$. The actual values of r and T_{eff} which correspond to sufficiently slow relaxation events have to be extrapolated from the fit in SM Fig. 32. There is also an outlier feature shown in SM Fig. 33 at $r = 2$, which we would like to point out. These features do occur sometimes and are the result of the system switching from relaxing into the "orange" ground state to relaxing into the "blue". The system is predominantly ordered according to the orange ground state and then tunnels into the blue ground state, suggesting a non-zero tunneling matrix element between these two states. This has no bearing on our results, but is a possible avenue for future work.



SM Figure 33 | Average rate versus T_{eff} for different values of r listed in the top right legend. The shaded area shows the standard deviation when averaging over 1000 experiments.



SM Figure 34 | Average chain break fraction versus T_{eff} for different values of r listed in the top right legend. The shaded area shows the standard deviation when averaging over 1000 experiments.

There is an important quantity to study within the scope of our simulation, in order to check whether we are not introducing any artefacts into the simulation. The chain break fraction (CBF) is defined as the ratio of the number of broken chains and the number of logical qubits in the system. A broken chain is a logical qubit comprised of more than 1 physical qubit, where

the physical qubits are not all measured to be the same value. For more details, see section "Applying the model on the D-Wave's machine". In our embedding of the problem on the DWave machine, we use 665 out of 2008 logical qubits as chains of 2 physical qubits, which means that the maximum fraction of faulty qubits is 0.331. SM Fig. 34 shows the average CBF for the cases shown in SM Fig. 33. It does reach substantial values at higher T_{eff} , but it does not come close to the maximum value of 1. For low T_{eff} dynamics it is even heavily suppressed, which is why we are confident in the validity of the physics presented in this work.

Finally, we also determine the parameters for H , which reproduce this 15 orders of magnitude separation in time-scales by repeating the same consideration also for P. From P we obtain $\tau_P \approx 1 - 200 \mu\text{s}$. In order to reach the same timescales as in M we estimate $r \sim 58$, which leads to a saturation of the rate at temperatures $T_{\text{eff}} \lesssim 32$ according to exponential fit extrapolation done in SM Fig. 32 and SM Fig. 30, respectively.

7.3 My Discussion

7.3.1 Reviewer Comments and answers to them

Reviewer # 1

In this manuscript, Jaka Vodeb et al. report a combined study of STM and quantum simulations about the time-evolution of the domain reconfiguration in 1T-TaS₂. The authors first prepare the domain structure in 1T-TaS₂ by the electrical pulse charge injection through STM tip. They record the domain structure periodically by STM and analyze the Hamming distance as a function of time. The authors further use the programmable noisy superconducting quantum simulator to simulate the reconfiguration dynamics. I am not convinced that simulating the domain reconfiguration dynamics in 1T-TaS₂ is important. I think this manuscript does not meet the high standard of Nature Communications. I do not recommend the publication of this manuscript in Nature Communications. Below are my detailed comments.

Author's response (AR): We thank the reviewer for his/her comments. We regret that the reviewer was not convinced of the importance of the simulations. In our response (and the didactically revised manuscript) we shall try and convince him/her otherwise. We also thank the reviewer for the detailed comments, which do not raise any major issues, and to which we respond below.

We first respond to the general statement of importance. (We note that in this regard the reviewer's opinion differs from the other reviewers.)

Simulations of low-temperature decay processes in 1T-TaS₂ are of interest for two main reasons:

- (1) for understanding the fundamental dynamics of a prototypical many-body quantum system with strong many-body correlations that displays topologically inhibited selforganized domain dynamics in 2D, and
- (2) for understanding the mechanisms that limit the performance of non-volatile charge configuration memristor devices based on 1T-TaS₂ (refs. 10,41,42) which display record speed and energy efficiency (ref. 10).

The domain reconfiguration is responsible for metastability, where topological effects inhibit classical dynamics (ref. 42) and quantum effects are those that are responsible for relaxation of the persistent state at low temperatures below 20K.

More generally, quantum simulation is an important contemporary field of study, which was recently demonstrated (also by this work) to be useful for addressing the problem of dynamics in open quantum systems, and noise-induced quantum dynamics in particular, which are beyond the reach of classical computers.

The processes that take place in 1T-TaS₂ are an excellent prototypical example for demonstrating and simulating emergent quantum decay with parallel experiment and simulation.

In summary, quantum simulations are a transformative tool, which we demonstrate here as a solution to problems that surpass the capabilities of classical computers. From the practical viewpoint, we address an extremely important problem: origins of the decay of the non-volatile state in an ultraefficient memory device.

In the revised manuscript we have highlighted why simulations of domain dynamics are important.

Response (1) What is the time interval for taking the STM topographies in Fig. 1c? Are the STM topographies in Fig. 1c taken on the same area?

AR: We thank the reviewer for pointing out the omission. (The information is implicitly given in Fig. 1 d, and also in the SI, but not explicitly stated in the main text, for which we apologise.) The images are of the same area. The time interval between images is 8 minutes.

(2) Since the author also report the temperature-dependent reconfiguration dynamics, in the

main text, they should also show similar series of STM topographies as in Fig. 1c, but measured at different experimental temperatures.

AR: In fact, this is how Fig.1e is obtained: by measuring the reconfiguration dynamics rates at different temperatures. Hundreds of such images were recorded at different temperatures. The actual series of images at different temperatures could be included, but this would require a presentation of more than 100 images, which we judged to be impractical. We considered that the one example shown in Fig.1c is sufficient to present the concept, and some more pertinent examples are given in the SI. Perhaps the editor might suggest how to resolve this presentation issue.

(3) For the fixed temperature, does the reconfiguration rate change for different areas?

AR: Indeed, the reconfiguration rate depends somewhat on the position. That's why in the supplementary information, in Fig.S10, at any given temperature, we have many different measurements in each interval. In the main text we show the average.

(4) In comparison with Fig. 1e, there are only a few data points in Fig. 1f. In order to make better comparison, the authors should measure more data points with the STM tip retracted.

AR: The purpose of the procedure of measurement with the tip retracted is to ascertain that the system is not affected by the presence of the measurement. It is not possible to add points if the tip is retracted. That is the point of the procedure.

We believe that the presented measurements unambiguously show that the tip does not significantly influence the rate of reconfiguration. This is confirmed by other controls and checks given in the SI.

(5) The authors perform the experiment with STM tip retracted to confirm that the noise in M does not originate from the STM tip. But it could originate from the electric field of the STM tip, because the electric field is long ranged. The authors should try to retract the tip, and reduce the bias voltage at the same time.

AR: In contact mode used for obtaining images, assuming a tip-to-sample distance of typically $\sim 300\text{pm}$, so the electric field is $\sim 3 \times 10^8 \text{ V/cm}$. When the tip is retracted to $50 \text{ }\mu\text{m}$, the field is $\sim 200 \text{ V/cm}$. The difference is a factor of $\sim 10^6$. We conclude that if there is an electric field effect, then the 10^6 difference in field should have an effect in the rate, but we see that changing the field from $3 \times 10^8 \text{ V/cm}$ to 200 V/cm has no measurable effect on the relaxation rate. We conclude that the electric field cannot be responsible for the relaxation.

(6) Why the authors do not fit the last data point in Fig. 2g?

AR: The quantum hardware used to perform our quantum simulations does not allow us to sample from arbitrarily low temperatures. See next point for further clarification.

(7) Since there are several parameters in the simulation, I am not surprised to see that the authors can more or less fit the reconfiguration rate. The authors should provide stronger evidence that their quantum simulation is indeed applicable to the domain reconfiguration dynamics in 1TTaS2.

AR: The comment from the reviewer suggests that they believe we are experiencing an overfitting problem in our quantum simulation of the experiment. Since we cannot know for certain how the reviewer came to this conclusion, we assume that they misinterpreted the definition of our Hamiltonian used to describe the system of polarons in 1T-TaS2. We assume that they understood that we fit all of the qubit couplers J_{ij} and qubit biases h_i to the experimentally obtained curve, which would give a valid concern for overfitting. However, as is stated in the

main text, we map all of these parameters to a physical model of two-dimensional polarons with nearest neighbour repulsion. This automatically fixes all J_{ij} and h_i such that precisely this model is realized on the quantum simulator. The only TWO parameters that we are left with are the effective temperature of the system and the ratio $r = A/B$ of kinetic and potential energy amplitudes. The simulated curve is therefore not a simple fit to the data, but rather an emergent behaviour of the system, which coincides nicely with the data for only one value of $r = 58$ as explained in the paper. We further clarify and emphasize this point in the revised text.

Reviewer # 2

The manuscript by Vodeb et al. reports a joint experimental and theoretical work on the relaxation dynamics of macroscopic domains in a 2d electronic crystal and its modeling using a quantum annealer machine.

The relaxation dynamics of complex many-body or quantum field systems brought out of equilibrium and trapped into metastable states is presently a very active field of research from both the theoretical and experimental point of view. This is a very interdisciplinary field of research that connects concepts of condensed matter physics and quantum dynamics and has deep implications even in cosmology for the so-called 'false vacuum decay'.

The present work specifically attacks the phenomenology of domain wall relaxation: in contrast to the traditional cosmological false vacuum decay where the decay process connects two spatially-homogeneous configurations differing by some macroscopic observable (aka two vacuum states), here the decay process consists of the motion of domain walls spatially separating different crystalline arrangements. As a common feature of the two phenomena, the temporal dynamics involves overtaking some potential energy barrier to exit from a metastable local minimum of the energy landscape. Whereas the physics of domain wall relaxation is -at least to my eyes- less intriguing and challenging than the traditional false vacuum decay, still the topic of the manuscript can be of some general interest for a wide community of physicists. In any case, I strongly recommend the authors to update the title of the manuscript and several parts of the text to faithfully match the actual content of the work and avoid misleading the readers.

AR: We thank the reviewer for acknowledging the importance of this work for a wide community of physicists. The comments have proved extremely valuable, and we have used them to motivate an extended rewriting of the manuscript, particularly the simulations, with significantly more attention to didactics that may arouse additional interest in the comparison of false vacuum decay (FVD) and quantum domain reconfigurations that lead to emergent behaviour. The differences reveal some fundamental aspects of noise-assisted quantum processes in relation to FVD.

We agree with the reviewer that while there is a connection of domain wall relaxation with false vacuum decay, it is important to highlight the differences. We have done this in the substantially revised manuscript and updated the title to "Non-equilibrium quantum domain reconfiguration dynamics in a two-dimensional electronic crystal: experiments and quantum simulations".

As a most interesting experimental observation, the dynamics of a complex, density-modulated electronic state is followed in real time by taking successible STM snapshots of the temporal evolution of the electron configuration after the system has been initialized in a domain state with a suitable current pulse. The main observation is that the relaxation follows an exponential law and its rate tends to a constant value at low temperatures and follows an thermally-activatedlike behaviour at higher temperatures. No study of the dependence of the rate on other physical parameters is provided and only a

generic interpretation of the activation energy value is provided. Such thermal activation behaviours are well-known in the literature on domain walls; also the specific material system under investigation, its electronic density-modulated states, and its STM imaging are well-established in the community, so they can be hardly considered as a key novelty of this work.

AR: We are glad to see that the reviewer finds our experimental observation 'most interesting'. While thermally activated domain wall motion has been observed previously in magnetic systems and ferroelectrics for example, this is the first time it has been observed in a CDW system, and first time it has been directly measured in a time-resolved experiment by STM. We agree that T-activated behaviour is not the key novelty of this work. The cross-over to T-independent processes is novel.

Given the extremely slow rate of the motion (on the order of minutes) I can hardly believe that the low-temperature dynamics is dominated by quantum tunneling processes (as the attempt of using a WKB model would instead suggest). A noise-induced activation processes (as mentioned by the authors at some points) is a much more convincing explanation. Generally speaking, the discussion of the physical interpretation of the experiments is carried out in a quite obscure way in the manuscript, with the consequent risk of being misleading for the readers.

AR: This comment is very valuable, and as lead us to significantly rewrite the paper, with much more succinct description of the processes involved, with more careful definition of terminology. We acknowledge that the physical interpretation of the experiment might not have been explained as well as it could have been as is evident from the misinterpretation of the reviewer in that we try and explain the temperature independent processes with pure quantum tunnelling. This is in fact not the case, and we only use the WKB estimation as a probe for estimating the viability of quantum tunnelling as an explanation. We then elaborate that the presence of noise is KEY in describing the dynamics observed in 1T-TaS₂ and it is precisely for this reason that we make the choice of using a NOISY quantum simulator in order to reproduce the experimental dynamics. In light of this misunderstanding, we rewrote major parts of the text relating to the physical interpretation of data in order to clarify our point. We updated the abstract (and title) to make clear that we describe noise driven dynamics, and we dedicated 3 paragraphs in the new Discussion section to detailed explanation of noise driven dynamics. We also removed the WKB discussion in order to avoid misleading the reader.

In parallel to the experiments, the temporal dynamics of the material system is simulated on an annealer machine. This is operated in a way to encode a transverse-field Ising model, which is a standard model where false vacuum decay processes are being studied in the theoretical

literature. This model shares some general features with the electronic system and the annealer machine is subject to a similar $1/\nu$ noise spectrum, but (as the authors confirm at several points of the SM) the modeling protocol has no direct mathematical link with the physics of electrons in the material, in particular for what concerns the role of the kinetic energy term.

AR: We acknowledge the reviewer's concern that our transverse-field Ising model does not exhibit the same kinetic energy term as a typical electronic Hamiltonian would. However, as we argue in the revised text the model shares the same kinetic energy term in the limit of strong

interactions. This is based on a paper we were not aware of before (Balducci, F., Gambassi, A., Leroise, A., Scardicchio, A. & Vanoni, C. Localization and Melting of Interfaces in the TwoDimensional Quantum Ising Model. *Phys. Rev. Lett.* 129, 120601 (2022)), where the authors show that domain walls in the transverse field Ising model behave as free particles in the background of strong interactions. This leads to an overall Hamiltonian that is the same as we use to describe polarons in 1T-TaS₂ in the limit of strong interactions. We add and emphasize this point in the revised version of the manuscript.

As another concern, I do not understand how information on the temporal quantum dynamics can be obtained using an annealer machine rather than a true quantum simulator. Unfortunately, the arguments offered by the authors (e.g. on the 'reverse annealing' feature) do not give much insight to justify this choice. If the authors had in mind to only focus on an incoherent relaxation dynamics (possibly with some activation by the noise), they should correspondingly and consistently amend the presentation to avoid misunderstandings. In this case, I am no longer sure that the wording 'false vacuum decay' would still be relevant; surely, 'macroscopic quantum tunneling' would no longer be relevant.

AR: Indeed, our focus was specifically on incoherent relaxation dynamics and we have already agreed in a previous point to amend the title to "Non-equilibrium quantum domain reconfiguration dynamics in a two-dimensional electronic crystal: experiments and quantum simulations", which moves us away from claiming that we study traditional false vacuum decay. However, the authors disagree that there are no quantum dynamics present even in the incoherent case. This is precisely why we decided to introduce the concept of incoherent macroscopic tunnelling (IMT) processes into the manuscript. There is a large body of literature dealing with the influence of various noise sources on quantum dynamics in the presence of an external bath. In the manuscript we cite for example: Leggett, A. J. et al. Dynamics of the dissipative two-state system. *Rev. Mod. Phys.* 59, 1-85 (1987); Grabert, H., Olschowski, P. & Weiss, U. Quantum decay rates for dissipative systems at finite temperatures. *Phys. Rev. B* 36, 1931-1951 (1987); Whiticar, A. M. et al. Probing flux and charge noise with macroscopic resonant tunneling. *Phys. Rev. B* 107, 075412 (2023); and we add extra references

- Boixo, S., Smelyanskiy, V., Shabani, A. et al. Computational multiqubit tunnelling in programmable quantum annealers. *Nat Commun* 7, 10327
- Boixo, S. et al. Evidence for quantum annealing with more than one hundred qubits. *Nat. Phys.* 10, 218-224 (2014).
- Boixo, S., Albash, T., Spedalieri, F. M., Chancellor, N. & Lidar, D. A. Experimental signature of programmable quantum annealing. *Nat. Commun.* 4, 1-8 (2013).
- Denchev, V. S. et al. What is the computational value of finite-range tunneling? *Phys. Rev. X* 6, 1-19 (2016).

All of these references together show clearly that quantum tunnelling is possible (not just in theory but also in practice on the quantum annealer) in the presence of noise as well as temperature, which is also the main study of this work. The issue then becomes that of semantics. We assume that the referee has in mind pure coherent quantum tunnelling when the system is not coupled to a bath. We agree that this is not the case here. However, if a system+bath quantum description is necessary to describe dynamics, we argue that incoherent quantum tunnelling is still applicable and indeed appropriate in our case.

The reverse annealing feature is used to introduce the kinetic energy term into the system, which then together with the interaction term causes IMT relaxation processes in the context of external noise and a bath. The best analogy we can use to help understand what the reverse annealing feature does is with an iterative measurement process, just as it is performed in

experiment. The STM measures 1T-TaS₂ iteratively with a certain time step. What happens in between measurements is subject to noisy, thermal, and quantum dynamics of the system. Reverse annealing, on the other hand, emulates this process by iteratively turning on and off the kinetic energy term and measuring the qubit configuration at every »turned off« point. We apologize for not explaining this point well enough and make our best effort to do so in the revised version. We have also made an effort to explain what we mean by IMT processes in the revised version.

In summary, I am not convinced that the scientific content and the quality and clarity of the presentation are at the level required for publication on Nature Communications. As such, my recommendation is that the authors make a willing effort to improve the manuscript by clarifying all obscure points and removing all potentially misleading and/or overselling sentences and, then, resubmit the revised manuscript to some more specialized journal. When revising the manuscript, they should also take care that the main text is fully intelligible without having to continuously refer to the SM.

AR: We thank the reviewer for their constructive criticism, which helped to greatly improve the revised manuscript version. We hope that we have addressed all of the concerns of the reviewer and that they find the revised version suitable for publication.

As minor issues:

-on pag. 16 of the SM, I do not understand the sentence '... the domain walls cost zero energy in terms of interaction. However, the energy could be lowered still by getting rid of domain walls'. If the energy is not in interaction energy, where is it stored?

AR: This is a good question. The energy is stored in the chemical potential term. If the domain walls were gone, the interaction energy would still be the same, because the repulsion is only between nearest neighbours, while the distances between polarons on each side of the domain wall is more than that. However, by introducing more polarons into the system, we could lower the contribution from the chemical potential, thereby lowering the energy of the whole system. The domain walls turn out to be difficult to get rid of in a Monte Carlo algorithm because a large number of polarons would have to be introduced in precisely the right locations within the domain wall, which is a highly unlikely event. We elaborated this point in the revised SI.

-I suspect that on pag. 24 of the SM, '...them to the minimal possible value...' should be corrected into '...them to the maximal possible value...')

AR: No, that is incorrect. The couplings need to be ferromagnetic (negative values) in order for physical qubits to tend to assume the same value. The value is set to be -1 in our case. We thank the reviewer for the comment and add this point to the SM to avoid further misunderstandings.

-The list of references may be reinforced with specific theoretical and experimental works on the relaxation dynamics of domain walls in different physical systems. This will facilitate the reader in assessing the points of novelty of this manuscript.

AR: We have added appropriate references to the manuscript.

Reviewer # 2

(Remarks to the Author):

While the authors have made important improvements to the manuscript and have removed most of the questionable statements, I am still not fully convinced by several of the authors' arguments in reply to my first report. On top of that, I keep feeling that its scientific content is not at the level that is required for publication on Nature Physics.

Should the authors decide to resubmit the manuscript to some other, more specialized journal, I urge them to address my previous questions on the reason for using an annealer (rather than a quantum simulator) and, even more important, on the relation between the actual physical system to the transverse-field Ising model used in the simulations. I am in fact not satisfied by the arguments that the authors put forward in support of mapping the physical system onto the transverse-field Ising model.

AR: We thank the reviewer for their constructive criticism, which did in fact help us to greatly improve our manuscript. In light of this, we provide a rebuttal to the final points made by the reviewer:

(i) The reason for using an annealer rather than a quantum simulator:

In our experiments we study polaronic domain reconfiguration events of tens of domains with domain sizes of several tens up to hundreds of polarons, where each polaron takes up to 13 atomic lattice sites. Even by reducing the requirement from 13 to 3 atoms per polaron in our theoretical model, a small single domain (~ 24 polarons) requires close to 100 atomic lattice sites ($\sim 24 \times 3 = 72$ atomic sites). Quantum simulators capable of simulating the Bose-Hubbard model have 80 atomic sites in total available at best [Chiu et al., 2019. String patterns in the doped Hubbard model. *Science*, 365(6450), pp.251-256.] which is simply not enough to create tens of domains with an average domain size of 100 polarons, required to emulate our experiments. The same argument holds for quantum simulation using digital quantum computers [Mi et al., 2024. Stable quantum-correlated many-body states through engineered dissipation. *Science*, 383(6689), pp.1332-1337.]

(ii) The relation between the actual system and the transverse field Ising model used in simulations:

The authors remain convinced that in the limit of a small kinetic compared to interaction energy, domain walls govern the dynamics of the extended transverse field Ising model and they exhibit a hopping-like kinetic energy term. The main reason is the observation of similar domain wall dynamics in both the experimental system 1T-TaS₂ and the quantum annealer, which is substantiated also theoretically by Balducci et al [Balducci, F., Gambassi, A., Leroise, A.,

Scardicchio, A. and Vanoni, C., 2022. Localization and melting of interfaces in the two-dimensional quantum Ising model. *Physical Review Letters*, 129(12), p.120601.].

We reiterated these points in the revised manuscript.

Reviewer # 3

In this article, the authors use two systems to show the metastable many-body states. One is the quantum material 1T-TaS₂, the other is an array of 2008 qubits in a programmable noisy superconducting quantum simulator. They claim that the simulations clearly display a crossover from T -activated dynamics to T -independent quantum domain melting that is experimentally observed in the STM measurements, and give remarkable insight into the mechanism for the

emergence of false vacuum states in a microscopic system. I have a few comments on this article,

- This article makes too much unrelated statements. For example, those statements, "Emergent metastability in non-equilibrium systems is a subject that touches everything from the origins of life..." "Understanding the dynamics of such systems is crucial for developing new quantum technologies..." are all beyond what can be claimed basing on their experiments.

AR: We thank the reviewer for the comments. While the statements hold we concede that without further explanation they may appear unrelated. We have revised the MS to revise such statements that may appear unrelated or vague, such as the ones mentioned. By the time the Conclusions are reached, the relation to the topics mentioned in the beginning become clear (to the reader who persists to read the Conclusions).

2)Both a thermal activation process and a quantum tunneling process are involved in the reconfiguration process. But the quantum tunneling process is not well explained. For example, it is contradict to the classical Monte Carlo simulation. Why don't they try quantum Monte Carlo simulation? Or a quantum Monte Carlo in the presence of noise?

AR: We apologize for the lack of clarity and make our best effort to better explain the quantum tunnelling process in the revised text. What we mean by quantum tunnelling or, more specific to our text, incoherent macroscopic tunnelling processes, are large reconfiguration events of the system of polarons in 1T-TaS₂ or qubits on the quantum annealer, enabled by quantum dynamics in the presence of noise and a bath. The dynamics would not be possible if not for the presence of both the interaction and kinetic energy term in the system's Hamiltonian, which do not commute with each other. The comparison with classical Monte Carlo was done on purpose, to show that if we only keep the interaction term and a bath, the temperature independent dynamics would not be possible in 1T-TaS₂.

The use of quantum Monte Carlo (QMC) is a very good suggestion and may be explored in a future study. Unfortunately, it falls outside the scope of this work because it is still an open question whether it would even be possible to perform such a non-equilibrium QMC simulation. One approach would be to simply cut off the sampling in the algorithm and check whether the distribution of states really does correspond to the experimentally observed one. We could also implement different kinetic energy terms in order to emulate the system of polarons more accurately. However, we want to emphasize that we are NOT sampling from an equilibrium distribution, which is what QMC is designed to do. In both 1T-TaS₂ and the quantum annealer, we are sampling the non-equilibrium trajectory towards equilibrium. In fact, if we would have waited for our system to equilibrate (in both 1T-TaS₂ and the quantum annealer), the measured T-independent rate of polaronic movement would simply always be 0. Furthermore, QMC sampling is done in an inherently unphysical manner, such that it can be efficiently implemented on classical computers. The quantum annealer, on the other hand, is actually performing the incoherent quantum dynamics that we are interested in probing.

3)The energy landscape should be multiple dimension, why is it safe to use a simple one dimensional case.

AR: A multidimensional version of the Kramers-Caldeira-Legget theory that we could apply

to our experimental data currently does not exist. With this work, we hope to stimulate research into this direction. We agree with the reviewer that the assumption of safe usage of a onedimensional case may be misleading. We thank the reviewer for the remark and add this point in the revised text.

4)How to obtain the reconfiguration rate from $f(t)$? It is unclearly explained.

AR: We apologize for not clearly explaining the reconfiguration rate R . It is obtained from $f(t)$, which measures the fraction of polarons that moved from one STM image to the next, by simply dividing it with the time interval between two sequentially measured images. We added the explanation in the revised text.

5)The Fig1.d and Fig2.f are quite different. From Fig1,d we can clearly see the metastable state while in Fig2,f the metastable states are not clear.

AR: We agree that the presentation of metastable states should be made more clear for a fair comparison of both figures. Therefore, we added lines that indicate the location of metastable states during the relaxation sequence as well as an explanation in the figure caption.

6)How the $1/\nu$ noise affect the tunneling?

AR: This question suggests that we have not clearly explained the influence of $1/\nu$ noise on the system. In essence, the noise broadens any energy level that the system has. So, if we imagine an entire energy spectrum of, for example, a system of polarons in 1T-TaS₂, the energy gap that has to be bridged for a transition between different polaronic states to occur is effectively reduced by coupling to an external two-level system. The broadening of energy levels is given by the integral of the $1/\nu$ noise spectrum. For more details, we refer the reviewer to a paper that is cited in the revised version on the manuscript Amin, M. H. S., Averin, D. V. & Nesteroff, J. A. Decoherence in adiabatic quantum computation. Phys. Rev. A 79, 022107 (2009). In the revised text we explain the effect of noise more clearly.

Reviewer # 4

(it is maybe reviewer 3)

It seems as though the authors have significantly modified their manuscript to remove somewhat spurious claims addressed by reviewer 3. The authors address questions about Monte Carlo simulations as well as including a note in the manuscript on how Quantum Monte Carlo simulations with noise are not developed for non equilibrium systems. They mention in their response how QMC is designed to sample from an equilibrium distribution whereas the manuscript specifically studies non equilibrium dynamics. The authors address the need for a multidimensional version of the KLC theory in the manuscript and have added explanations for the reconfiguration rate as well as the effect $1/\nu$ noise has on the system. In summary, I see the primary concerns of reviewer 3 as having been dutifully addressed.

7.3.2 My Conclusion about the Article

(It is not clear how some useful information can be extracted from the system and why they are interested in that R value. maybe it is useful for practice in the quantum computation, but in terms of physics, there are a lot of gaps in the explanations. maybe I'll understand them later. also, the limit of applicability of the model is not clear)

7.3.3 My General Questions about the Physics Here

How many electrons are in one “ball” of electronic density?

Can we see that there is exactly one electron there? Maybe there are several of them???

Suppose we have a CCDW phase. Now we add electrons. The energy of the system increased (if no particle has left the system) and there are now DWs. Does it mean that DWs have more energy than how much particles would have in the same area?

(?? or particles always escape the system???? then why the chem. pot is not changed to another value????)

Suppose we add more electrons. Then they should be packed more dense (if they don't exit the system). So the lattice itself changes. Is it taken into account?

(???? why do we have the same lattice always????? sounds like another big problem)
(?? or particles always escape the system????)

Do electrons go away from the material during the reconfiguration?

(?? I think that yes, but if so, how does it taken into account in the model? does the energy decrease?)

Suppose we plug NCCDW phase, will we see no reconfiguration?

(this is what we should see, but there is nothing written about NCCDW. so, based on this theory which does tell us any dependence on how many electrons were inserted, we might expect that there will be also reconfiguration, since it is not written that extra NCCDW symmetry will stop the reconfiguration. but it shouldn't be, since NCCDW is stable. another big problem...)

Is the reconfiguration only relaxation, but also some special dynamics?

(?? maybe both... I don't understand the contributions to the observed reconfiguration?)

So what exactly the dynamics of the DWs give us?

(??? there are unclear statements in the article, so I am writing this question separately)

Why the same noise is present in the simulation and in the measurement?

(??? is there a reason for it or just a coincidence???)

What would be if we didn't have the noise? Would there be no reconfiguration?

(??? I don't know, since reconfiguration should arise from coming to the ground state and we don't need a noise for it. maybe noise somehow influences the rate of coming to the GS??? how???)

What about other materials, is this simulation applicable for them?

(???????????????????????????? nothing is written about them here. We just use TaS2 because we like it and the applicability for other materials looks like an open research question... I'll think later about it)

(what about applicability not to TMDCs?)

(why at all they have chosen TaS2? "paradigmatic" example is a strange explanation)

7.3.4 My Questions about Methods and Models

What happen with kinetic term?

(??? which role does it play? I still don't understand)

How to get the free energy f functional (that washboard potential)???

(???? I don't know, there are no formulas in the article...)

It is very expected that the R will decrease and then saturate to a constant. Are there some alternative models to the PQA?

(???)

What is finally the influence of the tip to the dynamics?

Does it give extra noise or what? I don't understand it still.

How to derive the QPA Hamiltonian from the CLG Hamiltonian?

(???? I don't know, I'll try to understand it later)

What is not explained here because of which we need a kinetic term?

(??? is it written, why do we need the kinetic term?)

What is the origin of a noise in this system?

(??? maybe there are only guesses, I'll read again the article and try to understand)

How exactly the $1/\nu$ noise is used?

(??? I did not understand)

How the initial domain state is set up in the experiment and in the simulation?

(??? I did not understand)

(By electrical pulse charge injection through an STM tip, but how????)

(in simulation - by some initialization?)

What about other regimes, SC, CCDW, is this model valid there???

(??????? maybe no, but why nothing is written about it here???)

7.3.5 My Other Questions

Are there are other PQA-s?

what if they took another PQA, not the D-wave advantage??

Are there really no influence from the tip???

(the averaged τ is still changed, maybe there is still an influence of the tip???? what is stated about it???)

What if we restricted electrons and did not allow them to leave the material?

(??? would there be a reconfiguration at all?)

Is the distortion of atomic lattice big or small because of polarons?

(this is well-known for me question which I'll try to answer some day. we assume that it is little (even though we say "there is a strong electron-phonon interaction"). how can it be - I'll think later)

How to get the polaronic bandwidth w from the rate of tunneling?

(???? there are some comments in discussion about it)

Why are we so focused on 1T phase? What about 1H phase?

(??? this is rather not important question, but still)

7.3.6 Possible Next Steps for Research Using These Results

Do similar calculations for other materials (use different V_0), find this way the limit of applicability of this model

(!!! elaborate this idea!!!!)

8 Configurational Electronic States in Layered Transition Metal Dichalcogenides by Vodeb, Kabanov, Gerasimenko, Venturini, Ravnik, van Midden, Zupanic, Sutar, Mihailovic (2019)

Abstract

Mesoscopic irregularly ordered and even amorphous self-assembled electronic structures were recently reported in two-dimensional metallic dichalcogenides (TMDs), created and manipulated with short light pulses or by charge injection (in which article these different electronic structures were reported? how they are created exactly?) .

Apart from promising new all-electronic memory devices (I doubt that it is really applicable, I'll check later) , such states are of great fundamental importance, since such aperiodic states cannot be described in terms of conventional charge-density-wave (CDW) physics. (todo: learn better, what can and what can't be described by CDW? here, there are citations and authors say "we'll just use the CLG")

In this paper we address the problem of metastable mesoscopic configurational charge ordering in TMDs with a sparsely filled charged lattice gas model in which electrons are subject only to screened Coulomb repulsion.

The model correctly predicts commensurate CDW states corresponding to different TMDs at magic filling fractions $f_m = 1/3, 1/4, 1/9, 1/13, 1/16$. (the filling factor is the number of electrons per unit cell) (why didn't they write also 7, 12, so on??? there are more these numbers)

Doping away from f_m results either in multiple near-degenerate (why near-degenerate?) configurational states, or an amorphous state at the correct density observed by scanning tunneling microscopy.

Quantum fluctuations (there are no quantum fluctuations in this article, why is it in the abstract?) between degenerate states predict a quantum charge liquid at low

temperatures (what is the def. of quantum charge liquid?) , revealing a new generalized viewpoint (which? I don't agree, I see no new viewpoint) on both regular, irregular and amorphous charge ordering in transition metal dichalcogenides.

8.1 The Article

8.1.1 Introduction

(SUMMARY: there are TMDCs, which have different phases, there are several theories about them, but we focus on CLG model and we will have a filling factor in it as a main parameter)

Recently (when?) , scanning tunnelling measurements in transition metal dichalcogenides have revealed irregular charge ordered textures - nanoscale mosaics of charge-ordered domains separated by domain walls which could be created and manipulated by light or by charge injection ¹⁻⁷. (todo: look at this literature!!! this might give some similar pictures like in this article)

TMDs form a large family of materials have been of significant interest in the past because they exhibit a variety of charge density wave phenomena (CDWs) at low temperatures ⁸⁻¹⁰.

Upon doping or the application of pressure, they give rise to a generic phase diagram that usually includes a superconducting state ¹¹ (Fig. 1) ¹²⁻²¹. (read cited papers! does doping give the same effect as a pressure???)

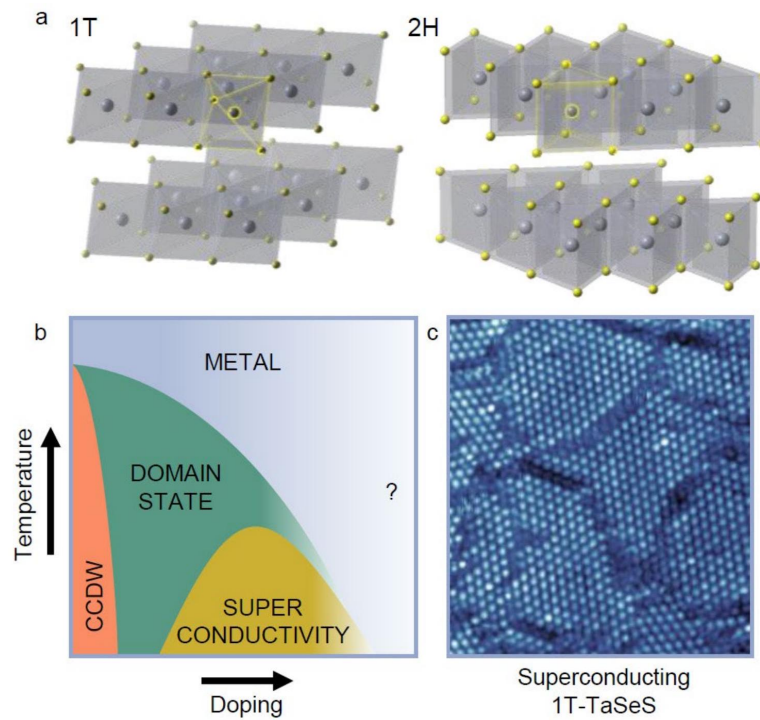


Fig. 1 A schematic representation of a typical crystal structure in layered materials, which exhibit a CCDW.

a This specific case shows two polytypes (1T and 2H) of TaS₂. (why are they called T and H?? is the difference in the arrangement of S atoms?)

The unit cell is emphasized in yellow, the yellow spheres represent sulphur and the gray spheres are metal atoms.

b The generic phase diagram of doped TMDs (this is a very confusing plot, it should not be taken into account seriously!!! first of all, there is no scale of a doping. naturally one might think that it goes from 0 to some high value, but no, in this case it would contradict the main figure of this article. so one way how to think about this plot is to see it as a little plot in the middle of the doping axes. there is the symmetric reflection of this plot right at the left of it.) (the superconductivity is at all irrelevant here, because it is not there in the model, and it is not the tiny region, it is a big region somewhere at the far right from this plot.) (what if we had a pressure on the X axes, how would these scheme change???) . (also, we assume that NCCDW phase is inside of the domain state. it would be better to call it NCCDW, but there are ordered domains, and here we have random domains)

STM experiments show that doping immediately results in the formation of domains which persist in the superconducting state.

The ? indicates that this part of the phase diagram is poorly understood (and what is not known there? read that another article and write it here) .

c The domain structure measured at 1.1 K in the superconducting state of 1T-TaSeS ($T_c = 3.2$ K). (we need the domain state, which is not ordered. why the SC phase is chosen???? why not the NCCDW phase?)

The most commonly considered mechanisms for the formation of conventional long-range ordered CDW states in TMDs are related to a Fermi surface nesting (FSN) instability²², electron-phonon coupling²³, and most recently exciton condensation^{10,24,25}. (work out at least one article about each of them!)

(what is the FSN??? answer it in another note and then add answer here)

In this context it is intriguing that the low-temperature CCDW states in very diverse systems are very similar (why similar? how the same state in different materials can be similar or

different?) , yet their proposed formation mechanisms are completely different (maybe because only one mechanism is real and others are nonphysical?) .

The FSN nesting mechanism for CDW formation is often questioned ^{26–30}. (why??)

Eiter et. al. ³¹ suggested that an enhanced EPC (Electron–phonon coupling. Here, authors do not distinguish the FSN and EPC, so it is not clear what do they mean out of these two) can contribute to or even entirely determine the selection of the ordering vector in ErTe_3 for example. (add it to part of theoretical papers on TMDCs!)

Johannes and Mazin have pointed out that FSN also fails in NbSe_2 and TaSe_2 , and have proposed that EPC can account for the CDW²⁶. (add it to part of theoretical papers on TMDCs!)

Similarly, Zhu et. al. have shown that the CDW in NbSe_2 can be explained by EPC, predicting the correct CDW wave vector ³². (add it to part of theoretical papers on TMDCs!) (many people wrote many things, but what is the outcome of them???)

(this paragraph was deleted from the latter version) Coupling of the electrons to the collective mode in the Lee-Rice-Anderson model ³³ (LRA) (what is the Lee-Rice-Anderson??? no one uses it now, the article is also not available, some registrations are needed. There is no sense to spend time to learn what is it?) predicts an incommensurate phase and metallic behavior in 1D, but doping by impurities, or interchain coupling predicts the appearance of a gap in the electronic spectrum, which is usually not born out experimentally.

Thus, the anomalous peak in resistivity in $1\text{T}-\text{TaS}_2$ with doping at 8.5% with Ti and Hf in $1\text{T}-\text{TaS}_2$ ³⁴ (check, what is this peak???) could not be understood in terms of the LRA model, and already $> 1\%$ of cation doping introduces metallicity - opposite of what is predicted. (this is a strange statement that anyway was deleted from the final article)

The absence of observed CDW sliding (CDW sliding???) ³⁵ and recent transport measurements which suggest that topological defects (topological defects?) govern transport at low fields ³⁶, and anomalous behavior at higher fields ⁵ highlights the need to re-address not only the transport problem, but the nature of the state itself. (re-address comparing to which approach???) (this is a strange statement that anyway was deleted from the final article)

Tossatti and Fazekas have pointed out the importance of Coulomb interaction in the commensurate (CCDW) state of $1\text{T}-\text{TaS}_2$, which was proposed to lead to a Mott insulator ³⁷, explaining the large gap and onset of metallicity (onset of metallicity???) with doping and pressure ^{3,4,11,34,38}. (read it, I don't know about the Coulomb interaction there!!!)

On the other hand, band structure calculations have reproduced many of the features of the CCDW state such as the in-plane gap (in-plane gap???) without strong Coulomb correlations ^{39,40}, but fail to reproduce the highly insulating out-of-plane resistivity ⁴¹.

In trying to reconcile the viewpoints, Rossmagel suggested that the degree of correlations (degree of correlations??) determines whether the state is an ICCDW or a CCDW in 2D dichalcogenides ¹⁰.

More recently, arguments have also been presented for a significant role of the EPC in $1\text{T}-\text{TaS}_2$ ^{42,43}. (was someone arguing before that there was a little EPC in this material???)

Thus, in spite of the fact that the problem is known since the 1970s, there are many open issues that have not been resolved even in $1\text{T}\text{TaS}_2$, let alone universally in the TMD materials.

Recent scanning tunneling microscopy (STM) experiments have shown that doping introduces densely packed domains and sharp domain walls (DWs) that are not easily understood using the established CDW physics discussed above. (not easily understood = understood or not? useless sentence)

Such textures also seem to appear under various external perturbations such as photodoping^{5,38,44}, charge injection^{2–5,45}, non-isovalent⁴⁶ and isovalent^{47,48} transition metal substitution, chemical doping by chalcogen ion substitution⁴⁹ or even intercalation of transition metal ions⁵⁰. (read one day some article from these)

Apart from DW textures, a few examples of amorphous states have been reported as a consequence of photodoping or charge injection⁵¹ as well as alkali or N₂H₄ vapor deposition^{52,53} and possibly Nb intercalation⁴⁷. (is it important?)

The states created through non-equilibrium methods are of particular interest for ultrafast memory devices^{5,54–61} (check if they really are, there is no sense to believe this claim), but the mesoscopic metastability associated with these phenomena are not easily explained with conventional CDW theory.

Superconducting 2H – NbSe₂ exhibits a domain wall structure even in its pristine state with no lock-in transition (lock-in transition??) to a CCDW as in other 2 H compounds⁶².

Superconductivity thus seemingly coincides with the appearance of a textured state not only in 2H – NbSe₂, but also in 1T- TiSe₂¹⁵ (and 1T- TaS₂¹¹, another generic feature which conventional theories do not address.

Thus, in spite of intense current interest, it is clear that none of the above-mentioned models which discuss k -space interactions (k -space interactions?) in a homogeneous periodic lattice can describe the intricate irregular topologically non-trivial mesoscopic features that universally appear in doped and metastable photoinduced or charge-injected structures^{2–4,38,44}. (too complicated sentence, they wanted to say "previous theories are not applicable for this material")

Such discommensurations were discussed theoretically to some extent by McMillan²³ (???) based on Landau theory in 2H – TaSe₂, and Nakanishi and Shiba^{63,64} for 1T-TaS₂, but only as regular structures. (read this later)

In this paper we approach the problem of describing irregular charge configurational states from the viewpoint of strong correlations between electrons involved in CDW formation (which strong correlations??? we just have a hopping model, what do we say about the correlations??) in the spirit of the Mott state introduced by Fazekas and Tossatti^{37,65,66}. (read these papers!!! what did they do there? not what is done here??)

Our approach has its origins in CLG modelling of strongly correlated polarons on a square lattice as applied originally to oxides^{67–70} and extended by Brazovskii⁷¹ to investigate the CCDW state of 1TTaS₂. (read the papers!)

DW formation resulting from doping was suggested by Karpov and Brazovskii^{45,71}. (read the papers!)

Here we examine the phase diagram of a sparse charged lattice gas (CLG) of electrons on a triangular lattice at different filling (i.e. doping) levels using extensive Monte Carlo CLG simulations.

The experimental evidence for local lattice distortions associated with the CDW implies that the electrons are effectively coupled to the lattice, which is usually discussed in terms of polarons, justified in part by the large difference between static and high-frequency dielectric constant that implies substantial screening (as discussed later). (it is a not explained and not clear statement which it is better to just forget. yes, of course they are are coupled, nothing is informative here) (how the amount of screening is connected to existence of polarons???)

The charged lattice gas (CLG) interpretation of a physical system is typically a very crude oversimplification, yet its intuitive nature is very appealing.

In our case it consists of a system of charged repulsively interacting electrons whose motion is slowed down by interaction with the lattice (multipolaronic model) .

Despite its simplicity, it has been utilized successfully as a model for a variety of seemingly unrelated physical systems (are they unrelated) .

Superconducting vortices either in Josephson junction arrays ^{72,73} or superconducting layers in the presence of periodic pinning ^{74–78} have been studied extensively by Monte Carlo simulations and analytical approaches ^{79–89} as well as molecular dynamics simulations ^{90,91}. (it is irrelevant)

Adsorbed atoms on a crystalline surface ^{92–97}, colloidal systems on templates ⁹⁸, organic conductors ^{99,100}, as well as magnetic bubble arrays ¹⁰¹ also exhibit CLG characteristics. (it is irrelevant)

Recently, the configuration of a system of polarons in 1 T – TaS₂ at very low temperatures has been investigated using the CLG model. Remarkably, this model describes well not only the equilibrium state ⁷¹ but also two different photoinduced states ^{45,51}. (read these papers, they should be very relevant)

This success may be considered as justification for attempting to generalize the CLG model for understanding the phase diagram and properties of polaron gases.

Remarkably, we find that the low temperature CCDW states in all the aforementioned systems correspond to electronic crystals, where the filling of the system is one of the many possible magic fillings f_m (it is meant that CCDW state has some of the magic fillings, here is a bad formulation of this idea) .

We find that there exists an infinite number of polaron arrangements (ways how the extra electrons are align) at non-magic fillings, where the energy gap between the analytically predicted ground state and the first excited long range ordered state can be made arbitrarily small in the thermodynamic limit.

Therefore, there exists a whole spectrum of energetically low lying states and this is where an amorphous state is very close in energy to the analytically predicted ground state. (what do we know about the amorphous state?) (how do we analytically predict ground state?)

(so the idea is that if the gap is little, then only low states of low energy will be occupied, so total energy of the system will be lower compared to the case of a big gap.)

Monte Carlo simulations extrapolated into the thermodynamic limit show for a finite amount of cases that this is indeed the case (that the GS is similar to the analytical predicted) (how do they do the analytical prediction?) .

Moreover, we prove that a triangular lattice cannot exist at $f \neq f_m$ due to the frustration (frustration??) .

We conclude that a translationary invariant state with hexagonal symmetry at $f \neq f_m$ indeed needs to exhibit a specific domain wall structure. (why??? what is the condition for the DW???)

This is consistent with previously developed theories concerning domain walls ^{102,103}. (which and how???)

From these findings we can draw parallels with a quantum spin liquid. (with what??? which formula is assumed by quantum spin liquid?)

On a triangular lattice a spin liquid is typically understood as a superposition of an infinite number of valence bond states, which all break hexagonal symmetry and have the same energy. (what is meant here? example?)

The spin liquid ground state then entangles all the states (ground state entangles all the states????) preserving hexagonal symmetry while lowering the energy at the same time ¹⁰⁴.

We find a similar situation with the polaron charge configurations in our calculations in the sense that the low lying energy configurations entangle into a quantum charge liquid. (there is no sense even to try to understand this, looks very senseless)

The MC simulations also confirm a clear absence of a first order phase transition (what tells us that there is no first order phase transition?) in a wide temperature range in all cases where $f \neq f_m$, which supports the idea that there are two quantum critical points (quantum critical points??) present at $T = 0$ around each magic filling.

This is shown on the phase diagram of the CLG on a triangular lattice presented in this paper.

Our conjecture also has important consequences regarding the current paradigm of glass formation ¹⁰⁵. (later, in the discussion it is explicitly written that not always minimal energy is a crystalline state, so they claim that this paradigm is in general not correct)

The paradigm states that upon cooling a system down to low temperature, a glass is formed due to the system getting stuck in a local minimum of free energy.

There is an overwhelming probability in favor of this phenomenon due to an extensive number of local minima present in the energy landscape of the system.

One of the main assumptions in the glass formation paradigm is that the global minimum of the system is the crystalline state, which is challenged by our calculations. (so they calculate energy for different configurations and see if the one with minimal energy is crystalline or no?)

SM: Charged Lattice Gas Model in Different Fields of Physics

(SUMMARY: they say "CLG is seen in other setups". Irrelevant knowledge.)

In order to illustrate the connection between different fields of science in using the CLG model, we list some terminology and the reasons behind its usage.

(what is the def. of CLG????)

In the field of superconductivity f has been dubbed as the frustration parameter (never heard about frustration parameter???) and the CLG model as the uniformly frustrated XY model (???) .

This comes from the fact that there exists a CLG interpretation of the classical XY model obtained via the Villain transformation ¹ (Villain transformation??) .

In the surface science community f has been dubbed as coverage and usually denoted as θ (really?) .

The reason for using a CLG model comes from the assumption that atoms adsorbed on crystalline surface behave classically and interact via some long range repulsion.

In the study of polarons in solid state physics it turns out that in the case of strong electron-phonon coupling a system of polarons reduces to a system of hopping fermions which repel each other ² (check that theory of polarons uses something from CLG. I doubt that it is there, a tight binding model is not a CLG. right?) . (what about the case of weak EPI?)

If we neglect the hopping and the spin, the CLG interpretation emerges immediately.

8.1.2 The Model

(SUMMARY: we take this TB model because common sense tells us to do it)

The model we employed in this paper is based on the CLG Hamiltonian

$$\mathcal{H} = \sum_{i < j} V(i, j) n_i n_j \quad (1)$$

where n_i is the occupational number of a polaron at site i with values either 0 or 1 and $V(i, j) = \frac{V_0 \exp(-\frac{r_{ij}}{r_s})}{r_{ij}}$ the Yukawa potential that describes the screening, where $V_0 = e^2/(\epsilon_0 a)$ in CGS units, $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$, where $\mathbf{r}_i$ is the dimensionless position of the i -th polaron and r_s is the dimensionless screening radius.

(there are no reason except common sense for this morel to be true. I don't know any derivation of it)

The value 1 for both $|\mathbf{r}_i|$ and r_s corresponds to one lattice constant a and ϵ_0 is the static dielectric constant of the material.

Polarons can occupy only the sites of the underlying triangular lattice (which can be different, since it is the PL, not the AL) with the lattice constant a and the ratio of polarons in the system divided by the number of lattice sites is defined as the filling f .

We studied the phase diagram of such a system at fixed values of f and r_s as well as the temperature dependence.

The idea for the use of polarons in a CLG comes from chapter 4.2 in ¹⁰⁶, where a system of repulsive electrons and phonons interacting via the electron-phonon interaction is canonically transformed into a system of interacting small polarons in the strong electron-phonon coupling limit. (why in all the TMDCs exactly the strong EP interaction is present?? shouldn't all of them have different EPI and it will be a different constant in some effective model?) (no, it is not clear how this model is not connected to that model. You'll not derive it, it is just a model which is justified by a common sense. moreover, this is a famous shitty derivation from the ch. 4.2, you need to find a good one, then cite it)

In this paper we neglect spin effects (which spin effects? yes, there is no spin, but which effects?) , assume that the hopping of polarons $\tilde{t} \ll V_0$ (the tilde is irrelevant, it is meant just t , typical hopping parameter, which could have been if there were hopping) , justified by the static nature of charges, and assume a screened Coulomb interaction (yes, we have seen already this model) .

For further discussion regarding the use of this model see the SI. (is there something useful?)

SM: Estimation of V_0 and Δ in the case of 1T-TaS₂

We can estimate the values of V_0 and Δ in the case of 1 T – TaS₂.

The magnitude of V_0 comes from the Coulomb interaction and is defined as $\frac{e^2}{\epsilon_0 a}$ in CGS units, where e is the charge of a polaron and ϵ_0 is the static dielectric constant.

Using the value for $a = 3.4 \text{ \AA}$ and $\epsilon_0 = 1.510^{45}$ (check these values in the literature!) we can estimate $V_0 = 2.810^{-4} \text{ eV}$.

This corresponds to a temperature of 3 K, therefore the energy gap Δ is of the order of 1 to 10 mK per particle.

8.1.3 Analytical Considerations

SM: Details of the Tiling Algorithm

(SUMMARY: there is a good illustration below of the fillings and primitive cells)

(I wrote it here from SM, because this is way more understandable then the unclear text from the main article)

Tiling of a polaron configuration can serve as a good visual illustration of the different nearest neighbor distances present between polarons.

To this end, we construct the so-called Voronoi diagram for the point pattern.

When a set of points (polaron centers) on a plane is given, the plane can be partitioned into regions.

Each point is assigned a region of points in the plane, which are closer to it than to any other points.

This is done for all figures exhibiting a polaron configuration.

After the Voronoi diagram is complete, one can construct a different set of tiling polygons from the Voronoi diagram's polygons.

Each new polygon has 4 vertices and represents a distance between two neighboring coordinates.

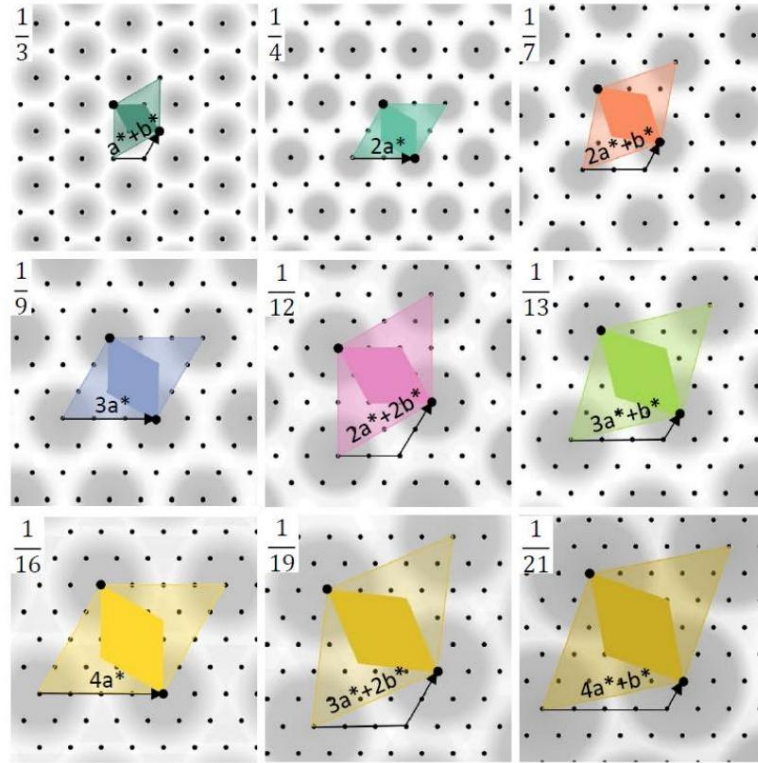
The first two vertices are the two neighboring coordinates from which the distance that the polygon represents is calculated.

The other two vertices are the two points, which are part of the Voronoi polygons containing the two coordinates and are also the closest to both coordinates.

This can be done for any two coordinates, which share two vertices of a Voronoi polygon.

Because the distances between polarons in the model are discrete due to the perfect underlying hexagonal lattice, one can specify a color for each tiling polygon based on the distance between the two coordinates it connects. (yes, we know it from the main plot of the article)

This is indicated by the legend present in each figure with polaron configurations. An example of one tile for each of the magic filling cases considered in the main text is presented in SM Figure 12.



SM Figure 12 A schematic representation of the polaronic crystalline phases present at magic fillings f_m . (how to get the numbers 4, 9 so on from the image??? If we use the formula $1/f_m = x_i^2 + y_i^2 + x_i y_i$, then I don't get the 4 and 9???? (and maybe others))

Each image is associated with a magic filling in the upper left corner.

The large gray circles represent individual polarons and the little black dots represent the underlying atomic lattice.

The unit cell is the parallelogram with a slightly faded out color, where one of the primitive vectors is drawn in terms of the underlying atomic lattice primitive vectors a^* and b^* .

The boldly colored parallelogram in the unit cell together with the two black points in the centers of polarons, which it connects, represents an example of one of the tiles generated from our tiling algorithm. (so which of these two parallelograms will be on the picture in the article?? or both of them??)

In these specific cases of course all of the tiles would be of the same color.

Analytical Considerations

(SUMMARY: we define coordinates of lattices, magic fillings and give some comments)

(write this idea of these analyt. methods better here!!!)

(!!!! it is not explained at all here how the analytical calculations of the gap, energy or anything else was made!!!! read other papers or ask other people to learn it.)

From the structure of the Hamiltonian in Eq. (1) it is obvious that the polarons will always tend to arrange themselves in a triangular lattice with the lattice constant $b = a/\sqrt{f}$ (why $b = a/\sqrt{f}$???) , as the most closely packed structure in 2D. (no, it is not obvious, why??)

However, we need to take into account that polarons can only reside on a triangular underlying atomic lattice (AL) (since there is a polaronic lattice in the Hamiltonian, not the atomic lattice) .

The problem is trivial in the case where the polaron lattice (PL) coincides with the AL. (it is meant "overlays", so that for each polaronic site, there is an atomic site)

In this case, every point of the PL can be mapped onto a point on the AL.

This condition will be dubbed as the hexagonality condition and considered in the following paragraph.

Imagine a 2D plane on which the AL resides.

Let the origin of the coordinate system used to describe the points of the plane lie on some AL point (this is always of course so) and let an arbitrary point on the plane be parametrized by polar coordinates (r, θ) .

Also, let an arbitrary AL point be parametrized by polar coordinates (r_i, θ_i) , where i runs through the infinite set of AL points.

In order to find all the possible triangular PLs we have to find all the possible triangular lattice unit cells, which map onto the AL.

Therefore, we need to find two primitive lattice vectors of a triangular lattice unit cell such that both correspond to some two points on the AL (it is a paraphrasing) .

The hexagonal symmetry of the problem helps because we only need to find one primitive vector (why one vector??) .

The second one is immediately determined as a $\pi/3$ rotation of the first and will therefore also have to reside on the AL.

With the help of the hexagonal symmetry of the problem we can also reduce the search region from the whole plane to only the region of points $\{(r, \theta) \mid 0 \leq \theta < \pi/3\}$. (I don't understand it fully, maybe drawing of it will help? why at all we are looking only at triangles?)

With all of this in mind it becomes apparent that all AL points satisfied by the condition $0 \leq \theta_i < \pi/3$ uniquely determine all the possible triangular lattice unit cell's primitive vectors. (it is an unclear statement, but it means that we can change one AL vector by value and angle and this will give a condition for all PL vectors)

With this we have exhausted all of the infinitely many possibilities for a commensurate triangular PL.

(images are needed here!!!! it is a bad explanation without them)

If we switch to a cartesian coordinate representation for the AL points $(r_i, \theta_i) = x_i(a, 0) + y_i(a/2, a\sqrt{3}/2)$ (why such numbers are here??? is the angle fixed???) , then the primitive vector of a PL with filling f can be obtained via a simple law of cosines (law of cosines gives the distance, not the filling factor. why is it used here???)

$$1/f_m = x_i^2 + y_i^2 + x_i y_i \quad (2)$$

(here, there is $\cos 120$ degrees, which is fixed because of the AL) (how does this related to the $f = \kappa (k_0 n_0 - l_0 m_0)^{-1}$ formula from the appendix??)

The fillings which satisfy this condition are dubbed as the magic fillings. It is easy to see that $1/f_m = 13$ corresponds to $x_i = 3$ and $y_i = 1$ and $1/f_m = 7$ corresponds to $x_i = 2$ and $y_i = 1$ for example.

One interesting fact can be deduced from the mirror symmetry of the problem with respect to the $\theta_i = \pi/6$ axis in the region $0 \leq \theta_i < \pi/3$.

Every point (r_i, θ_i) representing a polaron lattice primitive vector which is not on the $\{(r_i, \theta_i) \mid \theta_i = 0\}$ or $\{(r_i, \theta_i) \mid \theta_i = \pi/6\}$ line segments can be reflected over the $\theta_i = \pi/6$ axis in order to obtain a primitive vector (r'_i, θ'_i) of a polaron lattice with the same f_m which is distinct from the original. (draw an image about it and put it here!!!! I understand it to 60%)

We define them as having two different chiralities (cannot be superimposed on its own mirror image) .

There is no notion of chirality for lattices with primitive vectors on the line segments $\{(r_i, \theta_i) \mid \theta_i = 0\}$ or $\{(r_i, \theta_i) \mid \theta_i = \pi/6\}$.

In terms of the cartesian coordinate representation the PL has a chirality associated with it whenever the integers x_i and y_i are both non-zero and have different values.

Now consider the case in which the hexagonality condition is not satisfied or in other words, when the system is frustrated.

Taking into account that we have just found all the possible cases of hexagonal symmetry in our system, this proves that all the (other) lattice type configurations of polarons must break hexagonal symmetry.

None of the 5 possible two-dimensional Bravais lattices possess hexagonal symmetry, except for the triangular lattice. (why??? draw!!!)

However, by introducing domain walls, it is possible to also preserve the translational and hexagonal symmetry in the system if the domains assume the shape of identical hexagons. (why “if the domains assume the shape of identical hexagons”)

This is consistent with previous theoretical work^{102,103} (read these works!!!) .

The amorphous states are of course isotropic (why isotropic??) but there is no long range order present (why is LRO important at all??) .

The two important questions now are how do long range ordered (non amorphous) lattice configurations look like and which of them is the most energetically favorable.

A lattice must have a periodic unit cell which is how we categorized all the possible configurations (= we categorize it by two primitive vectors) .

In our analytical considerations two lattice energy calculation schemes we used (calculation of what??? of the gap between the two lowest energy states? why is it needed???) proposed by Pokrovsky et al.⁹² and Arce et al.⁹⁵ (see SI). (learn these lattice energy calculation schemes!!! add these articles!!) (why the first is not used for the case of 2 and 3?)

The former was used to evaluate all the possible lattices with only one polaron in the unit cell and the latter with two and three. (check that I understand, what result is for 1,2 and 3 polarons per cell. I don't know it now...)

We stopped at three due the very large number of possible configurations. (are there reasons why more than 3 can't be in real world?)

SM: Details of the Analytical lattice energy calculations

(SUMMARY: a few extra formulas are here, but again, no good explanation is provided)

Any ordered structure of the particle lattice is characterized by two fundamental lattice vectors:

$$\mathbf{a} = k_0 \mathbf{a}_0 + l_0 \mathbf{b}_0, \quad \mathbf{b} = m_0 \mathbf{a}_0 + n_0 \mathbf{b}_0, \quad (1)$$

where k_0, l_0, m_0, n_0 are integer and $\mathbf{a}_0, \mathbf{b}_0$ are base vectors of the hexagonal lattice.

If the particle lattice has more than 1 particle per unit cell, the positions of additional particles in the unit cell in the case of 2 and 3 particles are determined by vectors

$$\begin{aligned} \mathbf{r}_1 &:= i_1 \mathbf{a}_0 + j_1 \mathbf{b}_0 \\ \mathbf{r}_2 &:= i_2 \mathbf{a}_0 + j_2 \mathbf{b}_0 \end{aligned} \quad (2)$$

respectively. The values of i_1, i_2, j_1, j_2 are also integer.

We performed the calculations only for the case of $\kappa = 1, 2, 3$ particles in the unit cell, therefore there are maximally only two additional positions of particles in the unit cell.

The filling of particles in the system is determined as (why is it so????????? think about it!!!!)

$$f = \kappa (k_0 n_0 - l_0 m_0)^{-1} \quad (3)$$

according to this formalism. (connect it with $1/f_m = x_i^2 + y_i^2 + x_i y_i!$)

The energy of the system per one particle (per one particle??? what do we mean by this formula?? do we fix one particle and calculate how it interacts with all the rest??) is determined by the following formula

$$E = \frac{1}{2} \sum_{k, l \neq 0} V(k\mathbf{a} + l\mathbf{b}) \quad (4)$$

where the primed sum omits the term with $k = l = 0$. This formula describes the energy per one particle in the case of the simple lattice $\kappa = 1$.

In the case of two particles per unit cell ($\kappa = 2$) the energy is defined as: (the last term tells us how the second particle interacts with the rest) (think more about it!!!)

$$E = \frac{1}{2} \sum_{k, l \neq 0} V(k\mathbf{a} + l\mathbf{b}) + \frac{1}{2} \sum_{k, l} V(k\mathbf{a} + l\mathbf{b} + \mathbf{r}_1). \quad (5)$$

For $\kappa = 3$ the energy defined as (why??) (what does the last term correspond to?)

$$E = \frac{1}{2} \sum_{k, l \neq 0} V(k\mathbf{a} + l\mathbf{b}) + \frac{1}{3} \sum_{k, l} \left(V(k\mathbf{a} + l\mathbf{b} + \mathbf{r}_1) + V(k\mathbf{a} + l\mathbf{b} + \mathbf{r}_2) + V(k\mathbf{a} + l\mathbf{b} + \mathbf{r}_1 - \mathbf{r}_2) \right). \quad (6)$$

The sum over k and l were calculated directly using the cut off $-K_0 < k < K_0, -L_0 < l < L_0$, where K_0, L_0 are chosen in the range $500 < K_0, L_0 < 1000$. (check that such values make sense. why are exactly them???)

The error was estimated by the integral $\iint_{K_0, L_0}^{\infty} V(k\mathbf{a} + l\mathbf{b}) dk dl$. The estimated error was typically less than 10^{-10} . (ok, I believe)

8.1.4 Numerical Methods

Monte Carlo Simulations

Results of MC simulations

(SUMMARY: MC simulations just give the phase diagram, there are a lot of phases. If we take Fourier of them, we can check long ranged order and figure out if we can label the state "glass" or liquid", then pretend that it is important)

(how does the MC simulation work???? write it in another note and then write here)

We performed MC simulations (for details on the parallel tempering method we employed see SI) with periodic boundary conditions and analytical considerations in order to find the ground state of the system at fixed fillings f ranging from $1/2$ to $1/21$ with the increment of 1 in the denominator.

The screening radius r_s ranged from a to $100a$ but here we focus on just one value of $r_s = 4.5a$ (others are presented in SI). (forgot, why r_s is chosen as this one?)

SM Table I (given in the SI) summarizes our results for this value of r_s by listing all the energies per polaron obtained analytically (E_a) and compares them with MC simulations (E_S). (reminder: read about them)

We also list the analytically obtained excitation gap Δ to the first excited state for each value of f . (do we need the Δ at all??)

It is clear that all the energies obtained from MC results agree remarkably well with the analytical results up to the accuracy of the MC calculation.

This confirms that MC converged very close to the global minimum of free energy.

From the order of magnitude of Δ we can also estimate the order of magnitude of the hopping parameter required to entangle (why entangle??? when do we talk about entanglement? there is just a one paragraph in the "discussion" about it...) the low lying states $t \gtrsim 0.001V_0$ (for an estimation of Δ and V_0 in the case of 1T-TaS₂ see SI).

The phase diagram of our model reveals four distinct phases which we define as follows.

The crystal phase consists of a perfect long range ordered superlattice of polarons.

The domain state is composed of a textured domain structure without long range order and the domains are local formations of the nearest crystal phase.

The glass phase exhibits no long range order and is amorphous with glassy dynamics.

The liquid phase also does not exhibit long range order, where polarons move around but do not exhibit glassy dynamics. (there is a typo, "liquid phase does not" and "but liquid phase do not", what should be there? anyway, there are a lot of unclear statements everywhere in this article)

Long range order can be defined via the Fourier transform or pair distribution function (PDF). (how do we check the existence of the long range order?)

In the main text we focused on the Fourier transform and the PDF for two cases are discussed in the SI.

Fig. 2 shows a comparison of real space ordering in the low temperature MC simulation and the analytically predicted configurations.

In almost all cases where the hexagonality condition (see section Analytical Considerations) is satisfied (at magic fillings $f_m = 1/3, 1/4, 1/7, 1/9, 1/12, 1/13, 1/16, 1/19, 1/21, \dots$) we observed a collapse of the system to a long range ordered commensurate triangular lattice.

The exceptions are at $f_m = 1/4$ and $1/9$, where topological defects (topological defects??) in the form of domain walls prevent full equilibration (why equilibration is here??? is it in

scope of MC simulations???) that is hard to achieve in our MC algorithm (for a discussion of the effect of topological defects on the simulations see SI (I'll look later)).

Even so, there is no doubt that triangular lattices are still strongly preferred in the two exceptions.

In all cases where the hexagonality condition is not satisfied, there is an absence of long range order.

This is particularly clearly shown in the Fourier transforms (FT) of the large scale real space (see SI) ordering in Fig. 3. (how the FT is related to long ranged order??? how to define in formula a long ranged order??)

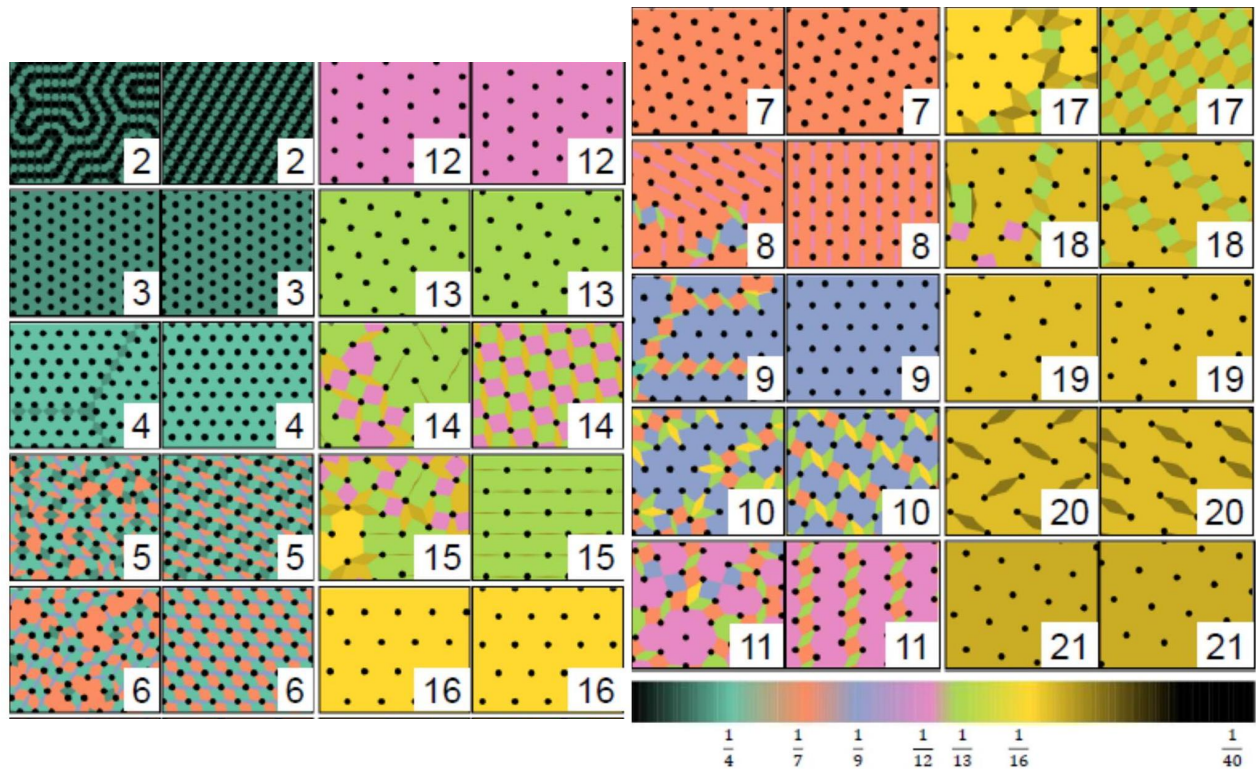


Fig. 2 Comparison of Monte Carlo simulation snapshots at low temperatures with analytical predictions of ground states at different values of $1/f$, where f is the filling of the system.

(how does the coloring work??? why some lines are wide and some are narrow??? i think it is a defect of the display)

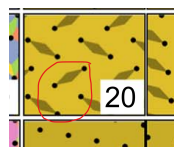
The figure is organized in two columns of pairs with the same value of $1/f$ denoted on each image.

The left image in the pair is always the simulation snapshot and the right is the analytical prediction (how can you get without numerics the right image???) .

The colors in the image represent distances between neighboring polarons and are presented according to the legend at the bottom of the figure.

For details regarding the tiling algorithm see SI.

(the distances look the same, but even if they are different, then the difference is very very tiny, but they are colored in a very different colors. looks like a bad idea to do such plots)



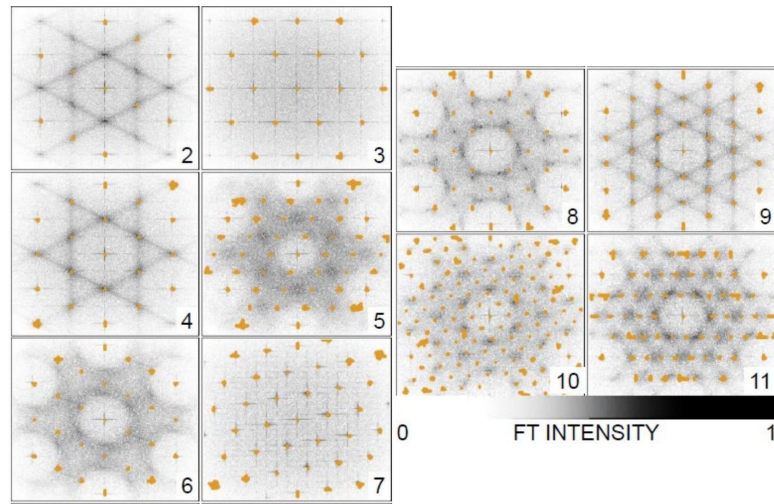


Fig. 3 Comparison of Fourier transforms (what is the formula for it???) of the large scale images in Fig. 2.

The peaks of intensity from the analytical cases are overlaid in orange on top of the simulated cases.

The number in each image represents the value $1/f$ like in Fig. 2.

(why these orange peaks are spots, not points???)

(how to get the peaks analytically??)

The orange points represent the FT peaks of intensity of the analytical long range ordered configurations and are superimposed on the FT of the simulated configuration.

The FTs confirm the presence of long range order in the magic filling cases (since peaks coincide) .

The cases $1/4$ and $1/9$ stand out due to the presence of intensity also in between the expected peaks, which originates from domain walls (why from domain walls???) .

The non-magic filling cases clearly show no long range order due to fact that the peaks of intensity are not located on the expected positions and that they are blurred compared to the sharp analytical peaks.

There is also a significant amount of intensity present in between the peaks.

We also performed MC simulations for different values of r_s . (yes, we remember that there is a discussion of r_s in the SI, it is another ref to it)

The overall trend is that the system becomes increasingly harder to equilibrate at larger values of r_s . (why the screening r_s is connected to equilibration? work out at least an article about the MC simulation!)

These calculations also reveal the presence of phase coexistence and ordering of domain walls, as well as higher energy amorphous states (see SI for examples).

In Fig. 4 we plot the phase diagram of the CLG model on the basis of MC simulations together with the effective (normalized) gap Δ/E_S .

Clearly, the transition temperature increases significantly at magic fillings.

This is also where the phase transition is of the first order, and not a glassy transition as it is for $f \neq f_m$.

By glassy transition we mean that MC simulations indicate the presence of a weak continuous transition at a certain temperature as is depicted in SM Figures 8 through 11, even though it is obvious from the low temperature configuration snapshots that no ordering is present (see SI).

We interpret this transition as the onset of glassy dynamics (onset of glassy dynamics?) , where correlations slow down the movement of polarons and eventually freeze the system.

Therefore, the transition temperature may be regarded as the interaction scale at which the entropy from all the different low energy long range ordered polaron configurations starts to dominate.

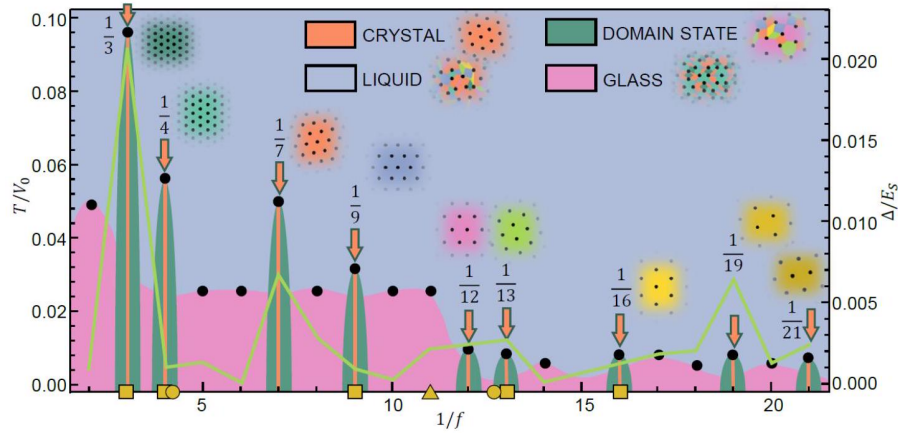


Fig. 4 Charge Lattice Gas phase diagram of temperature T versus $1/f$. ($V_0 = 2.810^{-4}\text{eV}$, as discussed in SI) (what is the value of T in K?) (why do we have a sharp transition from glass to liquid????) (which parameter is used at all to tell us the type of a phase???? or we need to look on the images????)

The liquid, crystal, domain and glass phases are colored in blue, orange, dark green and pink respectively and the boundary between them represents the phase transition.

Magic fillings are marked with arrows.

The green line is the calculated gap between the ground state and the first excited state (note that it has a different scale!) (what is E_S , forgot?) (if you look at the SM Table 1, you can see that the errors for the Δ are 100%, why they are not plotted???) .

The color coding of the commensurate phases is the same as in Fig. 2.

The experimental realizations of the polaron crystal phase are marked with yellow squares:

$$f_m = 1/3 (2\text{H} - \text{Fe}_{0.33}\text{TaS}_2),$$

$$1/4 (1\text{ T} - \text{TiSe}_2, 2\text{H} - \text{Fe}_{0.33}\text{TaSe}_2, 2\text{H} - \text{Fe}_{0.33}\text{NbSe}_2),$$

$$1/9 (2\text{H} - \text{TaS}_2, 2\text{H} - \text{TaSe}_2),$$

$$1/13 (1\text{ T} - \text{TaS}_2, 4\text{Hb} - \text{TaS}_2, 1\text{ T} - \text{TaSe}_2, 4\text{Hb} - \text{TaSe}_2) \text{ and}$$

$$1/16 (1\text{T-VSe}_2),$$

the domain states with yellow circles:

$$f \approx 1/12.6 (\text{photodoped } 1\text{T-TaS}_2, 1\text{TTi}_{0.07}\text{Ta}_{0.93}\text{Se}_2, 1\text{T-TaSeS}, 1\text{T-Ta}_{0.99}\text{Fe}_{0.01}\text{S}_2),$$

$$f \approx 1/4.2 (1\text{ T} - \text{Cu}_{0.08}\text{TiSe}_2)$$

and the glass phase with a yellow triangle:

$$f \approx 1/11 (1\text{ T} - \text{TaS}_2).$$

They are presented in more detail in figure Fig. 5 and main text.

(no, there is no metallic phase here in this model, which very much limits of applicability of it! nothing is explain here about it, so it is an unanswered hard question about obtaining it from some another model which in some limit is this model)

(no, there is no superconducting phase here in this model, which very much limits of applicability of it! nothing is explain here about it, so it is an unanswered hard question about obtaining it from some another model which in some limit is this model)

(another well-known for me problem is that these calculations are done only for TaS2, but it is said that the region of applicability of this model is only near 1/13. there was no

recalculation for other regions (with different V_0 and different screening, which will correspond to other materials). so, my conclusion is that this plot at all makes a very little sense)

(also, we see a lot of predicted glass and liquid state, however, in the article by Sipo there are no such phases at all!)

(another but not so big problem is that the lattice is also distorted because of electrons, and this effect is not taken into account here. but it can be extremely hard (or impossible now) to take this into account, so we can just expect that this effect is much smaller than the analyzed one)

We can speculate that in the quantum case of spinless fermions there are two quantum critical points (quantum critical points??) in the vicinity of each magic filling.

Karpov et al. ⁴⁵ have shown that in the case of $1/f = 13$ the crystal lattice is still present in the system at small negative or positive dopings with the addition of domain walls. (isn't it also shown here??)

If we define the order parameter of the system as the FT peaks (is ever the order parameter defined as a FT???? never heard about it) corresponding to the $1/13$ lattice, then it is obvious that the order parameter does not disappear immediately under doping (since peaks do not disappear) .

It is very natural to assume that this is the case for all magic fillings.

However, at the same time our MC simulations clearly show that if we dope the system enough, the first order phase transition becomes a glassy transition (see SI) (what is this first order PT here?? why is it 1st order???) .

This implies that the order parameter disappears in this case. (why??? there is no order in glassy phase, but was there an order in liquid phase?)

Likely, there is a quantum critical point somewhere in between(why??) .

This is the case for positive and negative doping but the two critical points are not necessarily symmetric around each f_m . (why??)

Also, it is possible that at low enough fillings the two critical points merge and even overlap and therefore disappear, as the magic fillings get closer and closer to one another. (why??)

In order to avoid the scaling of the gap Δ with f we overlayed the plot of the relative gap Δ/E_S (E_S is the energies per polaron, but what is it???) on top of the phase diagram.

The peaks in the plot agree well with the peaks in the phase diagram, which explains the emergence of a first order transition at f_m .

There is a well pronounced free energy minimum at f_m , which is not true in the frustrated case. The cases $1/4$, $1/9$ and $1/16$ stand out due to the fact that a square lattice is energetically very close to the triangular lattice.

This is probably true for every non-chiral lattice (see Analytical Considerations) and it is consistent with the emergence of domain walls in simulations for $1/4$ and $1/9$ fillings as the walls probably cost very little energy compared to the chiral cases.

The plot also clearly shows that even in the case of our limited analytical analysis the frustrated cases of $1/6$, $1/10$ and $1/14$ exhibit a gap which is almost zero (of the order of 10^{-8}) (how to get this value of the gap analytically???) .

We believe that if our analytical analysis would be extended to polaron lattices with 4 or more polarons per unit cell, a further reduction in the value of the gap will occur in all the other non-magic filling cases. (why??)

SM: Monte Carlo Method: Parallel Tempering and its Error Estimation

(SUMMARY: if needed to understand the MC, I'll read it, but now it is not the case, I also doubt that there is an extensive explanation here)

In order to efficiently sample the phase diagram at a substantial number of f and r_s we employed the parallel tempering (PT) Monte Carlo (MC) algorithm as it provides about an order of magnitude of improvement in time efficiency³. In the PT algorithm M replicas are simulated in parallel using standard MC procedures. Each replica has a fixed temperature T_i measured in units of V_0/k_B , where i is the replica index and runs through all M replicas. After a certain number of MC sweeps (MCS) an exchange between replicas is proposed and executed with the probability of

$$p(i \rightarrow j) = \min(1, \exp(-\Delta)), \quad (7)$$

where $\Delta = (\beta_j - \beta_i)(E_i - E_j)$, where $\beta_i = 1/k_B T_i$. There are two main issues with using PT. The question of how many replicas to use and how to distribute the temperatures among them. In our simulations we always used $M = 32$ replicas, as it turned out to be enough to simulate up to about 15,000 particles. With this relatively large number of replicas it was enough to distribute the temperatures in regular intervals ($T_i = T_1 + i(T_M - T_1)/M$). The lowest temperature was 0.001 and for equilibration purposes the highest temperature was always set to be just above the transition temperature of the phase transition at the particular point of phase space in play. For simulation of a single replica we used the standard Metropolis algorithm, where a proposed move consisted of one particle moving one lattice site in a random direction. This was done for 10 MCS between two successive PT exchanges. The proposed PT exchange between replicas was between nearest and next nearest neighbors. In a single equilibration simulation 1000 PT exchanges was typically superfluous in achieving convergence.

One contribution to the error in E_s comes from fitting in the scaling analysis done to obtain E_s in the thermodynamic limit.

Scaling was done from a system size of 100×100 to 175×175 lattice sites.

However, the main contribution comes from the estimation of the boundary effects in the system.

The estimation was done by comparing E_a with the energy obtained from the same scaling analysis as done in MC simulations, but with artificially constructed finite size analytical lattices.

SM: Details of the Fourier transform calculations

(SUMMARY: I'll look it when I need the FT. Right now I don't understand why at all we need to do it, it is not important to know, how to do it for me now.)

In order to highlight the features of interest in a Fourier transform (FT) of a real space particle configuration we employed image editing algorithms provided by the Mathematica programming language. Here is the code snippet use to produce a single zoomed in image of the FT of a plotted real space particle configuration. The variable "pts" represents the real space particle coordinates and "nin" represents $1/(f - 1)$.

```
ColorNegate[Image[ImageCrop[Image[ImageData[ImagePeriodogram[Blur[ImageEffect]
```

```
ListPlot [pts, Axes → False, AspectRatio →  $\sqrt{3}/2$ , ImageSize → 2000, PlotStyle  
→ Black ], { SaltPepperNoise, 2}], 10]]^4], N[300 + (nin - 1)(170  
- 300)/19]], ImageSize → 600]]
```

Exact Diagonalization of a Charged Lattice Gas With Quantum Tunneling

(SUMMARY: suddenly, we do the ED to get the density correlation, just because we are bored)

(what do we try to do with ED here?? calculate the gap????)

In order to substantiate our claim (which claim?? that there is a state of quantum charge liquid? what is even ment by it???) regarding the quantum charge liquid, we carried out exact diagonalization calculations using the Lanczos method in order to find the ground state.

The code used in the calculations was from the ALPS initiative, version v2.3 b1^{107–110}. (read it at least 1 time)

We were interested in how does the introduction of quantum effects such as the hopping of electrons alter the charge order compared to the classical case.

The model we used is the model of spinless fermions with a fixed filling and both nearest and next-nearest neighbor interaction

$$\mathcal{H}_{sf} = -t \sum_{\langle i,j \rangle} (c_i^\dagger c_j + c_i c_j^\dagger) + \sum_{\langle i,j \rangle} V_1 n_i n_j + \sum_{\langle\langle i,j \rangle\rangle} V_2 n_i n_j \quad ; \quad \sum_i n_i = N, \quad (3)$$

where c_i ($c_i^\dagger$) is the annihilation (creation) fermion operator on the i -th triangular lattice site, $n_i = c_i^\dagger c_i$, t is the hopping parameter, V_1 the interaction between nearest neighbors, V_2 between nextnearest neighbors and N is the number of polarons in the system.

We set the system size to 5×5 and $N = 5$ in order to explore the frustrated case of $f = 1/5$ (why this value??) and also set $V_1 = 10$, $V_2 = 5$ and varied t . (why so??)

SM Figure 13 shows the density correlation function $\langle n_i n_j \rangle$ for the classical case $t = 0$ and two quantum cases $t = 0.5$ and $t = 10$. (why do we need this figure at all???)

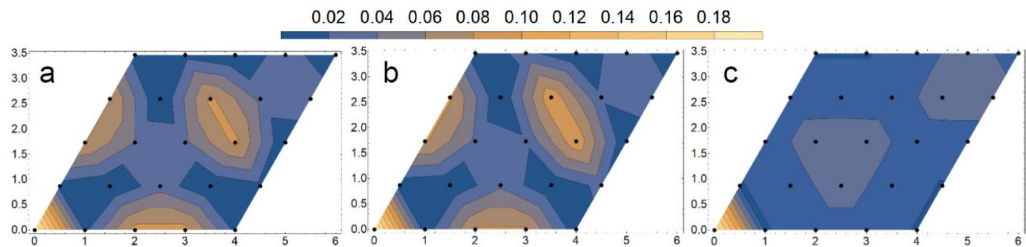
The correlation function clearly shows that for small values of t , the interaction driven charge ordering dominates in the system due to the fact that the correlation functions in the $t = 0$ and $t = 0.5$ cases are practically the same.

This is not the case for larger values of t , where a metallic phase is present as one would expect for a system where kinetic energy of electrons dominates.

These calculations by themselves do not prove the existence of a QCL (quantum charge liquid) because system size limitations limit the accuracy.

Indeed, the density correlation function of the small 5×5 system is substantially different from that from classical Monte Carlo simulations.

However, they do confirm that the presence of a large number of nearly degenerate configurations in the frustrated cases most likely plays a significant role.



SM Figure 13 Density correlation function of a next-nearest neighbor interaction spinless fermion model with nearest neighbor interaction $V_1 = 10$, next-nearest neighbor interaction $V_2 = 5$ and (a) $t = 0$, (b) $t = 0.5$ and (c) $t = 10$. (how it was calculated at all???)

The black dots represent the points at which the density correlation function was evaluated. The color legend for the magnitude of the correlation function is on the top of the figure and is the same for all three cases. The numbers on the frame of each of the three cases

are the real space coordinates.

8.1.5 Experimental Realizations of Predicted Charge Orders

(SUMMARY: there are a lot of TMDCs, which have phases which are described before, so here we collected them)

We have collected all of the experimentally studied systems for which our model is applicable in Table 1.

System	f	Phase
2H – Fe _{0.33} TaS ₂ ¹¹¹	1/3	crystal
1T-TiSe ₂	1/4	crystal
N ₂ H ₄ /1 T – TaS ₂ ¹¹²	1/4	crystal
N ₂ H ₄ /2H – TaS ₂ ¹¹²	1/4	crystal
1 T – Cu _{0.08} TiSe ₂ ⁵⁰	1/4.2	domain state
2H – Fe _{0.33} TaSe ₂ ¹¹¹	1/4	crystal
2H – Fe _{0.33} NbSe ₂ ¹¹¹	1/4	crystal
Alkali/1T-TaS ₂ ¹¹³	$\sim 1/8$	glass
N ₂ H ₄ /1 T – TaS ₂ ¹¹²	$\sim 1/8$	glass
2H – TaS ₂ ¹¹⁴	1/9	crystal
2H – TaSe ₂ ¹¹⁴	1/9	crystal

2H – NbSe ₂ ⁶²	$\sim 1/9$	domain state
Cu/1 T – TaS ₂ ¹¹⁵	1/9	crystal
Alkali/1T-TaS ₂ ¹¹³	1/9	crystal
N ₂ H ₄ /1 T – TaS ₂ ¹¹²	1/9	crystal
PD 1 T – TaS ₂	1/11	glass
1 T – Nb _{0.1} TaS ₂ ⁴⁷	$\sim 1/11$	possible glass
PD 1 T – TaS ₂	1/12.6	domain state
1T-TaSeS	1/12.6	domain state
1 T – Ta _{0.99} Fe _{0.01} S ₂	1/12.6	domain state
1 T – Ti _{0.07} Ta _{0.93} Se ₂ ⁴⁸	1/12.6	domain state
1 T – Nb _{0.04} TaS ₂ ⁴⁷	$\sim 1/13$	domain state
1 T – Nb _{0.07} TaS ₂ ⁴⁷	$\sim 1/13$	domain state
1 T – TaS ₂	1/13	crystal

4Hb – TaS ₂ ¹¹⁴	1/13	crystal
1 T – TaSe ₂	1/13	crystal
4Hb – TaSe ₂ ¹¹⁴	1/13	crystal
1 T – NbSe ₂ ¹¹⁴	1/13	crystal
1T-VSe ₂ ¹¹⁴	1/16	crystal

Table 1 A collection of all the experimentally studied systems for which our model is applicable. (what is the difference btw the models??? how did they find out that it is applicable there?? how did they find these f values???)

Every system in left column for which we were able to extract the filling f within the scope of our model is associated with its f and corresponding theoretical phase in the middle and right column, respectively.

In the six examples in which this was not possible, we specify the corresponding theoretical phase and only the closest f_m in the case of a domain state and the approximate f in the amorphous case with a $\sim$.

Perfect polaronic crystals according to ^{111–115} are realized for the following fillings (systems): (why??)

$f_m = 1/3$ (2H – Fe_{0.33}TaS₂),
 $1/4$ (1 T – TiSe₂, 2H – Fe_{0.33}TaSe₂, 2H – Fe_{0.33}NbSe₂, N₂H₄/2H – TaS₂, N₂H₄/1 T – TaS₂),
 $1/9$ (2H – TaS₂, 2H – TaSe₂, Alkali/1 T – TaS₂, Cu/1 T – TaS₂, N₂H₄/1 T – TaS₂),
 $1/13$ (1 T – TaS₂, 4Hb – TaS₂, 1T-TaSe₂, 4Hb – TaSe₂, 1 T – NbSe₂) and
 $1/16$ (1 T – VSe₂).

In Fig. 5 we show a number of very different examples of charge ordering for which we could determine the system's filling and in which doping is achieved by different mechanisms:

photodoping, isovalent transition metal or chalcogen substitution, non-isovalent substitution (i.e. chemical doping) or interstitial doping.

Most of the images were obtained using an Omicron 4-probe LT STM at 5 K.

The exceptions are the TaSeS image (obtained using a Specs JT-STM at 1 K), Cu intercalated TiSe₂ (images taken from ⁵⁰) and Ti doped TaSe₂ (images taken from ⁴⁸).

The experimental setup and sample growth were described previously ³⁸.

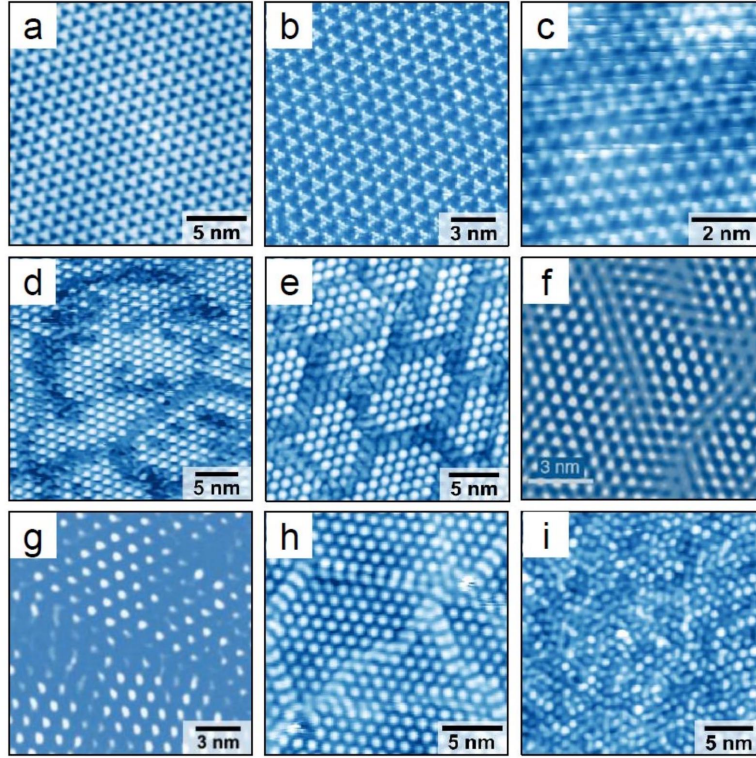


Fig. 5 Scanning tunneling microscope images for selected compounds showing the effect of doping, arranged in three successive groups of polaron crystals, domain states and a glassy state. (do this exercise: determine some f from the image!! how???)

The first three cases **a** – **c** represent polaronic crystals in 1T-TaS ($f_m = 1/13$), 1T-TaSe₂ ($f_m = 1/13$) and 1TTiSe₂ ($f_m = 1/4$) respectively.

The latter cases **d** – **h** represent domain states of 1T-Ta_{0.99}Fe_{0.01}S₂ ($f \approx 1/12.6$), photodoped 1T-TaS₂ ((what is fluence?) fluence $F \simeq 1 \text{ mJ/cm}^2$, $f \approx 1/12.6$), 1T-Cu_{0.08}TiSe₂ ($f \approx 1/4.2$), 1T-Ti_{0.07}Ta_{0.93}Se₂ ($f \approx 1/12.6$) and 1T-TaSeS ($f \approx 12.6$) respectively.

The last case **i** represents a glassy state in photodoped 1T-TaS₂ (fluence $F > 3.5 \text{ mJ/cm}^2$, $f \approx 1/11$).

The first case (Fig. 5a,e,i) of photoexcited 1T-TaS₂ shows the pristine state ($f = f_m = 1/13$), the lightly photoexcited "hidden" state ¹¹⁶ (learn more about the hidden state!!) and moderately photoexcited (moderately photoexcited??) "amorphous" state ⁵¹.

With light photoexcitation, the domain state is reached, while for moderate photoexcitation, an amorphous state is reached.

The measured values of f are $1/13$, $1/12.6$ and $1/11$ respectively.

For $f \neq f_m$, the density is determined by counting the polarons in the respective images using standard procedures described in ⁵¹.

In the amorphous state, f falls in between two magic numbers ($f_m = 1/9$ and $1/12$).

The second case (Fig. 5a,b,h)(why a) is also here???) shows non-isovalent chalcogen substitution from S to Se in $1\text{ T} - \text{TaS}_x\text{Se}_{2-x}$, where the main effect was recently suggested to be effective doping through broken-symmetry-induced hybridization upon local buckling⁴⁹ (broken-symmetry-induced hybridization upon local buckling???) .

The end cases (end cases???) $1\text{ T} - \text{TaS}_2$ (Fig. 5a) and $1\text{ T} - \text{TaSe}_2$ (Fig. 5b) both have $f = f_m = 1/13$, while the intermediate case is superconducting $1\text{ T} - \text{TaSeS}$ ($x = 1$, Fig. 5h) that clearly exhibits domain walls, as expected for $f \neq f_m$.

The estimated filling (by counting polarons) is $f \approx 12.6$, which is similar to the photoexcited hidden state. (how did they get the number 12.6?)

The third example (Fig. 5a,d)(why a) is also here???) shows Fe-doped $1\text{ T} - \text{Ta}_{1-x}\text{Fe}_x\text{S}_2$, which implies chemical doping. The undoped $1\text{ T} - \text{TaS}_2$ (Fig. 5a) has a filling of $f = 1/13$ and the estimated filling in the doped case is $f \approx 1/12.6$ ($x = 0.01$, Fig. 5 d).

The fourth example (Fig. 5b,g) is isovalent TM (isovalent TM?) ion substitution of $1\text{ T} - \text{Ta}_{1-x}\text{Se}_x$ ⁴⁸.

The filling is $f = 1/13$ in the undoped ($x = 0.07$, Fig. 5b) and $f \approx 1/12.6$ in the doped (Fig. 5g) case.

The fifth example presented here (Fig. 5c,f) shows doping of $1\text{ T} - \text{TiSe}_2$ by Cu intercalation⁵⁰. While undoped $1\text{ T} - \text{TiSe}_2$ (Fig. 5c) shows $1/4$ charge order, with $1\text{ T} - \text{Cu}_{0.08}\text{TiSe}_2$, domain walls are clearly seen (Fig. 5f). The estimated density of polarons from the doping level is $f \approx 1/4.2$, which suggests hole doping.

The final example that we highlight here is doping by alkali or N_2H_4 vapor deposition on the surface of $1\text{ T} - \text{TaS}_2$ ^{52,53} where a state emerges with $f = 1/8$, which was dubbed as a commensurate $c(2\sqrt{3} \times 4)$ rect CDW phase. It appears as a result of competition of three energetically equivalent $1/8$ rectangular lattices, which are rotated by 120 degrees relative to each other. The resulting structure is thus composed of small domains of superlattices, which are rotated relative to one another with domain walls in between. For a visual representation see SM Figure 3.

These examples were chosen because they display diverse doping mechanisms, but show generic behavior with doping as predicted by the phase diagram in Fig. 4.

There are also two other compounds worth mentioning, which could not be presented either in Fig. 5 or in the list of polaronic crystals. The case of intercalated $1\text{ T} - \text{Nb}_x\text{TaS}_2$ ⁴⁷ exhibits a $1/13$ polaronic crystal at $x = 0$, a domain state at $x = 0.04$ and $x = 0.07$ and a possible amorphous state at $x = 0.1$. However, we could not reliably determine the system's filling and therefore we excluded this case from the analysis in Fig. 5. It should also be noted, that the role of structural disorder is not clear in this case. The second case is $2\text{H} - \text{NbSe}_2$, which even in its pristine form does not exhibit a perfectly commensurate CDW. However, the work of Chatterjee et al.⁶² has shown that there are indeed local commensurate structures present with phase slips in between. Our polaron picture interprets this as a domain state, which is very intriguing, as it is the only domain state present in the absence of external perturbations to the system.

8.1.6 Discussion

(SUMMARY: there were a very big intro with a lot of irrelevant statements, so this subsubsection looks similar to the intro. Maybe there are interesting comments here, but it doesn't look like it is worth it to read it)

The presented calculations suggest a remarkably simple and generic model for understanding the phase diagram of TMDs with particular focus on correlated configurational ordering.

Our viewpoint intentionally neglects other interactions that may lead to competing or intertwined orders, for example the long wavelength (~ 50 nm) chiral states created by laser pulses ^{1,38}.

We neglect the fact that a Fermi surface instability may win at higher temperatures, when thermal fluctuations destroy local textures caused by Coulomb correlations, or the polarons themselves become unbound.

A good example is 1 T – TaSS₂, where Fermi surface nesting gives a nesting wavevector that gives a real-space charge modulation which is close to the 1/13 structure, and a series of transitions is observed from high-temperature incommensurate order to low-temperature correlated Mott state with 1/13 filling.

Many other TMDs exhibit an incommensurate CDW preceding the CCDW ¹¹⁴ (???) , which means that additional interactions, such as FSN need also be considered in such cases to describe the hightemperature orders.

The model does not address the electronic structure of the resulting compounds, and the emergent phases are not universally insulating as one would expect in a static polaronic crystal. For example, 2H – TaSe₂ is metallic in the CCDW phase down to the lowest temperatures, while others show anomalous resistivity ⁴¹.

The electronic band structure and transport properties may be modelled by DFT calculations of the folded structures ^{40,49} (read it, it can be very useful!!!!) , sometimes achieving quite good agreement with experiments such as angleresolved photoemission for example.

Nevertheless, transport properties still remain anomalous and are often not well understood. Resistivity relaxation measurements suggest that quantum configurational reordering processes may play a role in transport ⁴¹.

(some comments about doping are present below for the one who wants to hear something about doping)

The microscopic effect of doping in all the different compounds is not yet well understood and is not universal.

Substitution seems to cause the formation of more polarons in the system.

Intercalation also seems to cause the formation of more polarons, except for the 1T-Cu_{0.08}TiSe₂ case.

The role of fluence in photodoping has also not yet been fully explored, however the work of ^{1,51} suggest that larger fluences lead to more polarons being formed.

We also note that the isovalent Se for S substitution in 1T-TaS_{2-x}Se_x effectively introduces doping though strain induced by the size mismatch, but the end members (1T-TaS₂ and 1T-TaSe₂) both have $f_m = 1/13$ ¹⁷.

Dai et al. ¹¹¹ show that substantial Fe doping of 2H – TaS₂, 2H – TaSe₂ and 2H – NbSe₂ causes the formation of CDWs with smaller periodicities than the undoped materials (from $3a \times 3a$ to $2a \times 2a$, or $\sqrt{3}a \times \sqrt{3}a$, where a is the lattice constant) above a certain treshold Fe doping level (how is it relevant to the model here???) .

The apparent outlier of all the compounds is 1 T – TiSe₂, where exciton condensation is the proposed mechanism for CCDW formation²⁵. However, this approach on its own cannot explain the presence of the observed DW structure which emerges under pressure¹⁵ or doping with transition metal ions⁴⁸, nor does it take into account Coulomb interactions. We propose that 1T-TiSe₂ might be a good example of cooperation between strong polaron correlations enhanced by exciton crystallisation that favours the CCDW with $f_m = 1/4$.

The model presented in this paper is consistent with the observations in the work of Dai et al.¹¹¹ on Fe doped 2H – TaS₂, 2H – TaSe₂ and 2H – NbSe₂. The change of the superlattice type in experiments can be explained as the change of the magic filling of the present polaronic crystal. They also report on distortions in the superlattice, which is consistent with the domain wall state as well as the amorphous state in between magic fillings.

One interesting fact is the absence of the 1/7 superlattice predicted by the model (where is this absence ??? on the fig. 2, there is a superlattice, no??) , which has not been observed anywhere else.

Doping also seems to increase the importance of the role of correlations in the system due to the onset of commensurability from incommensurability in 2H – TaSe₂ and 2H – NbSe₂. (onset of commensurability from incommensurability?? where is the incommensurability?)

From the presented analytical calculations and the MC results it is clear that for all magic filling cases there exists a global minimum of free energy that corresponds to a triangular polaron lattice.

It might seem that similar magic number filling might appear also on square lattices⁸¹, or other more complex periodic lattices, but this is not the case: Triangular packing is a global energy minimum because a triangular arrangement of polarons with an isotropic interaction is densest possible packing in 2 dimensions.

So a square lattice may give rise to a local minimum of sparse periodic filling, but cannot yield a state that is a global energy minimum. (so there can't ever be square lattices?? sounds strange)

Indeed, as far as we aware, there are no examples of square regular sparse CCDWs on a square (tetragonal) lattices amongst either chalcogenides or oxides. Instead, various frustrated textures form, such as stripes, nematic phases and bipolarons^{67,68,81}.

The induced frustration in all the non-magic filling cases causes the system to break hexagonal symmetry and an amorphous state becomes very close in energy to the analytical ground state. The resulting hyperuniform jammed packing is the densest possible maximally correlated state in 2D that is not periodic. We interpret the fact that an amorphous state is so close in energy to the analytical ground state to be a consequence of the presence of a large amount of entropy even at very low temperatures. There seem to be a large number of states available to the system at low temperatures and they are mixed into an amorphous state even if the temperature is only slightly above zero. We conjecture that in every case where the hexagonality condition (see section Analytical Considerations) is not satisfied, the gap between the ground state and the first excited state can be made arbitrarily small.

From the fact that there are many broken-symmetry states present at low energies, we can speculate that for the quantum case of the CLG model (spinless fermions), where one introduces even a very small amount of nearest neighbor hopping t ($t \ll V_0$) and fixes the system's filling, the ground state will entangle the low lying energy states ($|\psi_i\rangle$) into a quantum charge liquid ($|\psi\rangle = \sum_i c_i |\psi_i\rangle$, where $\langle\psi|\psi\rangle = 1$) analogue of a quantum spin liquid with no long range

order.

The system would therefore have an amorphous ground state which breaks the current paradigm of glass formation by which a crystalline state is the eventual ground state of a glassy system.

It is important to note that t needs to be small enough so that correlations are still dominant in the system but large enough to retain entanglement between the low-lying states. At larger values of $f \neq f_m$ a so called "pinball liquid" state was proposed to be the ground state^{100,117}. However, due to limitations in the system size of quantum calculations, we believe that true long range order is still elusive in the two abovementioned studies. A much larger system size would be necessary in order to achieve conclusive results. An amorphous ground state has already been proposed within the context of frustration between two different length scales of the interaction^{118,119}. In our case frustration emerges from the competition between the interaction-driven polaron lattice and the underlying atomic lattice on which the polarons reside (see Analytical Considerations). The QCL in both the domain state or the glassy regime would in the theoretically ideal case exhibit a homogeneous real space structure, assuming quantum coherence across the whole system. However, in actual experiments impurities would force the system to choose a specific configuration as observed in^{38,51}. Therefore, only states local to the energy of the chosen state would be susceptible to entanglement. An interesting implication which follows is that any kind of observed polaron tunneling or even tunneling between different configurational states could be explained by the QCL concept.

Finally, let us estimate the macroscopic tunneling rate τ between the near-degenerate configurational states. The barrier tunnelling rate depends on the barrier height E as $\tau \sim \exp(-W\sqrt{E})$, where W is a constant. The energy of the system E is proportional to the number of particles involved N , and therefore in the thermodynamic limit as $N \rightarrow \infty$, the tunneling rate $\tau \rightarrow 0$. However, there may be processes in which a finite number of particles N_{eff} are involved, so τ is finite. If the configurations do not differ significantly, the tunneling rate may be significant, and observable.

Reconfiguration processes should show a cross-over from tunneling to thermally-activated classical behavior above some threshold temperature. Experimentally this should be observable as a cross-over from temperature-independent tunneling to thermally activated behavior at some characteristic temperature. Such processes may be observed when a small number of polarons are involved in a slight reconfiguration of domains, for example.

In the amorphous state jamming may inhibit the relaxation process⁵¹, and the system is exceptionally stable, in agreement with observations.

8.1.7 Conclusions

(SUMMARY: Conclusion like Discussion and Introduction maybe has some other interesting comments here, but it doesn't look like it is worth it to read it)

Remarkably, the generic physical picture which emerges appears to predict the CCDWs wavelengths at:

$f_m = 1/3 (2H - Fe_{0.33}TaS_2)$,
 $1/4 (1 T - TiSe_2, 2H - Fe_{0.33}TaSe_2, 2H - Fe_{0.33}NbSe_2, N_2H_4/2H - TaS_2, N_2H_4/1 T - TaS_2)$,
 $1/9 (2H - TaS_2, 2H - TaSe_2, Alkali/1 T - TaS_2, Cu/1 T - TaS_2, N_2H_4/1 T - TaS_2)$,
 $1/13 (1 T - TaS_2, 4Hb - TaS_2, 1 T - TaSe_2, 4Hb - TaSe_2, 1 T - NbSe_2)$
 and

1/16 (1 T – VSe₂).

To our knowledge, other f_m values are not experimentally known until now, but particularly the 1/7 state has a sufficiently distinct energy minimum that it might exist (aren't they saying that all of them should exist?) .

The fact that doping away from f_m leads to the formation of charged domain walls presents a straightforward interpretation of where doped charges reside. Simply counting sites in STM images (Fig. 5) gives the doping level which agrees with the chemical composition. Of course, one needs to take into account that diverse domain wall patterns are present which are both electron-rich and hole rich ^{3,38,45}.

At half-way points between successive f_m values the amorphous phase appears to be experimentally realized by photoexcitation at $f = 1/11$ ⁵¹ or possibly Nb intercalation ⁴⁷. The phase diagram thus suggests that in the quantum case of the CLG (including quantum hopping) two quantum critical points ($T = 0$ transitions) could emerge, separating each f_m state from the amorphous states in between. Due to the extreme near degeneracy present in the domain wall or the glassy case, we speculate that an entangled quantum charge liquid might also emerge in the quantum case of the CLG.

It appears that the ground state of many TMDs forms crystalline polaron order, which seems to not be correlated with Fermi surface properties at high temperatures. Which f_m appears apparently cannot be easily correlated with the band structure. Fermi surface nesting thus appears to be an additional effect, not the underlying cause for the formation of the low-temperature commensurate state. Instead, within our approach, f_m is determined primarily by an interplay between the magnitude of the electronphonon interaction that determines the electron bandwidth in relation to the Coulomb repulsion to satisfy the Mott criterion. The beauty of this viewpoint is that it gives insights into the formation of domain walls and the amorphous order that cannot be obtained from conventional reciprocal space models or DFT.

As the charge ordering within the CLG model emerges (how does it emerge? they just wrote this model and this is all) from the presence of strong screened Coulomb correlations present in the system, all of the listed systems would therefore appear to be dominated by strong correlations at low temperatures.

The temperature where the picture breaks down is related to either the point where polarons become mobile or polaron dissociation, which may be roughly estimated from their binding energy ¹²⁰ (why????????? why mobility of polaron is a case when CLG if not applied? dissociate to what and according to which law of physics???)

$$E_p = \frac{1}{2\kappa} \int_{BZ} \frac{d^3q}{(2\pi)^3} \frac{4\pi e^2}{q^2} \quad (4)$$

where $\kappa^{-1} = \epsilon_\infty^{-1} - \epsilon_0^{-1}$ and ϵ_∞ and ϵ_0 are the high frequency and the static dielectric constant respectively.

Using the published values for the lattice parameters from ¹²¹ and the static ³⁶ and high frequency ¹²² dielectric constant, we obtain $E_p \approx 0.19\text{eV}$ in the case of 1T-TaS₂.

The temperature which corresponds to this energy is about 2200K, which is much higher than any reported phase transition temperature in these materials.

We conclude by highlighting the model's predictions in relation to observed peculiarities which are not easily otherwise understood.

The most obvious is the ubiquitous and immediate emergence of domain wall structures under various kinds of doping of TMDs. The prediction of an amorphous state, as recently observed under specific and unusual photoexcitation conditions⁵¹ in between magic fillings is another.

The model also finally explains the anomalous peak in resistivity with Ti or Hf doping of 1TTaS₂ which occurs at $f_m = 1/12$ ($p \simeq 0.085$) that has been a puzzle since the 1970s³⁷ and has led to the original proposal of a Mott state^{37,65}.

Another beautiful experiment that begs for an explanation is alkali-vapour doped 1T-TaS₂ by Rossnagel et al.^{52,53}, where continuous tuning the electronic correlations by surface Rb deposition reveals a 1/8 state. (check it!! does he write this 1/8 there??)

The experiments of Dai et al.¹¹¹, that reveal a transition from one magic filling to another under substantial doping show that it is possible to move between magic fractions along the doping axis within a single compound.

Finally, given that superconductivity appears in between f_m and coincides with the appearance of domain textures, this work suggests that new superconductors may be searched for in other areas of the phase diagram that were not previously investigated for superconductivity. (which areas??? a useless sentence)

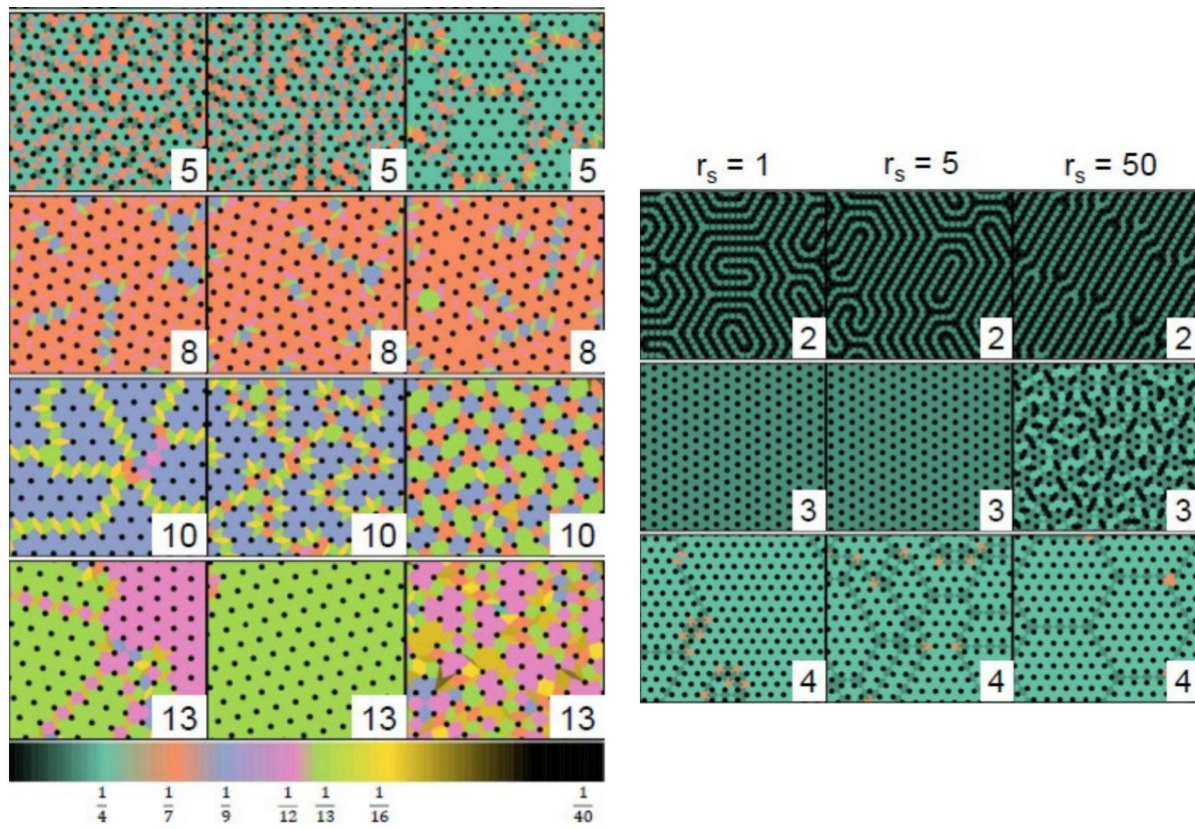
This may also reveal some valuable insight in answering the question how the appearance of textures is related to superconductivity - a question that has wider and persistent significance in cuprates and other textured high-temperature superconductors. (which insights??? a useless sentence)

8.2 SM for “Configurational Electronic States in TMDCs”

(I'll move it later to the theory)

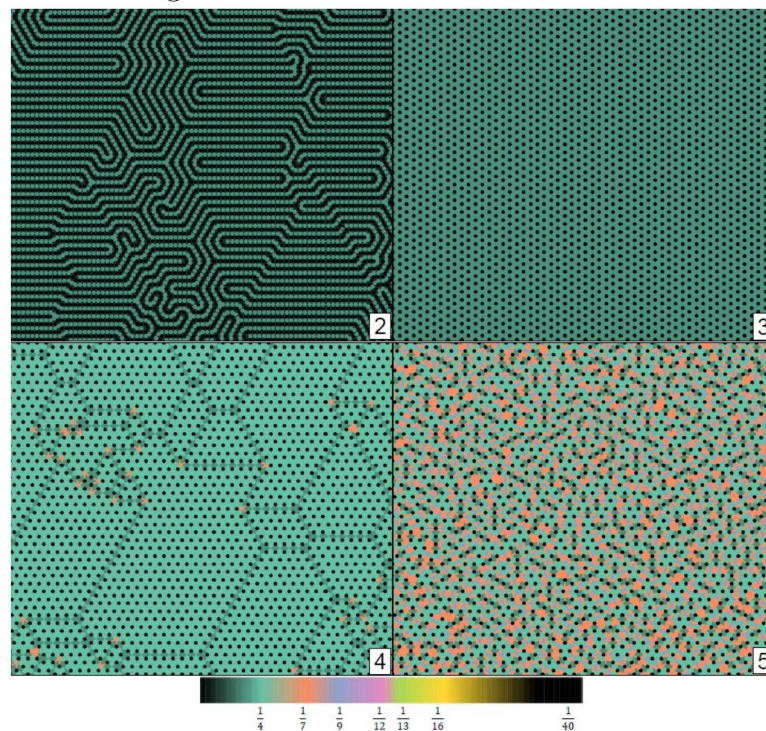
SM: Full Scale Real Space Images of the Cropped Versions in the Main Text

(SUMMARY: just images for your enjoyment)



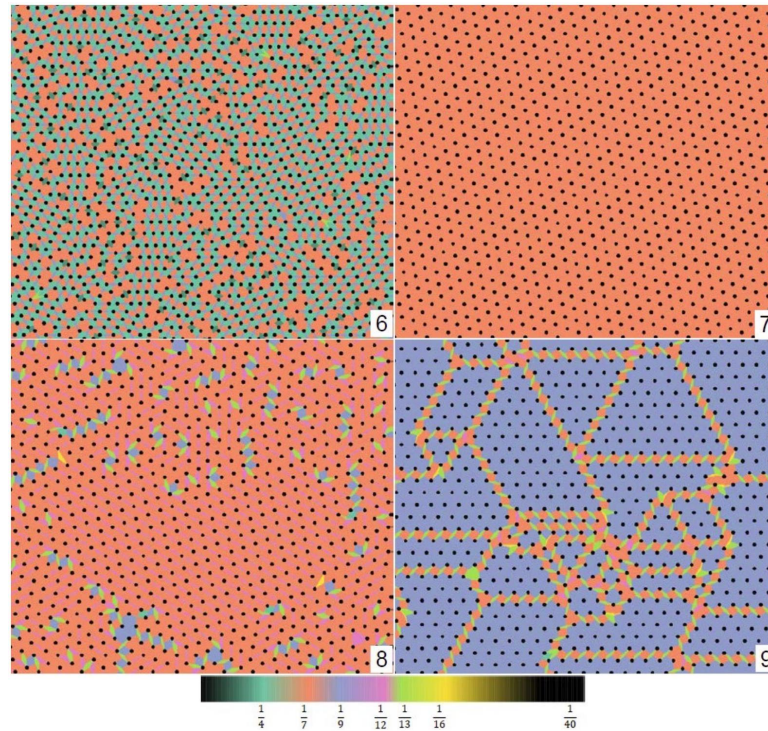
SM Figure 1 Selected cases of low temperature snapshots in MC simulations at different values of $1/f$ and r_s . The values of $1/f$ are in the bottom right corner of each image and the different values r_s are presented in three columns and listed above each column. The colors in the image represent distances between neighboring particles and are presented according to the legend at the bottom of the figure.

Full scale MC snapshots at lowest temperature, which were cropped and used in the main text in Fig. 2 are shown in SM Figures 2-6.

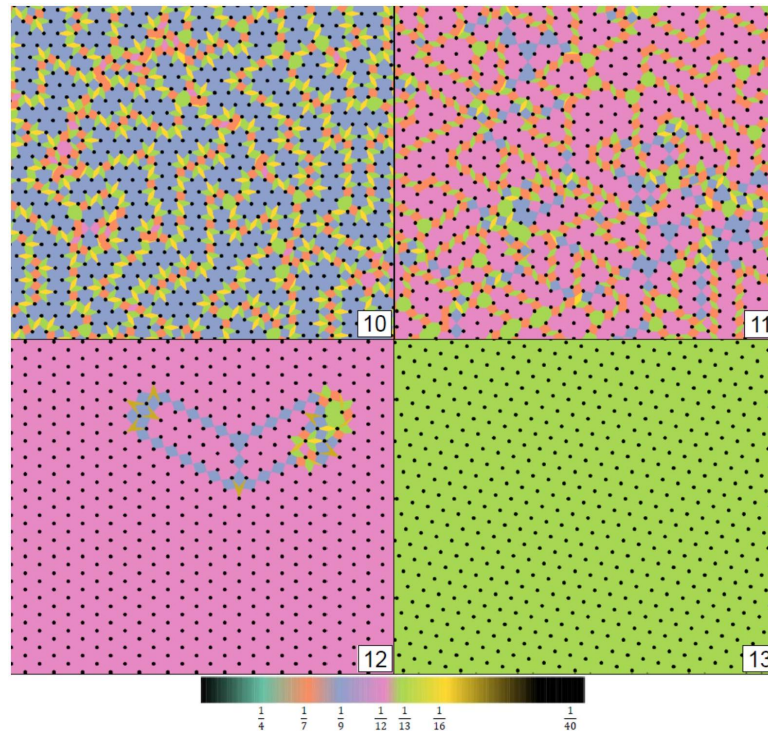


SM Figure 2 Low temperature MC snapshots of particle configurations. The values of $1/f$

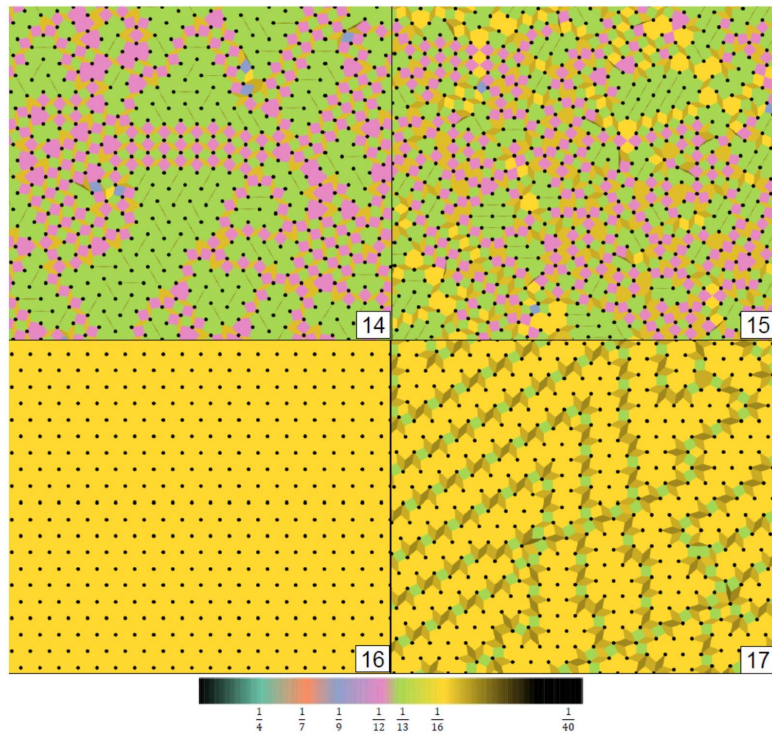
are in the bottom right corner of each image. The colors in the image represent distances between neighboring particles and are presented according to the legend at the bottom of the figure.



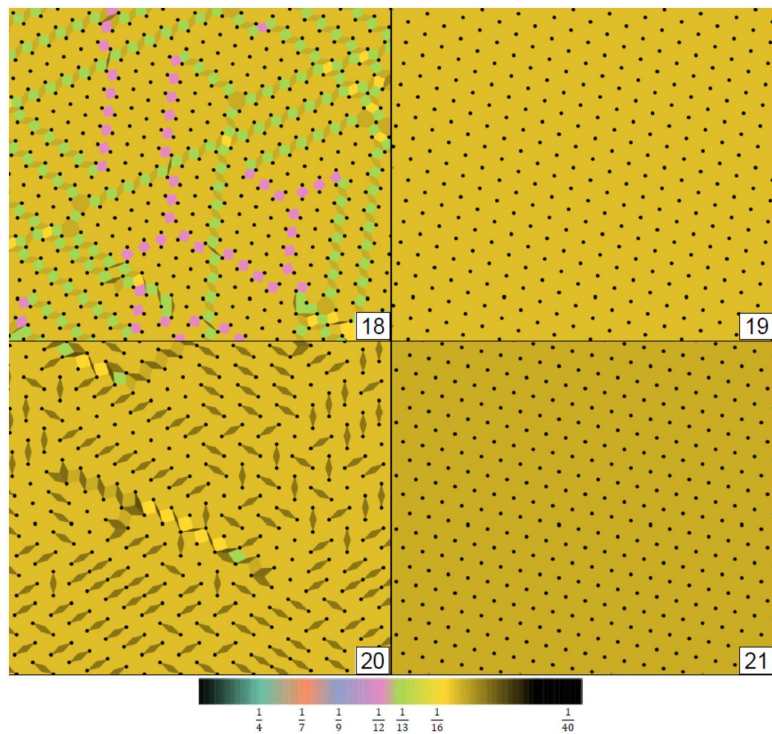
SM Figure 3 Low temperature MC snapshots of particle configurations. The values of $1/f$ are in the bottom right corner of each image. The colors in the image represent distances between neighboring particles and are presented according to the legend at the bottom of the figure.



SM Figure 4 Low temperature MC snapshots of particle configurations. The values of $1/f$ are in the bottom right corner of each image. The colors in the image represent distances between neighboring particles and are presented according to the legend at the bottom of the figure.



SM Figure 5 Low temperature MC snapshots of particle configurations. The values of $1/f$ are in the bottom right corner of each image. The colors in the image represent distances between neighboring particles and are presented according to the legend at the bottom of the figure.



SM Figure 6 Low temperature MC snapshots of particle configurations. The values of $1/f$ are in the bottom right corner of each image. The colors in the image represent distances between neighboring particles and are presented according to the legend at the bottom of the figure.

SM: Details of the Scaling Analysis

(SUMMARY: it is related to MC, since I wasn't doing the MC, I am not interested in the ideas here)

In our scaling analysis we assumed the following scaling relationship between the energy of the system and the size of the system $L \times L$

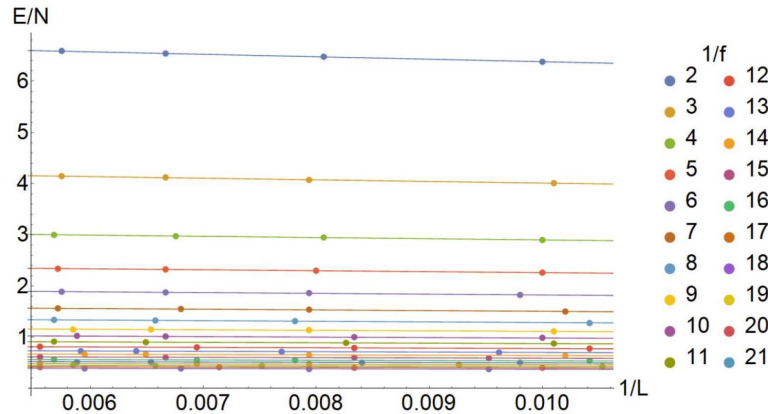
$$E = \alpha L^2 + \beta L \quad (8)$$

where α and β represent the volume and edge scaling constants respectively. Therefore, if we divide the energy of the system by the number of particles which itself scales as L^2 , we obtain

$$\frac{E}{N} = E_s + \frac{\beta'}{L}, \quad (9)$$

where E_s is the energy per particle in the thermodynamic limit used in SM Table 1 and β' is the edge effect contribution. The latter is taken into account as the main contribution to the error of MC simulations. The system sizes used were 100^2 , 125^2 , 150^2 and 175^2 . From the plot it is obvious that the sizes are not exactly the listed values for each f . We varied them slightly around the listed values in order to obtain the exact ratio of particles to lattice sites f .

SM Figure 7 shows the E/N dependence on $1/L$ obtained from simulations.



SM Figure 7 E/N dependence on $1/L$ obtained from simulations together with linear fits for each value of f .

SM: Results at Different Screening Radii

(SUMMARY: I skipped it, looks like there are some extra comments, maybe also about topological defects. It is not written that this theory is useful)

Selected cases of low temperature MC simulation snapshots, which summarize all of the various behaviors we observed is presented in SM Figure 1.

Firstly, topological defects in all the commensurate cases become more difficult to annihilate during simulations due to their nonergodicity.

Due to the interaction between them, which becomes more pronounced at larger values of r_s , topological defects order into a hexagonal lattice. This is very clearly seen in the $1/4$ case.

The $1/2$ case is similar, but due to the symmetry breaking lattice domains, the ordering of defects also breaks hexagonal symmetry.

The $1/3$ case is an example of the fact that MC simulations fail to converge well with increasing r_s .

The hexagonal lattice is still the ground state in this case, yet simulations show an amorphous state.

The $1/5$ case is interesting at large values of r_s because it forms a $1/4$ lattice with point defects which is ordered into a hexagonal array of topological defects.

The $1/8$ case interestingly enough does not change qualitatively with increasing r_s .

In the $1/10$ case there is a change of the type of domain walls from the ones present at small values of r_s ($r_s = a$) to the ones at intermediate values ($r_s = 5a$).

Also, an interesting amorphous structure is present at large values of r_s .

Mind that the amorphous structure need not be the same every time.

It is different depending on which local minimum MC gets stuck in. The $1/13$ ($1\text{ T} - \text{TaS}_2$) case is pointed out due to the fact that phase separation is present at small values of r_s ($r_s = a$).

The two phases are the $1/13$ and $1/12$ lattice.

SM: Table of Analytical and Simulated Energies per Polaron and the Energy Gap

(I still don't understand how it was calculated!!!)

SM Table 1 summarizes our results for the value of $r_s = 4.5a$ by listing all the energies per particle obtained analytically (E_a) and via MC simulations (E_s). We also list the analytically obtained excitation gap Δ to the first excited state for each value of f .

$1/f$	E_a/V_0	Δ/V_0	E_s/V_0
2	6.86443	0.006 ± 0.01	6.864 ± 0.01
3	4.33172	0.09 ± 0.006	4.327 ± 0.006
4	3.13364	0.003 ± 0.005	3.136 ± 0.005
5	2.45051	0.003 ± 0.003	2.449 ± 0.003
6	1.97909	0.00000006 ± 0.003	1.979 ± 0.003
7	1.64005	0.011 ± 0.002	1.641 ± 0.002
8	1.4028	0.004 ± 0.006	1.409 ± 0.006
9	1.21494	0.001 ± 0.002	1.217 ± 0.002
10	1.0766	0.0002 ± 0.002	1.078 ± 0.002
11	0.95727	0.002 ± 0.002	0.958 ± 0.002
12	0.854387	0.002 ± 0.002	0.856 ± 0.002
13	0.773243	0.002 ± 0.002	0.774 ± 0.002
14	0.706357	0.000001 ± 0.001	0.707 ± 0.001
15	0.64818	0.0004 ± 0.002	0.648 ± 0.002
16	0.594414	0.0007 ± 0.002	0.594 ± 0.002
17	0.552821	0.001 ± 0.001	0.551 ± 0.001
18	0.512662	0.001 ± 0.001	0.514 ± 0.001
19	0.475777	0.003 ± 0.002	0.476 ± 0.002
20	0.445802	0.0005 ± 0.002	0.447 ± 0.002
21	0.416978	0.001 ± 0.001	0.418 ± 0.001

SM Table 1 Comparison of energies per particle calculated from analytical considerations E_a and Monte Carlo simulations E_s for different filling of the system f . The value of the screening radius is $r_s = 4.5a$. (why the arrow bars are so big for the Δ ???)

It is clear that all the energies obtained from MC results agree with the analytical results up to the accuracy of MC.

SM: Topological defects

(SUMMARY: just some statement, nothing is important or explained is here)

A topological defect in this case is the shift of at least three lattice domains with respect to one another (sounds not connected to topology) , where the three lattices have the same filling and chirality.

They are caused by incommensurate boundary conditions (incommensurate boundary conditions?) , where the lattice which wants to form is not commensurate with the finite sized system on which it is simulated.

The reason why we call it a topological defect is the fact that only a change in the boundary of the crystal would annihilate it (why??) (again, sounds not connected to topology) .

The mechanism of formation of topological defects is a consequence of the nature of the first order transition (from liquid to crystal?) in the magic filling cases (why??) .

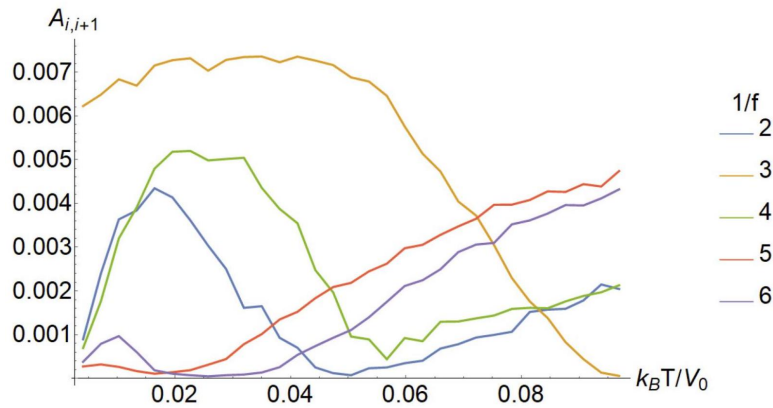
Multiple nucleation sites emerge in the system at the critical point from where the crystalline phase spreads through the system.

They meet in the form of line shaped domain walls and domain wall crossings, which are the topological defects.

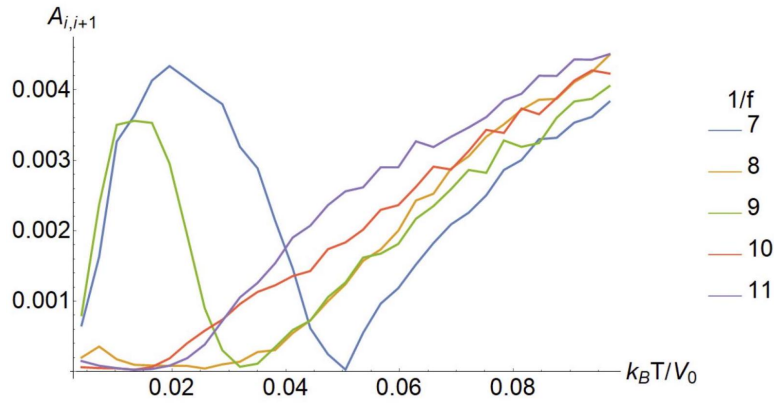
SM: Details on Obtaining the Phase Diagram

(SUMMARY: I skipped this, there is a new strange parameter A , which might be connected with the pattern of electrons which we see. It is not clear how is it connected, so I consider it as a some auxiliary not successful attempt to predict a state from the knowledge of f)

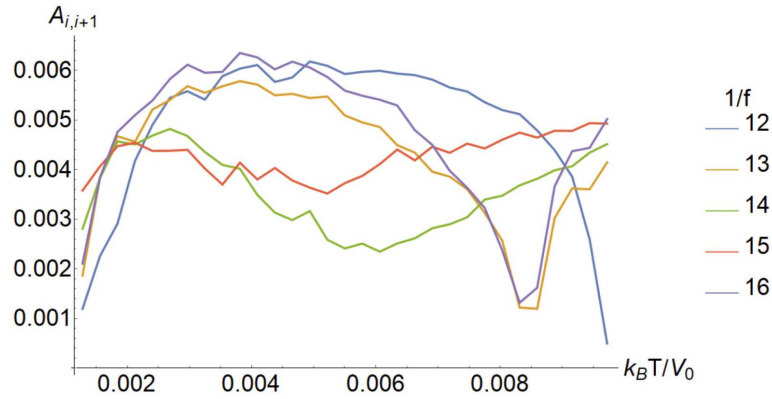
The phase diagram presented in Fig. 4 of the main text was obtained with the help of the acceptance ratios between nearest neighbor replicas $A_{i,i+1}$ dependence on the replica index i within the parallel tempering MC scheme. $A_{i,i+1}$ is defined as the ratio between the number of accepted nearest neighbor replica exchanges and the number of proposed exchanges. It is well known that the acceptance ratio gets suppressed in the presence of a phase transition ^{6–8}. Since each replica represents a fixed temperature, we can use this fact as a measure of the type of transition and the transition temperature. SM Figures 8-11 show the stark difference between magic filling and non-magic filling cases.



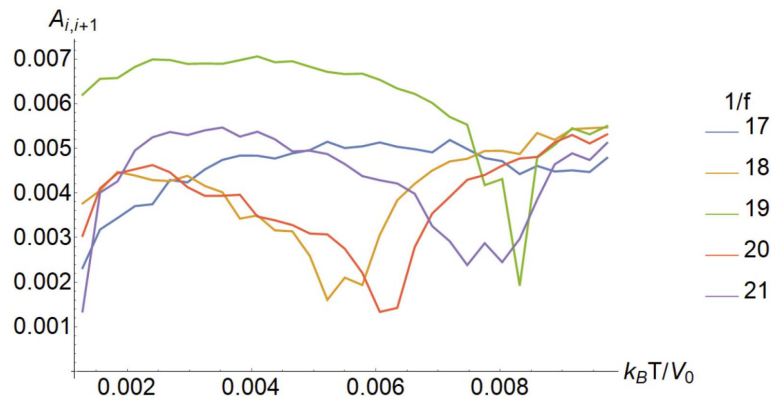
SM Figure 8 Acceptance ratio between nearest neighbor replicas $A_{i,i+1}$ dependence on temperature for one of the magic filling cases $1/f = 2 - 6$.



SM Figure 9 Acceptance ratio between nearest neighbor replicas $A_{i,i+1}$ dependence on temperature for one of the magic filling cases $1/f = 7 - 11$.



SM Figure 10 Acceptance ratio between nearest neighbor replicas $A_{i,i+1}$ dependence on temperature for one of the magic filling cases $1/f = 12 - 16$.



SM Figure 11 Acceptance ratio between nearest neighbor replicas $A_{i,i+1}$ dependence on temperature for one of the magic filling cases $1/f = 17 - 21$.

It is obvious that in SM Figure 9 in the case of $f_m = 1/7$ there is a first order phase transition at the temperature $0.05k_B T / V_0$ due to the sharp suppression of $A_{i,i+1}$.

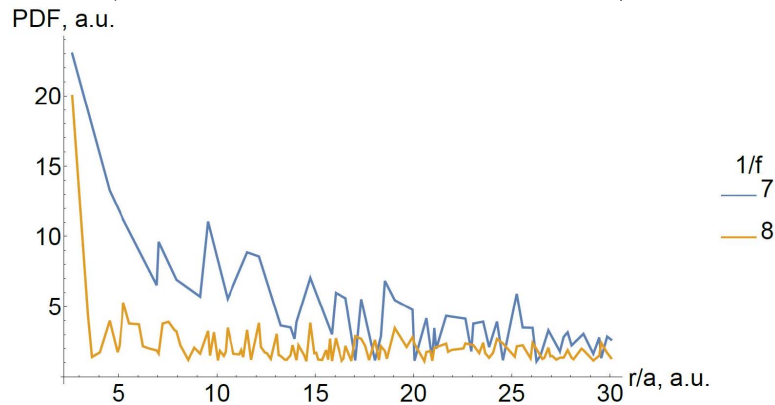
This is how a first order phase transition to a crystalline state is exhibited in terms of the $A_{i,i+1}$ temperature dependence.

However, for example in the frustrated case of $f = 1/8$ there is a gradual decrease of $A_{i,i+1}$ present down to very low temperatures. Another example is in SM Figure 10 in the case of $f = 1/14$, where there is an upturn in $A_{i,i+1}$ after the descent. Both of these examples are a signature of a continuous glassy transition to a low temperature frozen state. The two examples only seem different, when in fact, there is also a slight upturn in the $f = 1/8$ case, only it is not as easily seen due to the large range of the $A_{i,i+1}$ scale. These faint minima of $A_{i,i+1}$ compared to the sharp ones in the case of crystallization ($f_m = 1/7$) are interpreted as the glassy transition temperature. The critical temperature was taken to be right before the acceptance ratio reaches the end of its descent.

SM: Pair Distribution Functions of MC Simulation Results for $f_m = 1/7$ and $f = 1/8$

(SUMMARY: I skipped this, I believe that some consequences for the PDF measurements can be obtained from MC simulations. Maybe. If needed, I'll read it later)

The case of $f = 1/8$ is an interesting one, as three degenerate rectangular lattices represent the three possible ground states exactly as presented in ⁹. However, in simulations, even at very low temperatures, the three lattices are always present in mesoscopic domains, separated by domain walls. This structure does not exhibit long range order, which can be seen from comparison of the pair distribution functions in the case of an ordered structure ($f_m = 1/7$ lattice) and the $f = 1/8$ case. The comparison is presented in SM Figure 14. The absence of long range order and the glassy phase transition presented in the previous section (Details on Obtaining the Phase Diagram) has convinced us to label the $f = 1/8$ case as a glassy phase.



SM Figure 14 Pair distribution function (PDF) dependence on distance between polarons in the case of $f_m = 1/7$ and $f = 1/8$. In both cases all the values below 1.1 have been omitted for clarity's sake. In the case of $f_m = 1/7$ a clear power law dependence is seen as expected in the case of long range ordered structures. In the case of $f = 1/8$ a fast exponential decay is clearly evident as is expected in the case of short range correlated structures.

8.3 My Discussion

8.3.1 My Conclusion about the Article

(A confusing model is presented in this article. it does not predict the metallic state. it predicts a lot of peaks, which are not present for the same material (at least I don't know an experiment where the plot of doping was obtained to check it with predictions). the limit of applicability is not clear. I see nothing useful in this model right now. I see now way how to connect these results to other models, I need to read more articles and then I'll return to this one again. Also, I did not understand mathematics here because it wasn't well explained and

also because I didn't spend extra 5 hours on trying to guess what they mean. Maybe if needed I'll try it with chat GPT or just think myself again later)

8.3.2 Possible Next Steps for Research Using These Results

Do similar calculations for other materials (calculate V_0)

(!!! elaborate this idea!!!)

Check how well this theory is applicable for other 2D materials. Write explicitly the limit of applicability of it

(it is very unclear what this limit is)

8.3.3 Questions

Does this model reproduce the NCCDW phase, where there are ordered domains?

(????? no, but why??? it is a big problem. often there are ordered domains, as was exemplified by Sipos et al. so, my conclusion is that this model is barely applicable, this is why it does not reproduce the NCCDW phase)

To which materials this approach is applicable and to which it is not?

They write about a lot of materials, but why the model is applicable for such many of them? What about other 2D materials, why they are not writing about them???

Is CLG model applicable for all TMDCs?

(????)

Is the TaS₂ better than other TMDCs for this model? Why was it chosen as a main example? Why the TB model was calculated for the its parameters, but then applied to other materials, which should have different parameters?

(??? I forgot, do we focus in this article on it or no? maybe no, this article is about all the TMDCs... but I don't understand the limit of applicability of the formulas here)

Is the prediction for the states (glass/domain/pattern) applicable for all TMDCs?

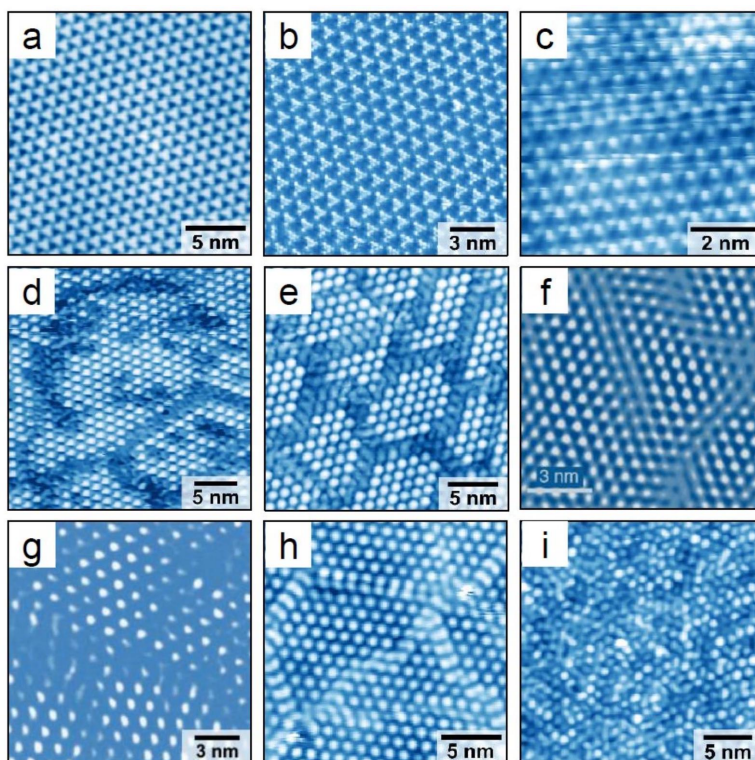
(???? they assume something so)

To which 2D materials the predictions of configuration is not applicable and why?

(???? I don't understand the clear criterion)

Which analytical methods and how can be used to tell us something about the results of fig. 5?

Fig. 5:



(????????? so okay, we can calculate the f , maybe, so what is next???? it is even not clear how to get the f ???)

Do at least one analytical calculation

(??? I don't know how to do it, I don't understand it well, it is a good practice)

Why is it important at all to know the long ranged order and glass/liquid transition?

What is the difference between glass and liquid here?

(maybe long ranged order, but what does it really mean??? and which formulas are used for both?)

Do we really need to consider electrons here as polarons?

(??? I am not sure, since we use just the CLG model, so maybe we can just call them electrons??? anyway we are not using explicitly the EP interaction)

9 Mottness collapse without metallisation in the domain walls of triangular-lattice Mott insulator 1T-TaS₂ by Skolimowski, Gerasimenko, Žitko (2019)

Abstract

1T-TaS₂ is a charge-density-wave (CDW) compound with a Mott-insulating ground state.

The metallic state obtained by doping, substitution or pulsed charge injection is characterized by an emergent CDW domain wall network (we are working in this hidden state which is obtained by laser pulse or something, this is why DWs are not present on a typical phase diagram) , while single domain walls can be found in the pristine (pristine=original) Mott state (Mott state also at some point will have a DW, it will not be a CCDW though all the material) .

Here we study whether and how the single walls become metallic. (can DWs be metallic or non metallic??? what is meant by this statement? I thought that they are always metallic, since other electrons travel through them, no?)

Tunneling spectroscopy reveals partial suppression of the Mott gap (Mott gap??) and the presence of in-gap states (in-gap states???) strongly localized at the domain-wall sites (why localized ???) .

Using the real-space dynamical mean field theory description of the strongly correlated quantum-paramagnet ground state (strongly correlated quantum-paramagnet ground state?) we show that the local gap (there is a different gap at each spatial coordinate) suppression follows from the increased hopping along the connected zig-zag chain of lattice sites forming the domain wall.

Also we show that full metallisation is preempted (preempt=to take action in order to prevent something from happening) by the splitting of the quasiparticle band into bonding and antibonding (antibonding, bonding?) sub-bands due to the structural dimerization (dimerization?) of the wall, explaining the presence of the in-gap states (in-gap states?) and the low density of states at the Fermi level.

9.1 Article

(SUMMARY: We have a model that gives results which coincides only qualitatively with experiment. the model is very complicated and it does not reproduce exactly the experimental results)

The interplay between superconductivity (SC) and correlated insulating phases, such as Mott insulators and charge density waves (CDW), is one of the central problems in condensed-matter physics (this statement shouldn't be taken seriously) .

Remarkably, their combination can be found even in simple (we know that they are not simple) material systems, such as transition metal dichalcogenide (TMD) van der Waals compound 1T-TaS₂ (why van der Waals compound??? can I apply the vdW theory for it???) .

The ground state is a Mott insulator [1, 2, 3] with CDW [4] and unconventional quantum spin liquid behavior [5, 6, 7, 8, 9, 10]. (learn more about the GS of TaS₂)

Upon Se substitution [11], Fe intercalation [12], or by applying pressure [13] it becomes superconducting, with both CDW and correlated behavior still present. (I know it, but it maybe these articles are well-written, so I'll read them later)

Further control over electronic properties is possible through non-equilibrium charge injection via ultrafast optical or electrical pulses [14, 15, 16, 17, 18, 19, 20, 21], which lead to drastic insulator to metastable metal transition.

The long-standing hypothesis for metallisation (hypothesis for metallisation??) and SC onset (hypothesis for SC onset?) is linked to the formation of CDW domain walls (are the domain walls really connected to sc and metallisation???) , seen in multiple TMDs with different techniques [22, 23, 24].

(are there metallic DWs in the Mott insulating state??? they shouldn't be there, maybe for a little time after some nonequilibrium process)

Recently, it was challenged experimentally with scanning tunneling spectroscopy (STS) [25], which showed the absence of metallisation in certain types of walls (what is the criterion of

metallisation? how a metallisation can be in the wall and not in the material? the current should flow in the wall and in the material both) .

First-principles calculations revealed that atomic reconstruction (atomic reconstruction??? is it a physical effect?) in the walls may cause the formation of bound states [25] and band reconstruction [24] (interesting, read about first-principles calculations for the DWs) , but the correlation effects were left out of scope.

Thus, the crucial question of whether the CDW distortion (is the CDW distortion the same as atomic reconstruction???) inside the wall can lead to Mottness collapse remains open. (what is the question and why is it important?)

In this paper we combine STS (scanning tunneling spectroscopy) and dynamical mean field theory (DMFT) (why the dynamical method is used for calculations of static properties??? (abstract question)) calculations to study the behavior of the Mott gap in CDW domain walls (can the wall be not a CDW domain wall but another wall (in this material)??) , finding Mottness collapse without metallisation. (what they did not see to conclude that it is without metallisation?)

In 1T-TaS₂, each layer is periodically modulated to form a $\sqrt{13} \times \sqrt{13}$ superlattice of David star deformations [4] (David stars are created of the Ta atoms, S atoms are on top and bottom of it and create another layer) (check this article, it should be useful) , resulting in a commensurate CDW state with a single half-filled electron band at the Fermi level [26, 27].

(half-filled electron band??? how is it??? draw. find the experimental plot of it)

The Coulomb repulsion opens a charge gap in this band, resulting in a Mott insulating ground state [2, 28, 36, 30, 31] (learn it deeper from the articles!) .

Single CDW domain walls (DWs) [17, 25, 32] can be found connecting large lattice inhomogeneities in freshly cleaved (=split or cut apart with force) samples or they remain after the relaxation of the metastable metallic mosaic state created with voltage pulse (what is the voltage pulse? electrons or extra field???) from the scanning tunneling microscope (STM) tip. (yes, two ways how they can appear) (I guess that if we have lattice inhomogeneities, then the DWs will be robust do external influence)

We study both (a bad sentence, there are no "both" something here. there is no sense in thinking about it) examples and find the relevant physics similar.

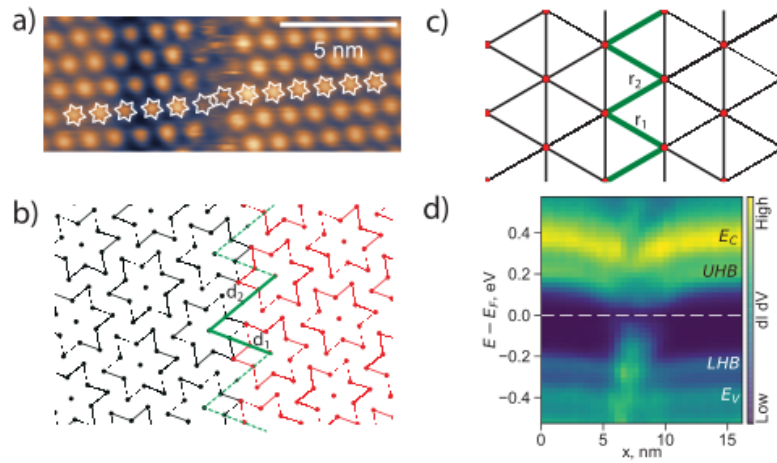


Figure 9.1: Domain walls in 1T-TaS₂. (a) STM topographic image of a single domain wall separating two adjacent CDW domains (other authors are assured that these are the polarons, not CWD, but maybe it is not important herer) ($V_{\text{tip}} = -0.8$ V, $I = 100$ pA, $T = 4.2$ K) (why exactly these parameters were used? below, we have a different V dependence, why exactly the 0.8 is chosen????) . (the David stars are not seen here, I see only balls, why still they are there?) (I see the same configuration of electrons at the left and right. what it I had a different configuration of lattice???)

(b) Schematic diagram of the configuration of David stars near the domain wall: the stars along the wall are brought closer together.

The modified center-to-center distances are indicated as d_1 , d_2 .

(c) Hubbard model description of the domain wall: one-dimensional zig-zag chain with modified hoppings (ratios r_1 , r_2 , green line) embedded in a two-dimensional Mott insulator environment.

(d) (how to understand this plot???) dI/dV map across the domain wall (domain wall A, DW-A, averaged over longitudinal direction).

LHB and UHB are lower and upper Hubbard bands (what are the lower and upper Hubbard bands???) , E_c and E_v indicate the additional conducting and valence bands associated with the Ta d -shell.

Topographic STM image, Fig. 9.1(a), reveals individual David stars as bright spots packed in a triangular lattice. (here we don't see stars, but ok, maybe another experiment has told us that exactly it is there)

The DW is seen as a misfit of the lattices on left and right sides: David stars partially overlap and are shifted with respect to each other.

(we see it as many misfits, so there are many different t -s between each site. this is why we have a plot over different t -s.) (is it correct???)

Among the twelve possible DW types (twelve possible DW types???) only a few are observed experimentally[17]: indeed, in the most commonly seen DWs, the stars are drawn closer together, Fig. 9.1(b), but still retain their shape; see Supplemental Material (SM) for an extended discussion.

The DW is very localized (how can the DW be localized???) , approximately two superlattice constants in extent, so that its core (core of a DW???) roughly consists of a 1D zig-zag chain of the nearest-neighbor stars, Fig. 9.1(c). (so this is how along only this line there can be hopping) (but the DW is though a lot of stars, not near neighboring stars???? I don't see on the STM that we have a one line)

The tunneling spectra, Fig. 9.1(d), reveal the apparent Mott gap closing at the DW (where is that line x , where the gap closes?) (I see that there is an increase in the gradient of current

at one region in x (and decrease in another part of energy in the same region in x) why the gap is closing????), while the clear bending of the Hubbard bands outside the DW indicates its charging (charging?? charging of a band??) .

The CDW gap is quite robust, except at the very center of the DW.

Changes to the Mott gap occur on significantly larger spatial scales(which spatial scales???) , allowing us to decouple the two gaps.

(so where is the CDW gap and where is the Mott's gap?)

The spectral weight is distributed unevenly along the DW (see SM), suggesting finite scattering(why finite scattering???????) .

Closer inspection of the high-resolution density of states (DOS) in the Mott gap, done on another DW sector, shows two more major features:

(i) inside the DW, the DOS (how the DOS related to the current??? maybe I was learning it ago, I just forgot..) is significantly reconstructed and a small non-zero weight (which weight???) appears at the Fermi level, and

(ii) in-gap states at -70 mV are present on top of a smooth spectrum, see Fig. 9.2(a).

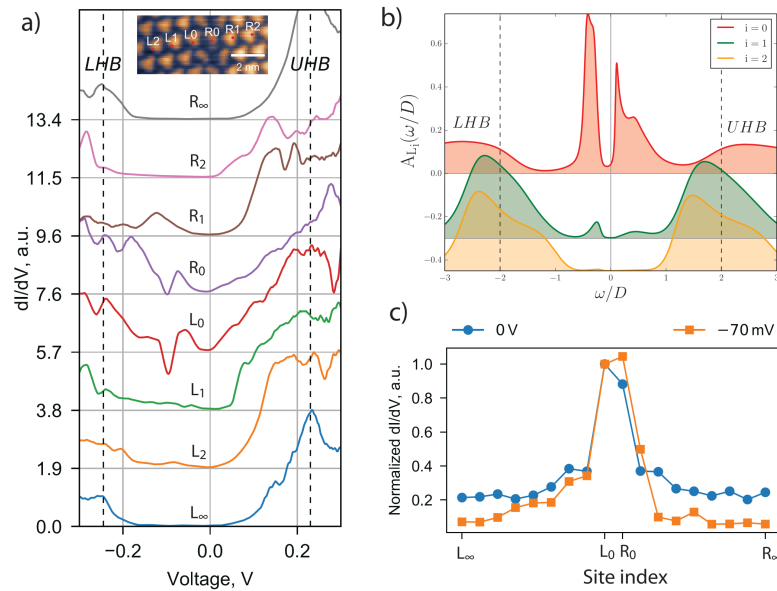


Figure 9.2: Sub-gap features in the domain wall.

(forgot, why we measure exactly the dI/dV ???) (a) Position-resolved dI/dV tunneling spectra across the domain wall B (DW-B(this is the one that is shown on insert)). (why we don't have even balls at all here??? they look more like triangles!!!)

L_i and R_i indicate left and right side; i counts the distance from the domain wall centre in units of supercells.(the index i is there in the subscript of A)

The spectra are offset for clarity, the horizontal grid lines correspond to $dI/dV = 0$ level for each curve. (there is the x position on the left axes)

(b) Theoretical prediction for the spectra at the domain wall and in its vicinity.(what does this spectra mean????) (!!!! HOW DOES IT RELATE TO OTHER OBTAINED PLOTS IN THE ARTICLE?????)

(c) Cross-sections of spectra at selected voltages: at Fermi level (blue line, $V = 0$) and at the in-gap level (orange line, $V = -70$ meV). (why exactly such voltage???)

Spectra are normalized to the value at the point L_1 .

We now construct an effective model to understand the observed low-energy behavior in the DW. (which exactly question should be answered, which phenomena should be explained???)

The minimal model for the Mott state in TaS₂ is the single-band Hubbard model on a triangular lattice at half filling [33, 34, 35, 36, 36, 30, 37]: (has it been used for TaS₂ somewhere successfully?)

$$H = \sum_{\langle i,j \rangle, \sigma} t_{ij} c_{i\sigma}^\dagger c_{j\sigma} + \sum_{i\sigma} \epsilon_i n_{i\sigma} + \sum_i U_i n_{i\uparrow} n_{i\downarrow}, \quad (9.1)$$

(??? why there is no interaction btw neighbours, only self interaction of different spins is present???)

(???? why at all we have a Hubbard model here???? was it derived somewhere from the Frohlich model?)

where i, j are site indices, $\sigma = \uparrow, \downarrow$ is spin, $c_{i\sigma}^\dagger$ are electron creation operators, $n_{i\sigma} = c_{i\sigma}^\dagger c_{i\sigma}$ are the local electron-occupancy operators, t_{ij} are the hopping constants between nearest-neighbors, ϵ_i are the on-site potentials, and U_i are the Hubbard repulsion parameters.

Down to the lowest temperatures, TaS₂ does not order magnetically [6, 9] (order magnetically? is it important???) .

A simple approximation to describe this experimentally observed paramagnetic Mott insulating state, theoretically predicted to exist in a range of U between the paramagnetic metal and the 120° Néel ordered state (what are these values???) [38, 39], is the DMFT [40, 36].

This approach can be generalized to the inhomogeneous case (is it the case here? how it is used then here???) [41, 42, 43, 44, 45, 46, 47, 48, 49, 50].

Here we assume the DW lattice structure (DW lattice structure ??? that it does not distort the lattice???) to be predetermined and fixed, and we focus on the effects of such a deformation on the electronic degrees of freedom (to the electronic degrees of freedom??? to the electrons??? what is meant by this??? that we have a static atomic lattice and it makes electrons hop somehow particular???) .

The modified separation between the stars in the DW is reflected in a change of the corresponding hopping constants t_{ij} (why don't we change the lattice itself????? lattice shouldn't also be fixed, maybe they just neglect this) due to a different overlap of the corresponding Wannier wavefunctions; see the adjacent black and red stars in Fig. 9.1(b), represented by the green line in Fig. 9.1(c).

The rescale factor for the hopping constants will be denoted as r . (In unperturbed bulk $t_{ij} \equiv t$, while $t_{ij} = rt$ for i, j belonging to the DW.) (so in both GSs (both sides of the DW) there is the same t , since we expect to have the same distance between them) (note that they always consider a DW as a line!!! other features of the DW are not included in this model (if DW is not a line))

The superlattice deformation along the DW has a longitudinal component (why longitudinal component??? do we see it on STM?) leading to a period-2 modulation of r along the DW (the values will be denoted by r_1 and r_2). (this is very strange!!! I thought these are the upper and lower values of the phase diagram, not related to the modulation... why???)

Next, we allow for a modification of the on-site energies ϵ_i resulting from the deformation of the stars. (how do they dependent on the deformation???)

The additional on-site potential at the DW sites will be denoted as δ (so they write $\epsilon_{\text{DW}} = \epsilon + \delta$. they are changed by a constant, there is no non-trivial dependence) .

(why the on-site potential is not also in U ???)

For simplicity we assume that the Hubbard constants remain uniform, $U_i \equiv U$. (shouldn't they because of the same argument be not constant?)

We set $U = 4D$ (why $U = 4D$???) , where $2D = 9t$ (why $2D = 9t$???) is the bandwidth of the triangular-lattice DOS.

We fix the chemical potential in the centre of the bulk Mott gap (bulk Mott gap???) .

We now study the effects of the inhomogeneity on the local DOS (LDOS) using the real-space DMFT approach as described in SM. (read it more!)

The main result is that in the DW the Mott state collapses (what collapses and where???) if at least one of r_1, r_2 is large enough, due to an increase in the kinetic energy of the DW subsystem.

However, the resulting state has a low Fermi-level LDOS for $r_1 \neq r_2$ due to the splitting of the quasiparticle band into bonding and antibonding subbands which tends to open a (pseudo)-gap. (this is what we see on the plots of the LDOS) (but why does this splitting give us the lowering of the LDOS??) (what is the difference btw LDOS and DOS??)

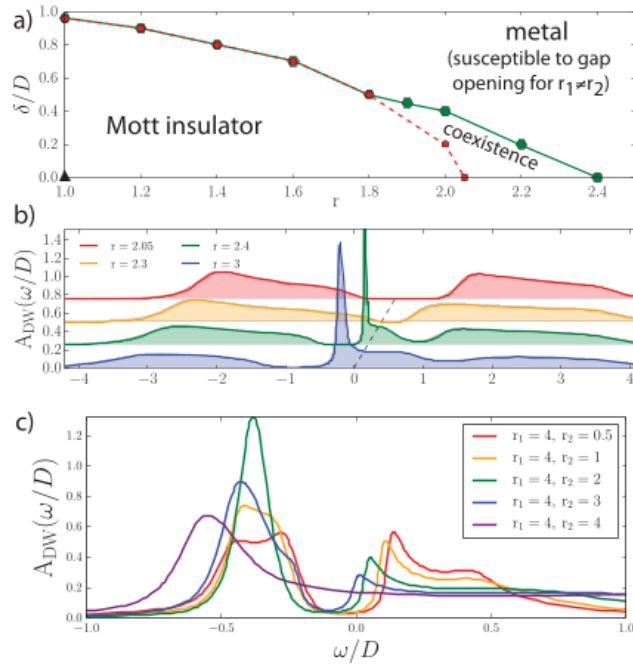


Figure 9.3: Insulating and metallic regimes. (why at all we have a plot over ω ????? what is this ω ????)

(do I understand correctly that there is no such thing in the experiment? we just increase and then decrease the r , since we start with CCDW and we finish at the CCDW phase???? so we start from $r = 1$ and finish at $r = 1$???) (a) (how this plot was obtained at all??? how to get this r ... by fitting?) Phase diagram of the domain-wall subsystem as a function of the hopping enhancement factor $r \equiv r_1 = r_2$ and the local potential δ (local potential δ ????) . (I have no idea about why there is this strange text on this image???)

(b) Domain-wall spectral function (Domain-wall spectral function ??? what is its meaning???) across the bandwidth-driven Mott transition.

(c) Effects of the dimerisation (dimerisation????) (=case, where r -s are different) , $r_1 \neq r_2$, on the quasiparticle band in a metallic wall (metallic wall??) .

In 1T-TaS₂, the lattice geometry effects are particularly important: The zig-zag nature of the lattice distortion makes the DW a connected linear system embedded in a bulk Mott insulator sheet (I don't see in STM any connected linear system ???) .

The homogeneous Hubbard model undergoes Mott metal-insulator (MIT) transitions of two types [33, 51, 52, 40, 53, 54, 55] (learn these articles, I don't understand physics of both) : interaction/bandwidth-driven (Hubbard repulsion U overcomes the kinetic energy proportional to hopping) or doping-driven (for sufficiently large U the electron occupancy approaches half-filling).

If the system lacks translation invariance, the MIT can also take place in a subsystem, e.g. on a surface, at an interface, or in a domain-wall [41, 42, 43, 44, 45] (it is interesting what is in that articles, but the statement is obvious, if we have locally the system which is described by a Hubbard model, then we will have there locally these transitions also) .

In TaS₂, the DW sub-system metallises if $r_1 = r_2 \equiv r$ becomes large (bandwidth-driven MIT (first type out of two above)) or if δ becomes large (doping-driven MIT (second out of two types)), see Fig. 9.3(a) (in which formulas, there is the δ ???) . (why???)

The “local charge gap”(charge gap? there were some gaps before, which is meant here??) is reduced inside the DW.

This is due to the enhanced hopping r that increases the effective bandwidth (which is the synonym of "reduction of the gap") so that local LHB and UHB become broader, while the band centers shift only little. (work out how)

Because of the particle-hole asymmetry in the triangular lattice, the top of LHB and the bottom of UHB have quite different shapes and (use the model, learn why?) the upper edge of the LHB moves towards the Fermi level with increasing r faster than the bottom edge of the UHB.

For high enough $r = r_1 = r_2$, the DW goes through a MIT and it metallizes: A quasiparticle (QP) band emerges inside the Mott gap (where do we see it? is it a criterion of metallization???) , Fig. 9.3(b), so that the Fermi-level local LDOS jumps to a finite value, Fig. 9.4(a). (that is the A_{DW} there??? Fermi-level local LDOS?)

The QP band has a highly asymmetric internal structure with a sharp maximum M in the occupied part of the spectrum (the maximum is not pinned to the Fermi level) and an extended flat plateau P in the unoccupied part, see Fig. 9.4(d), right panel. (how to get the right panel from the left???)

In addition, in the range $r \lesssim 2.5$ we find a weak secondary peak S (see SM for its interpretation). (what is the interpretation?)

Information about the in-gap states can be extracted from the momentum-resolved (partially Fourier transformed)(why by a FT???) spectral function, $A_{k,i}(\omega)$, where k is the longitudinal momentum in the DW direction, while i is the index of the DW site in the transverse direction.

An overview is shown in Fig. 9.4(c), and a close-up to the QP band in Fig. 9.4(d). (what is the meaning of this plot?? is the D just a constant?)

The dominant features (M and P) in the structure of the QP band are due to the one-dimensional nature of the DW which is a 1D zig-zag chain with nearest and next-nearest neighbour hopping constants differing by a factor of r . (why by a one-dimensional nature of the DW???)

The band dispersion for such a non-interacting tight-binding model with $r = 2.4$ indeed matches the QP dispersion (matches the QP dispersion???? what is it?? from what was it obtained?) , Fig. 4(d).

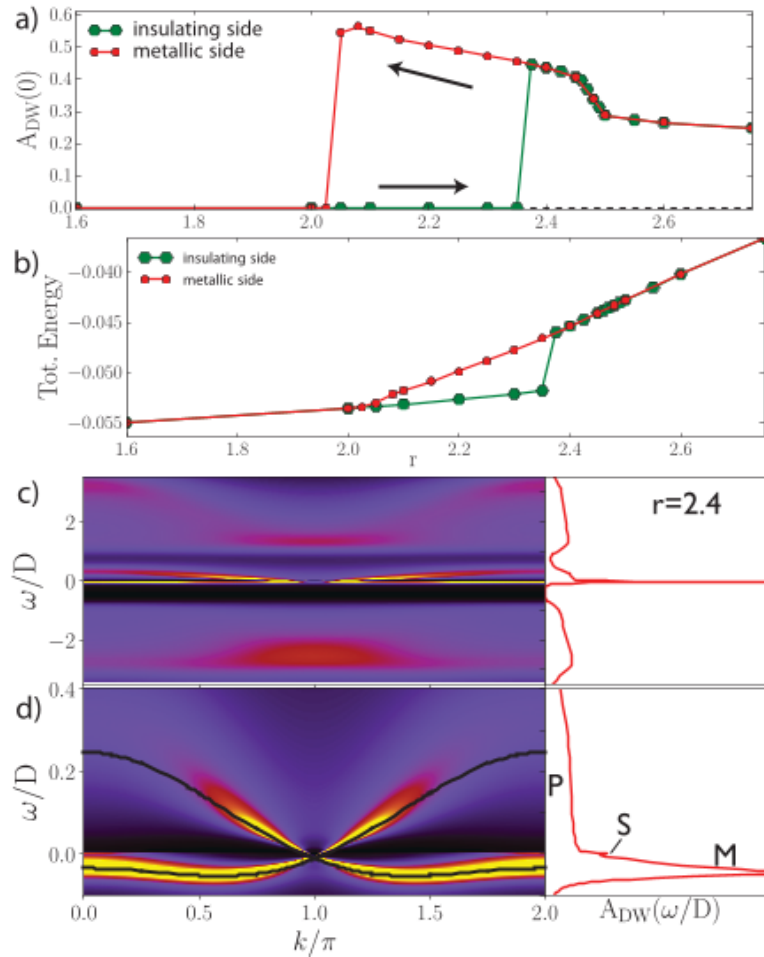


Figure 9.4: Effects of the hopping enhancement factor r with δ fixed at 0 ($\delta = 0$) .

(how did they get this plot???)

(a) Local DOS at the Fermi level across the bandwidth-driven Mott transition. The arrows in the hysteresis region indicate the direction of the changing parameter r .

(b) Total energies of metallic and insulating solutions. (how to calculate it?)

(c,d) Momentum-resolved spectral functions. k is the momentum along the DW (momentum along the DW???) .

The black line is the dispersion of a non-interacting 1D zig-zag chain tight-binding Hamiltonian.

Surprisingly, the boundary bandwidth-driven MIT (bandwidth-driven MIT, how is it??? what do we change???) is first order (why first order???) even at zero temperature, unlike the bulk MIT.

We find a sizeable region (region in r) with coexisting (because there is this strange hysteresis there, see the plot) DMFT solutions: with increasing r , the insulating solution metalizes at $r_{c,2}$, while with decreasing r the metallic solution becomes insulating at $r_{c,1} < r_{c,2}$.

The insulating solution is stable in the entire coexistence region, $r_{c,1} < r < r_{c,2}$, Fig. 9.4(b).

(and is the metallic solution stable? maybe it is also stable)

As a consequence, the bandwidth-driven transition from the insulating state happens at the moment when the Hubbard band (here LHB) touches the chemical potential (where was it before it touched???) , similar to the scenario for the disappearance of the metastable insulating DMFT solution (disappearance of the metastable insulating DMFT band???) in the bulk case.

We note, however, that for $r > r_{c,2}$ the LHB becomes clearly separated from the quasiparticle (QP) peak, i.e., at $r = r_{c,2}$ the LDOS changes discontinuously (where are they on the plot??? QP peak and band, I thought they are just different plots, no???) .

The doping-driven boundary Mott transition (doping-driven boundary Mott transition?) also proceeds by the mechanism of LHB crossing the chemical potential, but the QP peak is pinned to the top of the LHB right after the transition (see SM for more details). (I guess they mean some another transition, which is not seen here)

The superlattice deformation at the DW corresponds to an increase of hopping that can easily attain values of $r \approx 3$ or 4 (see SM for estimates corresponding to common DW types). (it is very interesting how this was obtained?)

One would thus generically expect to observe a strong metallisation and a prominent peak at (or close to) the Fermi level. (how would it look like, what we expect?) (metallisation maybe means that there are electrons near Fermi level, which are very easily to be excited)

In reality, however, the DW is naturally dimerized so that $r_1 \neq r_2$ (by dimerization they mean that there is one connected line in this DW. this is not maybe true, but this is how they see the physics. This is the synonym to have $r_1 \neq r_2$ for some different hoppings) .

For most DW types r_1 and r_2 can indeed be quite different. (since the length are different)

The Mott phase collapses at the DW if the kinetic energy of the 1D subsystem is high enough (this is the same as increase of the hopping constant) .

For this to occur, it is sufficient for one of r_1, r_2 to be large, even if the 1D subsystem in isolation from the triangular-lattice bulk would actually be gapped (a band insulator).

The alternation of hoppings gives rise to molecular orbitals localized on the nearby sites forming dimers (why???? if hoppings are both the same and little (??? or big), there should be also a localization???) , thereby splitting the QP band into bonding and anti-bonding subbands. (how the localized is connected to the creations of bonds???)

The resulting spectrum has a prominent peak in the occupied part of the spectrum ($\omega < 0$) and a gap-like strong suppression of DOS around the Fermi level, see Figs. 9.2(b) and 9.3(c).

The major observations from the tunneling spectra can thus be consistently understood within this model.

In the DW core, two effects dominate: reconstruction of spectra (reconstruction of spectra?) , and emergence of the bound state (emergence of the bound state?) .

If the in-gap resonance (in-gap resonance???) is disregarded, it can still be observed that the Mott gap is smaller (what should we see to say that Mott gap is smaller??) and the DOS distribution is smeared - the behavior reproduced by the intra-DW change of hopping (why? this is written before that we need to change the r -s, but why is it connected to the smearing of DOS distribution???) . (what is the DOS distribution??? I know DOS, not the DOS distribution)

The in-gap DOS peak at negative bias results from the QP band splitting. (didn't they write that the flattening arises from this splitting?)

(how at all splitting comes from the Hubbard model?????????)

(how at all low DOS comes from the Hubbard model?????????)

(how at all in gap states come from the Hubbard model?????????)

The features in the unoccupied part of the the spectrum are most likely pushed toward the UHB and are largely submerged into it.

We also observe a small yet clearly non-zero value of Fermi-level LDOS inside the DW, which results from the subband spectral tails(subband spectral tails? why from them? how?) of the split QP band (QP band? how exactly?) .

The spatial distribution of the Fermi level LDOS and the bound state LDOS are indeed quite similar, see Fig. 9.2(c), which confirms their common origin. (see discussion of this fig. later in the section of discussion)

Finally, the band bending outside the DW is effectively reproduced with the local potential.

Its role in metallization is unpronounced inside the DW, even when UHB is brought very close to the Fermi level (see SM).

We thus conclude that the structural change (change of positions of atoms) in an isolated DW does not yield a good metal in spite of the Mottness collapse (what is teh Mottness collapse???) . (why should it yield a good metal???)

The same result can be extrapolated to the DWs in the hidden state, which have an even larger structural distortion [17, 20]. (what about the hidden state) (something can be re-searched for a different configuration)

Optical or electrical pulses can, however, affect the orbital structure [56] or cause redistribution of electrons in the Brillouin zone, and lead to metallization independently of the density and the type of DWs. (another effect can cause metallization, maybe they mean that this is not what happens during the measurement?)

Finally, we mention the possibility that the superconductivity in this compounds is unrelated to the DWs (I thought that there is a current that comes through DW, no???) , and that upon doping, the SC state emerges directly from the quantum spin liquid state (connection of SC and quantum spin liquid???) , thus 1T-TaS₂ might be an unconventional resonating-valence-bound superconductor (resonating-valence-bound superconductor??? I heard that it is pseudogaped SC) . (anyway it is irrelevant)

9.2 SM

9.2.1 I. Hopping Amplitudes Inside the Domain Walls of Various Types

(SUMMARY: details about DW and r -s)

Here we discuss the magnitude of the relative hopping factor r arising from the change in the separation between the Wannier orbitals of David Stars forming the domain wall.

As discussed in Ref. 1, the hopping amplitudes in tight-binding Hamiltonians describing transition metals scale as d^{-5} , where d is the distance between the atoms. (why???? read the ref. 1, maybe it is essential to understand this article)

This fact, combined with the results of Rossnagel et al., Ref. 2 (read this paper!) , on the reconstructed phase in 1T-TaS₂ showing that the main contribution to the narrow band in the C-CDW phase comes from the orbitals (how to take into account orbitals at all?) centered in the middle of David stars, allows us to estimate the relative change in the hopping amplitudes inside a DW.

As an example, we consider here the three typical DW structures which we enumerate 1,2,4 following Ref. 3; the corresponding schematic plots are shown in Fig. 1. The resulting relative distances and hopping ratios are collected in Tab. I.

In a dimerized tight-binding chain with hoppings r_1 and r_2 the band gap is given by $2|r_1 - r_2|$, the width of the interval supporting both subbands by $2(r_1 + r_2)$, the bandwidth of each subband by $2\min\{r_1, r_2\}$, while the occupied band kinetic energy is proportional to $\sqrt{r_1^2 + r_2^2}$. It is this latter scale which controls the boundary Mott metal-insulator transition; for details see Section V.

Note that in all three cases considered one of the r values is large;

it is this dominant r which leads to an increased kinetic energy and Mottness collapse, with the other r value as a subleading correction. (why???)

The difference between r_1 and r_2 then additionally leads to the bonding-antibonding splitting of the quasiparticle band as a secondary effect.

DW type	d_1	d_2	r_1	r_2
1	0.83	1.11	2.51	0.6
2	1.21	0.73	0.38	4.7
4	0.73	0.83	4.7	2.51

Table I. Relative distances d_1 , d_2 and relative hoppings r_1, r_2 for commonly occurring types of single standing DWs. (how to calculate them???)

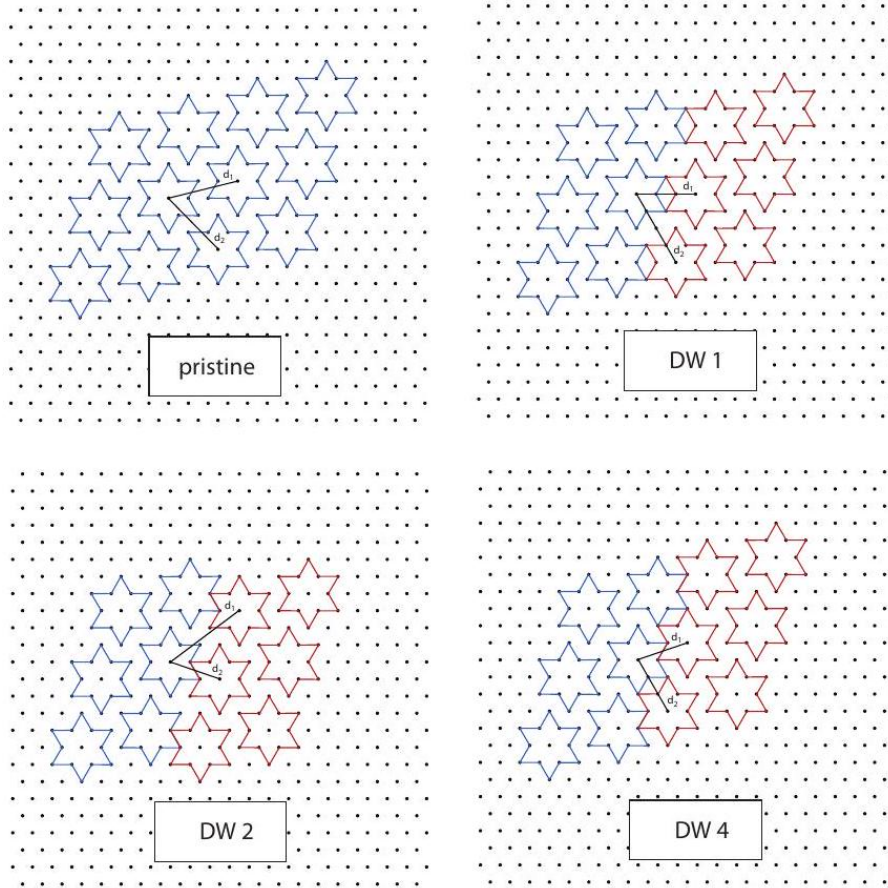


Figure 1. Schematic plot of the superlattice pattern in pristine 1T-TaS₂ and for three commonly occurring domain wall types (1,2,4)(where is the 3?) .(these images define the DWs)

9.2.2 II. Doping-Driven Transition

(SUMMARY: another maybe possible transition)

As described in the main text, the metallisation in the domain wall (what is the metallisation in the domain wall?) can also be triggered by modifying the on-site potential on the DW sites, see Fig. 2.

With increasing δ , the LHB and UHB shift with respect to the bulk Hubbard bands and the spectral density is redistributed within the bands, although the bandwidths are only weakly affected.

As the LHB crosses the Fermi level with increasing δ , the system metallizes at $\delta = \delta_c \approx 1.0D$, see Fig. 2(a), and a QP band emerges at the top of the LHB, see Fig. 2(b).

The transition has no hysteresis in this case. As δ increases past δ_c the electron density at the DW rapidly decreases, see Fig. 2(c), i.e., the DW becomes charged. A charged DW in

an infinite insulating bulk must be of finite length in order for the electric potential to remain finite and it must be furthermore in contact with a charge reservoir for the charge to flow into the DW during the metallisation: indeed the observed DWs are kinked and often terminate at large lattice inhomogeneities.

The modification of local potential leads to the experimentally observed gradual shift of the bands towards the Fermi level, see Fig. 1(d) in the main text. The band shift occurs on several sites adjacent to the DW core. On these peripheral sites the spectral shape is maintained but the band approaches the Fermi level. Such behavior results from the long-range part of the Coulomb interaction. From the symmetry of the shift we infer that the source of the potential is the DW core itself.

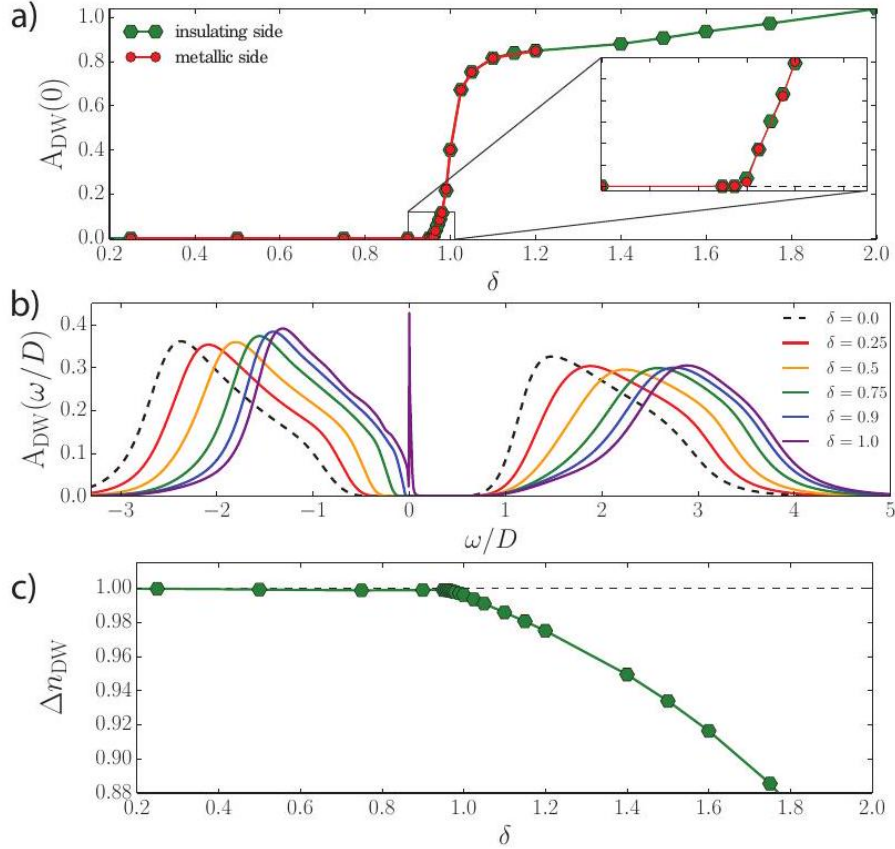


Figure 2. Effects of the on-site potential $\epsilon_{DW} = \epsilon + \delta, r = 1$. (a) Local DOS at the Fermi level across the doping-driven Mott transition. (b) Local DOS for select values of δ . (c) Local electron density n_{DW} vs. δ .

9.2.3 III. Fine Details in the QP Band in the Bandwidth-Driven Mott Transition

(SUMMARY: some comments (???))

The Mottness collapse due to increased hopping generates itinerant quasiparticles. These tunnel in the surrounding insulating lattice [4] with a hopping matrix element proportional to $\cos(k/2)$, producing a weakly dispersive spectral feature at $k \sim 0$ with energy close to that of the pole in the bulk self-energy function (the pole which produces the Mott insulating behavior). The resulting peak S , despite having rather small spectral weight, produces the sequence of two kinks at $r \sim 2.45$ and $r \sim 2.5$ in the Fermi-level LDOS seen in Fig. 4(a) of main text.

9.2.4 IV. Details of the R-DMFT Calculations

(important comments about their calculation, which I don't understand, I need to read 4 articles about it in order to understand what is below. also, there are very few comments here)

We employ the real-space DMFT (R-DMFT) to solve the model defined by Eq. (1) in the main text. Within this approach the assumption of spatial homogeneity is lifted and the lattice Green's function, instead of using the Hilbert transform (which Hilbert transform could be tried?) , is calculated using its real-space representation as

$$\hat{\mathcal{G}}_{\text{latt}}(z) = \left[z - \hat{\mathcal{H}}_{\text{kin}} - \hat{\Sigma}(z) \right]^{-1}, \quad (1)$$

where $\hat{\mathcal{H}}_{\text{kin}}$ is the hopping matrix in the Wannier basis (we are always in the Wannier basis, right?) .

The hats above $\hat{\Sigma}(z)$, $\hat{\mathcal{G}}_{\text{latt}}(z)$, $\hat{\mathcal{H}}_{\text{kin}}$ underline the fact that these are matrix quantities. (how do they look?)

From $\hat{\mathcal{G}}_{\text{latt}}(z)$ the site dependent hybridization function $\Delta_i(z)$ is calculated through

$$\Delta_i(z) = z - [\hat{\Sigma}(z)]_{i,i} - \frac{1}{\left[\hat{\mathcal{G}}_{\text{latt}}(z) \right]_{i,i}}. \quad (2)$$

To take advantage of the symmetries in the system (which symmetries???) we introduce a mixed basis representation (mixed basis representation?? why is it called so?) by performing a partial Fourier transformation along the domain-wall direction [5, 6] (read the literature, why do they do it?) .

As a result, the kinetic term in the Hamiltonian is given by (get this equation somehow!...)

$$\begin{aligned} \mathcal{H}_{\text{kin}} = & - \sum_{x,k,\sigma} \left(2t \cos(ka) c_{\{x,k\},\sigma}^\dagger c_{\{x,k\},\sigma} + \right. \\ & + \left(t_{1,x} e^{-ik\frac{a}{2}} + t_{2,x} e^{ik\frac{a}{2}} \right) c_{\{x+1,k\},\sigma}^\dagger c_{\{x,k\},\sigma} + \\ & \left. + \left(t_{1,x-1}^* e^{ik\frac{a}{2}} + t_{2,x-1}^* e^{-ik\frac{a}{2}} \right) c_{\{x-1,k\},\sigma}^\dagger c_{\{x,k\},\sigma} \right) \quad (3) \end{aligned}$$

where k is the quasi-momentum in the DW direction, x is the distance in perpendicular direction, and a denotes the inter-site distance. Any contributions coming from the nonorthogonality of the triangular lattice basis come as a phase factor and thus can be removed by a unitary transformation of the fermionic operators. In the mixed basis $\mathcal{H}_{\text{kin}}$ becomes block diagonal with each block describing a one-dimensional system in the x direction having k -dependent hopping amplitudes, cf. Eq. (3).

Explicit usage of hopping matrix in Eq. (1) for the lattice Green's function leads to artifacts if it is truncated to a finite size matrix in order to proceed with the numerical calculations.

To overcome this problem we add self-energy terms to the edge of the finite cluster to mimic the infinite environment in which this finite subsystem is embedded [7-9].

Due to the translation invariance along the DW direction it suffices to add the self-energy term $\Sigma_{\text{B-S}}(z, k)$ (B-S denotes what?) which depends only on the frequency and the quasi-momentum k .

Each k block describes a one-dimensional system with only nearest-neighbor k -dependent hopping and the formula for $\Sigma_{\text{B-S}}(z, k)$ can be written in closed form:

$$\begin{aligned}\Sigma_{B-S}(z, k) &= |t(e^{ik\frac{a}{2}} + e^{-ik\frac{a}{2}})|^2 G_{s-i}(z + 2t \cos(ka), k) = \\ &= \frac{z + 2t \cos(ka)}{2} \left(1 - \sqrt{1 - \frac{4|t(e^{ik\frac{a}{2}} + e^{-ik\frac{a}{2}})|^2}{(z + 2t \cos(ka))^2}} \right).\end{aligned}\quad (4)$$

(they could have used the ch function there)

In Eq. (4) G_{s-i} denotes the surface Green's function of a semi-infinite chain[10]. (read about it!!!)

Using the mixed basis and the boundary self-energy term, Eq. (1) becomes

$$\hat{\mathcal{G}}_{\text{latt}}(z) = \frac{1}{2\pi} \int_{-\pi}^{\pi} dk \left[z - \hat{\Sigma}_{\text{DMFT}}(z) - \hat{\mathcal{H}}_{\text{kin}}(k) - \hat{\Sigma}_{B-S}(z - \Sigma_{\text{DMFT}}^{x=\infty}(z), k) \right]^{-1} \quad (5)$$

where $\hat{\Sigma}_{\text{DMFT}}(z)$ is the self-energy matrix from the R-DMFT, $\hat{\mathcal{H}}_{\text{kin}}(k)$ is the hopping matrix within a k block and $\hat{\Sigma}_{B-S}(z - \Sigma_{\text{DMFT}}^{x=\infty}(z), k)$ is the self-energy matrix describing the coupling to the bath. In the latter the energy is shifted by the selfenergy term from the asymptotic limit ($x = \infty$) to include the correlations in the bulk. Here the assumption is made that at large distances from the domain wall its effects are damped out and the self-energy asymptotically approaches the homogeneous bulk results. Testing showed that this happens within 3-7 sites from the DW, thus the calculations in this work were done for systems where coupling $\Sigma_{B-S}(z, k)$ to the bath was placed 20 lattice constants away from the DW.

The self-consistency equations for a set of effective impurity problems are solved using the numerical renormalization group [11, 12] with the discretization parameter $\Lambda = 2$. We work in units of the half-bandwidth $D = 9t/2$. Hubbard repulsion is $U = 4D$, while $U_{c,2} \approx 3D$ for the triangular lattice within the DMFT. The calculations are performed at zero temperature.

To account for the imperfections inside real DWs in 1T-TaS₂, in the calculations for the dimerized case we also include a constant purely complex term $\eta = -0.05i$ at the DW sites. The role of this additional term is to mimic the scattering caused by the presence of kinks or termination of the domain wall that differentiate it from the pristine infinite case used in modeling.

9.2.5 V. Charge gap in $r_1 \neq r_2$ case

(SUMMARY: some exotic case (???))

In this section we discuss the influence of $r_1 \neq r_2$ on the Mott phase at the DW wall.

Fig. 3 shows the evolution of the gap when one hopping ratio r_2 is varied and the other r_1 is kept fixed.

Since the bare bandwidth (interval supporting both subbands) is given by $2(r_1 + r_2)$ and kinetic energy (in the first approximation) behaves as $\sqrt{r_1^2 + r_2^2}$, the shape of the curves in Fig. 3 clearly indicates that the later is indeed the energy scale controlling the gap width.

To highlight this fact, we collapsed the curves for different r_1 onto each other by rescaling them by their largest value (lower panel in Fig. 3).

For $r_2 < 1$ all curves display a very similar behaviour, but the deviation between them increases with increasing r_2 .

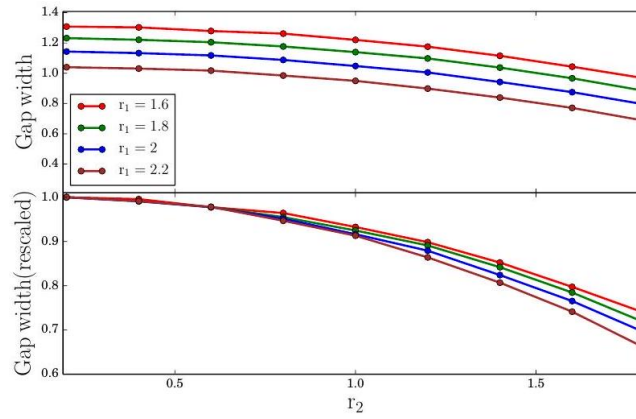


Figure 3. (Upper plot) Dependence of gap width on r_2 for different values of r_1 (how is it??? we don't have the r -s in the Hamiltonian, how to find such dependence???) . (Lower plot) Corresponding gap width rescaled by its maximal value.(why are the differ so much???)

9.2.6 VI. Details about Experimental STM/STS Measurements

(SUMMARY: a section which only experimentalists will read (???))

The topographic images that show the David-star pattern are taken at a high bias voltage of -800 mV. We have investigated two examples of the domain walls: one (A) was found connecting two large-scaled defects and another (B) was found after the relaxation of the metallic mosaic phase. The David-star overlap in both DWs investigated is equal to one atomic lattice period.

The DW-A was characterized with the dI/dV map shown in the main text Fig. 1, as well as in Figs. 6(a),(c) and Fig. 5 in the Supplement. The map was obtained in the ± 0.6 V range with 0.5 nm spatial resolution using the lock-in technique with 25 mV AC modulation. The map, Fig. 5(c), allows to see that the substantial spatial variations of the spectral weight are present along the domain wall at all energies of interest around the Fermi level E_F .

The tunneling spectra for DW-B [Fig. 6(b),(d)] were taken with small DC bias steps and large integration time to obtain high resolution and avoid convolution with the AC lock-in modulation. The raw $I - V$ curves inside and outside the DW-B (L_0 and L_∞ in the main text) are shown in Fig. 4. Clear difference in slopes demonstrate the elevated Fermi-level LDOS. The sharp jump indicates the high value of the LDOS in the in-gap state compared to the background, by analogy with the occurrence of N-type $I - V$ curves in tunnel diodes.

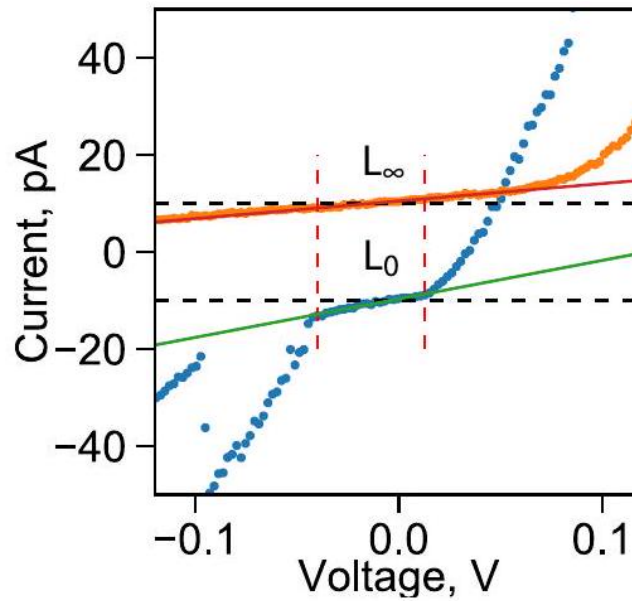


Figure 4. Comparison of the raw $I - V$ curves inside (blue, L_0) the DW-B and away from it (orange, L_∞). Solid lines are guide for eyes showing the slope around the Fermi level.

9.2.7 VII. Comparison of the Domain Walls of Different Origin

(SUMMARY: extra understanding of the DWs, I don't know if it is useful... I'd better understand the main theory, then I'll be learning it if needed)

Below we compare the two walls, DW-A and DW-B, in terms of the major spectral features discussed in the main text. (what is their def.??)

The side-by-side comparison of the spectra is shown in Fig. 6.

- The band bending is observed for both DW-A and DW-B. Its direction is the same.
- Spectral reconstruction is found for both DW-A and DW-B.
- The sub-gap states in the occupied part of the spectrum are observed in both cases, although no sharp resonance can be resolved for DW-A. This is likely linked to the convolution with the AC modulation from lock-in.
- Neither domain wall shows a significant change in the CDW E_V position.

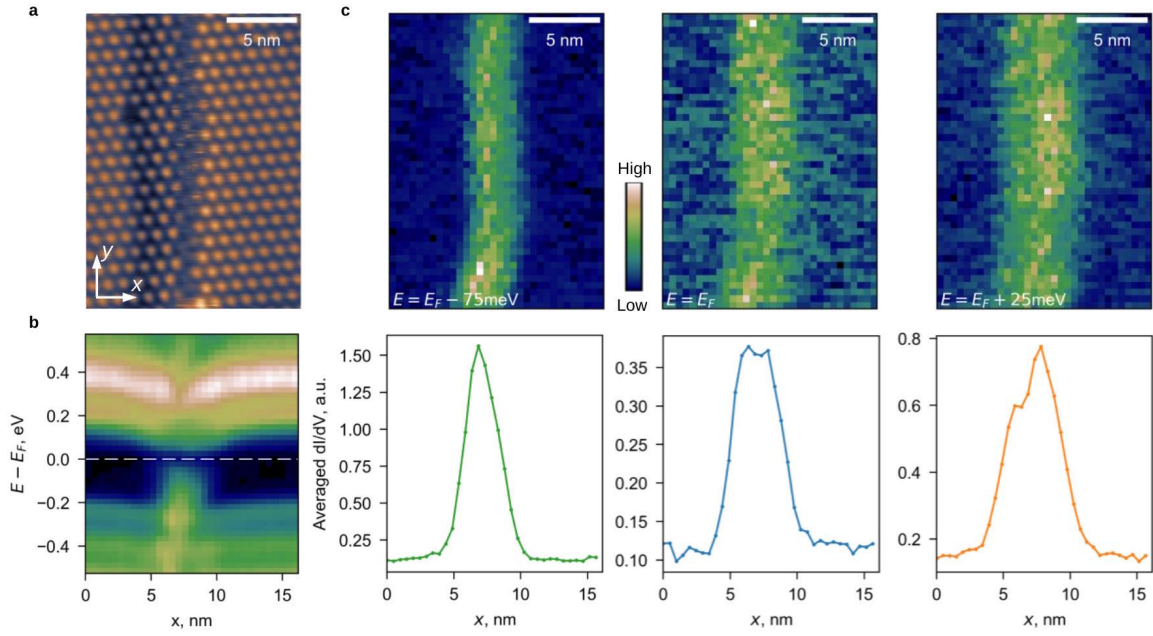


Figure 5. Spectroscopy maps for DW-A: a) Topographic image. b) Tunneling spectra evolution on crossing the wall from left to right in the x direction [see panel (a) for the coordinate axis orientation]. (what is th def. of colors here, in b)?)

For each position x , the spectra are averaged along the wall direction y .

c) Tunneling spectroscopy maps (Tunneling spectroscopy maps??) at selected energies within the split band emerging inside the domain wall.

The plots in the second row show the evolution of the average LDOS at the respective energy on crossing the wall (for each x position the averaging is done along the wall direction y).

In conclusion, the relevant physics is the same in both cases. The differences are: (i) the Fermi level position in the gap (which is sample dependent) and (ii) quantitative shape of the spectra (which is tip dependent).

In the DW-A case, the UHB comes very close to the Fermi level, see Fig. 7(a). It is interesting thus to compare the behavior with the predictions of the doping-driven metallization scenario. In the latter we would expect the appearance of a peak merged with the UHB lower edge. Experimentally, only minor increase of the spectral weight is observed above E_F , better seen if the spectra are subtracted, Fig. 7(b). It is almost indistinguishable from the UHB as is seen from comparing the spatial distribution with that at $E \leq E_F$. The behavior suggests that the hopping-driven scenario still dominates even in this case.

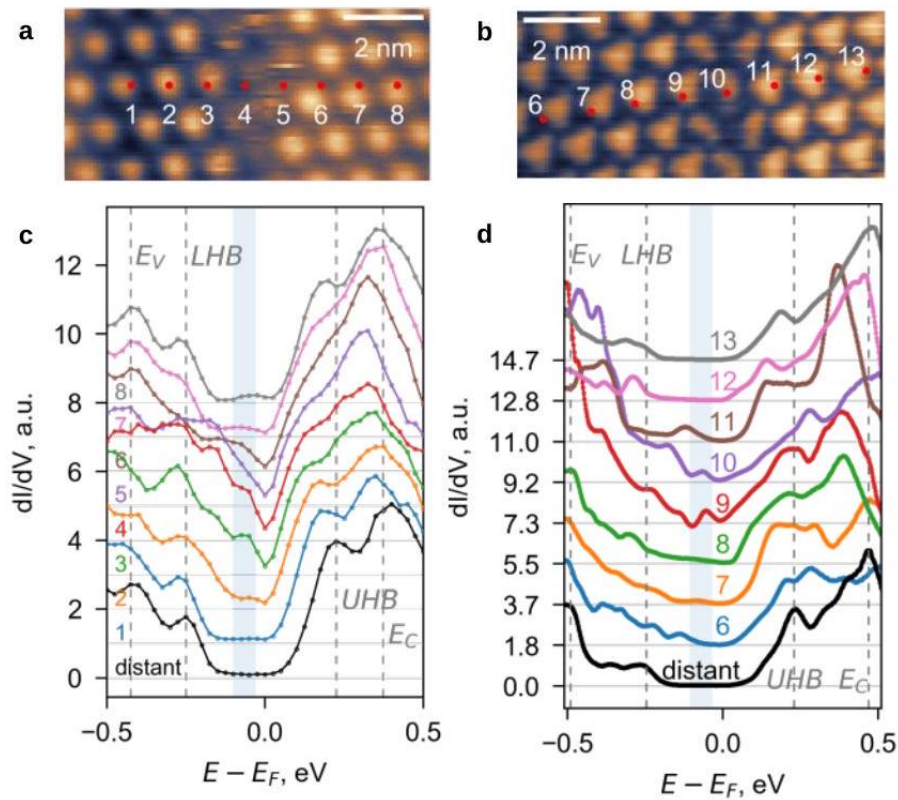


Figure 6. Comparison of the DW of different origin:

a, b) Topographic images of the DW-A and DW-B, respectively. (what is the key difference here?)

Red dots mark the positions where the spectra were taken. (how at all they move along the line E ???)

c, d) Individual spectra (why dI/dV is the individual spectra?) at different positions across the wall for DW-A and DW-B, respectively. The curves are offset for clarity.

The black curve shows the spectrum observed far away from the domain wall. (how to understand, why is it such?) (why on both plots the black line is different?) (here 8 is basically this black curve)

Dashed lines show the position of respective spectral features (respective spectral features??? not peaks, peaks are in different place) .

The shaded area marks the energy of the in-gap state. (why is it so?)

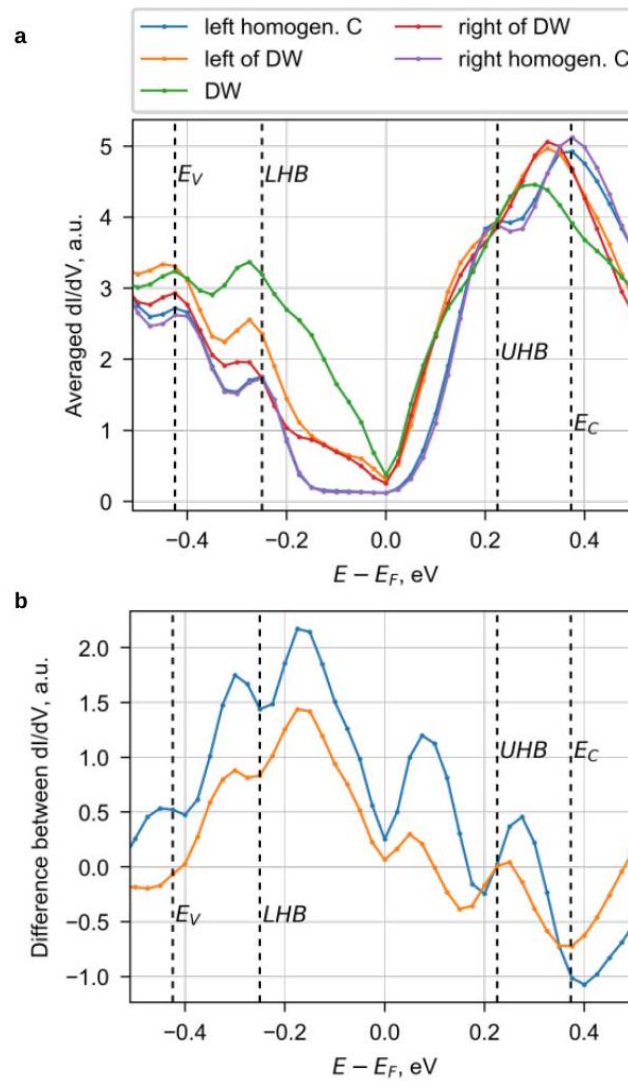


Figure 7. (idk what is here??) a) DW-A spectra spatially averaged in 5 different areas described in legend. b) Subtracted averaged spectra: blue - inside the DW and homogeneous C (green and blue curves in (a)); orange inside the DW and left of DW (green and orange curves in (a)).

9.3 Questions, Comments

9.3.1 Some answered questions for a later analysis

can DWs be metallic or non metallic??? what is meant by this statement? I thought that they are always metallic, since other electrons travel through them, no?

(GPT:)

A domain wall is a structural/electronic boundary and is not metallic by definition. Whether it is metallic depends on its electronic spectral function. A locally metallic domain wall should possess low-energy electronic states at the Fermi level,

$$A_{\text{DW}}(\omega = 0) > 0,$$

which can provide conducting states along the wall. Conversely, a domain wall can remain insulating or have only a very small Fermi-level density of states. This distinction is central

to the paper: enhanced hopping can destroy the local Mott state, but structural dimerization can split the resulting quasiparticle band and strongly suppress the density of states around the Fermi level. Thus, the presence of a domain wall does not by itself imply the presence of a metallic conducting channel.

what is the question "The crucial question is whether the CDW distortion inside the wall can lead to Mottness collapse" there and why is it important?

(GPT:)

The central question of the paper is whether the structural reconstruction of a CDW domain wall can locally destroy the Mott-insulating state and, if it does, whether this necessarily produces a metallic domain wall. This question is important because domain walls had been proposed as a possible origin of metallisation, and potentially of superconductivity, in modified states of 1T-TaS₂. The authors find that the first implication does not necessarily imply the second:

structural reconstruction $\rightarrow$ enhanced hopping $\rightarrow$ Mottness collapse,

but

Mottness collapse $\nrightarrow$ good metal.

In their model, dimerization of the domain wall subsequently splits the quasiparticle band and suppresses the Fermi-level density of states.

Why there is no interaction btw neighbours, only self interaction of different spins is present???

(GPT:)

$$H = \sum_{\langle i,j \rangle, \sigma} t_{ij} c_{i\sigma}^\dagger c_{j\sigma} + \sum_{i\sigma} \epsilon_i n_{i\sigma} + \sum_i U_i n_{i\uparrow} n_{i\downarrow}, \quad (9.2)$$

(??? why there is no interaction btw neighbours, only self interaction of different spins is present???)

The Hamiltonian used in the paper is a single-band Hubbard model and therefore retains only the local Coulomb interaction,

$$H_U = U \sum_i n_{i\uparrow} n_{i\downarrow}.$$

A more general extended Hubbard model could additionally contain a non-local interaction,

$$H_V = V \sum_{\langle i,j \rangle} n_i n_j.$$

The absence of V is therefore a modelling approximation rather than a statement that Coulomb interactions between neighbouring David-star orbitals physically vanish. The authors choose the minimal Hubbard description intended to capture the local Mott physics and investigate how modification of the hopping amplitudes at a domain wall affects that Mott state. Consequently, effects that specifically require non-local Coulomb interactions are outside the scope of this model.

Why at all we have a Hubbard model here???? was it derived somewhere from the Frohlich model?

(GPT:)

The Hubbard model is not obtained here from the Fröhlich model. The low-energy electronic structure of the C-CDW phase is described in terms of a narrow, approximately half-filled band associated predominantly with orbitals centered on the David stars. The kinetic motion of an electron between these effective orbitals is represented by hopping amplitudes t_{ij} , while the energetic cost of double occupation of one effective orbital is represented by the local Coulomb repulsion U . This leads naturally to the effective low-energy Hamiltonian

$$H = - \sum_{\langle ij \rangle, \sigma} t_{ij} c_{i\sigma}^\dagger c_{j\sigma} + U \sum_i n_{i\uparrow} n_{i\downarrow}.$$

The purpose of this effective model is not to describe the microscopic formation of the CDW itself, but to describe the correlated electrons living in the already reconstructed David-star lattice and, in particular, the Mott transition of its narrow half-filled band.

why don't we change the lattice itself????? lattice shouldn't also be fixed, maybe they just neglect this

(GPT:)

Yes, the lattice is effectively treated as an externally specified static structure in this calculation. The authors do not perform a simultaneous self-consistent optimization of the atomic positions and the correlated electronic state. Instead, the experimentally known structural deformation of the domain wall is mapped onto modified electronic parameters, primarily the hopping amplitudes $r_1 t$ and $r_2 t$ and the local potential δ . The DMFT calculation then determines the electronic state for this prescribed lattice geometry. Thus,

$$\text{DW structure} \longrightarrow \{r_1, r_2, \delta\} \longrightarrow \text{electronic DMFT calculation},$$

rather than solving

$$\text{electrons} \leftrightarrow \text{atomic positions}$$

self-consistently. This is an approximation of the theoretical treatment.

why the on-site potential is not also in U ???

(GPT:)

The local potential δ and the Hubbard interaction U describe fundamentally different terms in the Hamiltonian. The local potential is a one-particle term,

$$H_\delta = \sum_{i, \sigma} \delta_i n_{i\sigma},$$

so it changes the energy of an electron occupying site i independently of whether another electron is present. The Hubbard term,

$$H_U = U \sum_i n_{i\uparrow} n_{i\downarrow},$$

is instead a two-particle interaction: the energy U is paid only when both spin states of the same effective orbital are occupied. Therefore, δ shifts the local electronic levels, whereas U produces correlation effects such as the separation into lower and upper Hubbard bands. They cannot in general be absorbed into the same parameter.

but why does this splitting give us the lowering of the LDOS??

(GPT:)

Before dimerization, the metallic domain wall contains a quasiparticle band crossing the Fermi energy and therefore has finite spectral weight around $\omega = 0$. When the hopping amplitudes alternate,

$$r_1 \neq r_2,$$

the unit cell of the effective one-dimensional chain contains two sites. The quasiparticle band is consequently split into bonding and antibonding subbands. Spectral weight that previously occurred near the Fermi level is redistributed toward the lower and upper subbands,

$$\text{QP band} \rightarrow \text{bonding subband} + \text{antibonding subband}.$$

For an isolated non-interacting dimerized chain the corresponding band gap is

$$\Delta_{\text{dim}} = 2|r_1 - r_2|$$

in the normalized hopping units used in the Supplement. In the full interacting system embedded in the two-dimensional lattice the result is a strong gap-like suppression, rather than necessarily a perfect zero, of the LDOS around the Fermi level.

how at all splitting comes from the Hubbard model????????

(GPT:)

The bonding–antibonding splitting does not originate directly from the Hubbard interaction U . It originates from the alternating hopping amplitudes t_1 and t_2 in the one-particle part of the Hubbard Hamiltonian. The simplest illustration is an isolated two-site dimer,

$$H_t = -t_1(c_1^\dagger c_2 + c_2^\dagger c_1).$$

Its one-electron eigenstates are

$$|B\rangle = \frac{|1\rangle + |2\rangle}{\sqrt{2}}, \quad |A\rangle = \frac{|1\rangle - |2\rangle}{\sqrt{2}},$$

with energies

$$E_B = -t_1, \quad E_A = +t_1.$$

They are the bonding and antibonding states. In a periodic dimerized chain these states broaden into bonding and antibonding bands. The Hubbard interaction U then acts on top of this dimerized band structure and strongly renormalizes the electronic spectrum. Thus, the splitting appears within the Hubbard-model calculation because the kinetic part of that Hubbard model contains $r_1 \neq r_2$, not because U itself generates bonding and antibonding orbitals.

what is teh Motttness collapse???

(GPT:)

“Motttness” refers to insulating behavior caused by strong electron–electron correlations rather than by an ordinary single-particle band gap. In the present model, the bulk narrow half-filled band is split by the Hubbard interaction into lower and upper Hubbard bands, producing a Mott charge gap. At the domain wall, enhanced hopping increases the kinetic-energy scale relative to U . When this kinetic energy becomes sufficiently large, the locally

Mott-insulating DMFT solution disappears and a quasiparticle band develops inside the original Mott gap. This loss of the local Mott-insulating state is what the authors call *Mottness collapse*. Importantly,

Mottness collapse

means the destruction of the Mott mechanism for insulation; it does not by itself guarantee that the final state has a large density of states at the Fermi level, because another mechanism such as dimerization can subsequently suppress the low-energy states.

why should it yield a good metal???

(GPT:)

If the only important change at the domain wall were an enhancement of a uniform hopping,

$$r_1 = r_2 = r,$$

then increasing r increases the bandwidth relative to U and eventually drives the local subsystem through a bandwidth-driven Mott metal–insulator transition. The DMFT calculation indeed produces a quasiparticle band crossing the Fermi level and a finite $A_{\text{DW}}(0)$ in this case. Since realistic structural estimates give rather large hopping enhancements, $r \sim 3\text{--}4$, one might therefore expect a strongly metallic wall. The crucial additional ingredient is that a real wall is not uniform: generally $r_1 \neq r_2$. This dimerization splits the quasiparticle band and strongly suppresses its Fermi-level spectral weight. Hence the expectation of a good metal follows from considering hopping enhancement alone, while the failure to obtain a good metal follows from including the actual dimerized wall structure.

9.3.2 My general questions about meaning of the article

How is Fig. 1(d) connected to Fig. 2(a)?

(I'll think later about it!!! GPT:)

Although Fig. 1(d) and Fig. 2(a) look very different, they represent closely related spectroscopic information in two different ways. In Fig. 1(d), the horizontal axis is the position x across the domain wall, the vertical axis is the energy relative to the Fermi level,

$$E - E_F = eV,$$

and the color represents the measured differential tunnelling conductance,

$$\frac{dI}{dV}(x, V),$$

which approximately probes the local spectral density,

$$\frac{dI}{dV}(x, V) \propto A(x, E_F + eV).$$

Thus, Fig. 1(d) should not be interpreted as a single function $E(x)$. Instead, it is a two-dimensional spectral map

$$A(x, E),$$

in which every point (x, E) has a spectral intensity represented by the color. The visible curves or “bands” in this map correspond to maxima of spectral weight, such as the LHB and UHB, whose characteristic energies change with position; the authors describe this as the bending of the Hubbard bands near the domain wall. :contentReference[oaicite:0]index=0 In Fig. 2(a), by

contrast, several particular spatial positions $x_i = L_\infty, \dots, L_0, R_0, \dots, R_\infty$ are selected and the corresponding spectra

$$\frac{dI}{dV}(x_i, V)$$

are plotted individually as one-dimensional curves versus voltage. Therefore, conceptually, taking a vertical cut through a two-dimensional map such as Fig. 1(d) at a fixed position $x = x_i$ produces

$$A(x_i, E),$$

which is the type of spectrum displayed as a curve in Fig. 2(a). However, Fig. 2(a) is not literally obtained by taking cuts through the particular data shown in Fig. 1(d): the authors perform a separate higher-resolution measurement on another DW sector in order to inspect the Mott-gap region more closely. This reveals the small but finite spectral weight at the Fermi level and the in-gap state near -70 mV that are difficult to resolve in the broader measurement of Fig. 1(d).

Is there a metallization finally in the DW (in experiments and in theory)? And how does it connect to the the type of a wall????

(???????????? this is the main question, which I don't understand)

(there say in the abstract that walls become metallic by splitting the band, also there are such parameters r and δ which gives the metallicity)

Why at all we are dealing with $A(\omega)$ parameter at all?

(??? improve my theoretical understanding and answer it)

(???? how does the $A(\omega)$ connects to the LDOS and with dI/dV ???)

What is the criterion of metallisation?

(think more about it, what exactly they mean? how does it connect to the value of the current?)

what is the relation between fig. 2b and 3b? (!!!!)

(I don't understand where fig. 2b came from at all. AN IMPORTANT QUESTION)

What exactly is the Mottness collapse?

(???? read other papers to learn it. how the state can be neither metallic nor insulating?)

Is this theory not applicable for different lattices at the left and right of the DW?

(I see the same configuration of electrons at the left and right. what if I had a different configuration of lattice???)

(I think no, it is just not applicable, lattice should be the same or one should redo a lot of complicated calculations)

(looks like a big limitation of this theory)

What happens in the Hubbard model what is relevant for this case?

(????)

(how at all splitting comes from the Hubbard model????????)

(how at all low DOS comes from the Hubbard model????????)

(how at all in gap states come from the Hubbard model????????)

Why interaction with S atoms is not included?

(???? there is still this layer on the boom, right? electrons should also interact a lot with it)

Which U, ϵ and t are used exactly for the TaS₂?

(????? I don't know... maybe it is written in the SM...)

(GPT:)

The calculations in this work do not require an absolute value of the hopping t in eV because all energies are expressed relative to the half-bandwidth D of the non-interacting triangular lattice. The authors define

$$2D = 9t, \quad \text{or equivalently} \quad D = \frac{9}{2}t,$$

and choose the Hubbard interaction

$$U = 4D = 18t.$$

Thus, one can simply work in units where $D = 1$, in which case

$$U = 4, \quad t = \frac{2}{9}.$$

In the unperturbed bulk the nearest-neighbour hopping is $t_{ij} = t$, whereas at the domain wall it is modified according to

$$t_1 = r_1 t, \quad t_2 = r_2 t.$$

The structural deformation can additionally modify the local on-site energy; the authors describe this through a relative domain-wall shift δ , rather than specifying an absolute value of the bulk on-site energy ϵ . The chemical potential is fixed in the center of the bulk Mott gap. Therefore, the relevant quantities entering the calculations are dimensionless ratios such as

$$\frac{U}{D} = 4, \quad \frac{t}{D} = \frac{2}{9}, \quad \frac{\delta}{D}, \quad r_1 = \frac{t_1}{t}, \quad r_2 = \frac{t_2}{t},$$

and the resulting spectra can correspondingly be plotted as functions of ω/D . An absolute physical value of t (or D) in eV is therefore not required to reproduce the dimensionless theoretical plots; it would only be required to convert the theoretical energy axis into eV or meV for an absolute quantitative comparison with experiment. The paper explicitly states that $U = 4D$, $2D = 9t$, and that the chemical potential is fixed in the center of the bulk Mott gap. :contentReference[oaicite:0]index=0 The Supplement further states that the calculations are performed in units of $D = 9t/2$. :contentReference[oaicite:1]index=1

Interpretation of Fig. 4: hopping-driven Mott transition and momentum-resolved spectral function.

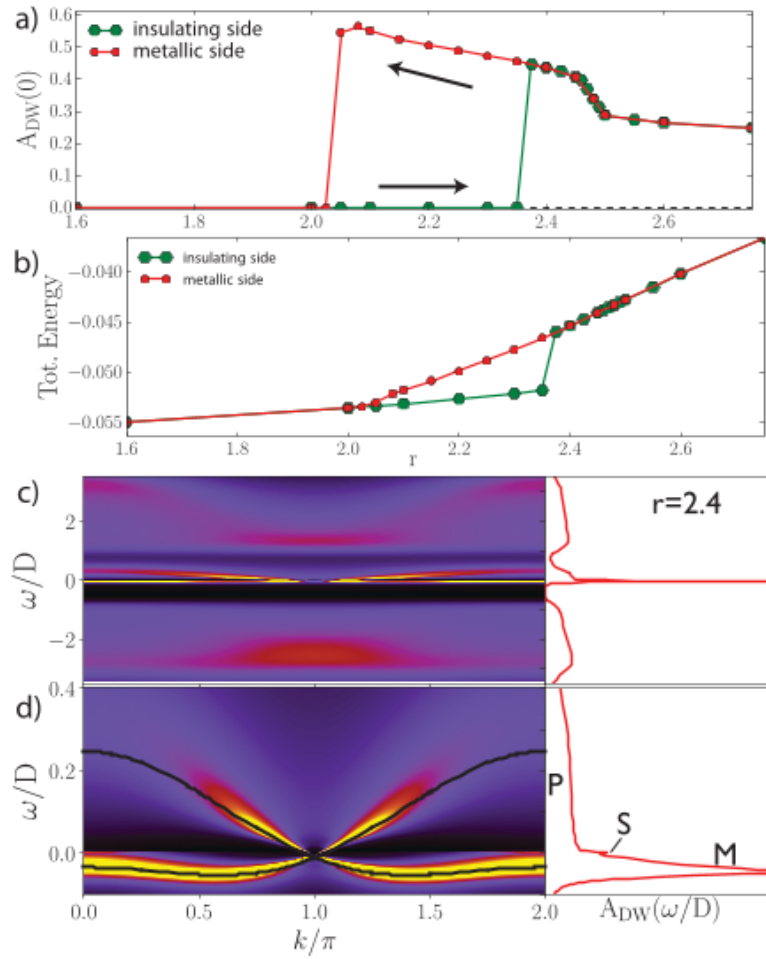


Figure 9.12: Effects of the hopping enhancement factor r with δ fixed at 0 ($\delta = 0$) .

(how did they get this plot???)

(a) Local DOS at the Fermi level across the bandwidth-driven Mott transition. The arrows in the hysteresis region indicate the direction of the changing parameter r .

(b) Total energies of metallic and insulating solutions. (how to calculate it?)

(c,d) Momentum-resolved spectral functions. k is the momentum along the DW (momentum along the DW???) .

The black line is the dispersion of a non-interacting 1D zig-zag chain tight-binding Hamiltonian.

(GPT:)

Figure 4 studies the effect of increasing the hopping enhancement factor r at the domain wall while keeping the local potential shift fixed at $\delta = 0$. Panel (a) shows the Fermi-level local spectral density $A_{DW}(0)$ as a function of r . Increasing r increases the kinetic energy and effective bandwidth at the domain wall until a bandwidth-driven Mott transition occurs and finite spectral weight appears at the Fermi level. The presence of two different transition values depending on whether r is increased or decreased demonstrates a coexistence (hysteresis) region: the insulating solution survives up to $r_{c,2}$ upon increasing r , whereas the metallic solution survives down to $r_{c,1} < r_{c,2}$ upon decreasing r . Panel (b) compares the total energies of these coexisting DMFT solutions and shows that the insulating solution is stable throughout the coexistence region; the paper therefore identifies the boundary transition as first order

even at zero temperature. Panels (c) and (d) show the momentum-resolved domain-wall spectral function

$$A_{\text{DW}}(k, \omega) = -\frac{1}{\pi} \text{Im } G_{\text{DW}}^R(k, \omega)$$

for $r = 2.4$, where k is the momentum along the domain wall. Panel (c) displays the spectrum over a broad energy range, whereas panel (d) is a close-up of the low-energy quasiparticle (QP) band. The color intensity represents the magnitude of $A_{\text{DW}}(k, \omega)$, so bright dispersing structures indicate energies at which electronic excitations carry large spectral weight. The red curve on the right is the momentum-integrated local spectral function,

$$A_{\text{DW}}(\omega) = \int \frac{dk}{2\pi} A_{\text{DW}}(k, \omega),$$

and therefore features such as the sharp occupied-side maximum M , the unoccupied-side plateau P , and the weaker feature S originate from the momentum-resolved structures visible in the color map. The paper attributes the dominant M and P structures to the effectively one-dimensional zig-zag geometry of the domain wall. The black line in panels (c,d) is *not* another calculation of $A(k, \omega)$ and is not obtained from DMFT; it is the dispersion $\epsilon_{\text{zigzag}}(k)$ of a non-interacting one-dimensional zig-zag tight-binding Hamiltonian whose nearest- and next-nearest-neighbour hopping constants differ by the factor $r = 2.4$. It can be plotted directly on the (k, ω) spectral-function map because for a non-interacting band

$$G_0^R(k, \omega) = \frac{1}{\omega - \epsilon(k) + i0^+}, \quad A_0(k, \omega) = -\frac{1}{\pi} \text{Im } G_0^R(k, \omega) = \delta[\omega - \epsilon(k)],$$

so the non-interacting spectral weight lies precisely along the curve $\omega = \epsilon(k)$. The agreement between this black dispersion and the bright QP structure in the interacting $A_{\text{DW}}(k, \omega)$ demonstrates that, although the quasiparticle band emerges from the correlated DMFT solution after the collapse of the Mott state, its momentum dependence is largely governed by the one-dimensional zig-zag geometry of the domain wall. The paper does not specify whether the black tight-binding dispersion was evaluated from an explicit analytical formula or obtained by numerical diagonalization; it only states that it is the dispersion of the corresponding non-interacting zig-zag-chain tight-binding Hamiltonian.

How r is dependent on a distance? Why r is bigger than 1, what if it was lower than 1?

(???? I don't understand this physics, maybe it is obvious because of common sense behind the TM model, but I don't have an answer now)

Hopping - это интеграл перекрытия двух локализованных орбиталей:

$$t = \langle \phi_i | H | \phi_j \rangle.$$

Поскольку орбитали экспоненциально затухают,

$$\phi(r) \sim e^{-r/\xi},$$

то и hopping тоже примерно экспоненциально зависит от расстояния:

$$t(d) \approx t_0 e^{-\beta(d-d_0)},$$

где

- d_0 - расстояние в объёме,
- d - расстояние в доменной стенке,
- $\beta \sim 1/\xi$.

если $d_{\text{DW}} < d_{\text{bulk}}$,
 (is it true?? but then, если $d_{\text{DW}} > d_{\text{bulk}}$, $r > 1$, so we should have $r < 1$, no?)
 $r < 1$.

(learn more intuition about r and connection of the value of t with its physical meaning)

How finally did they create the DW?

(by injection or how? is it a stable property, or there will be a reconfiguration later?)

Does this model dependent on how exactly they created the DW?

(nothing is also written about it, it assumes that there is only a static DW)

Why do we have a wide DW and there is a more contrast region there? this model ignores it, right???

(this model is not telling us anything about this darker region. right???)

How do we name the limit of applicability of the model if it doesn't take into account the reconfiguration of the DW?

(sounds like this is a very bad model, since there will be a reconfiguration later, and this model does not predict it. what does it miss???? looks like suddenly it becomes just not applicable because of the unknown reason. You just need to wait for like 20 min and you'll see that there are some dynamics in STM that goes beyond this model)

I thought that the Fermi model is applicable for a bulk. Why at all we can write it locally? Locally we don't have a 3D bulk where there is this box quantization and semiclassics?

(????? I don't know, I need to think more about it.)

Why at all they consider the DW as a one line with different r -s?

I don't see one line, I see an turbid area of several atoms there.

What exactly this model does not explain?

(the collection of this will be here, for now, I feel that there are very a lot of effects that are not explained)

Why do we have the change of the background intensity in the DW???

(okay, there is a region between walls which is blurred, but then there is the first material and it has black background, not slightly orange. why????)

(??? also, what if not one but several slots are missing??? maybe this goes beyond this model, since here a wall is 1D object....)

Where is each of the gaps?

(??? there are a lot of gaps in this article, I am confused, where is which)

What about nonequilibrium effects, all of them are beyond this model?

(??? there are a lot of gaps in this article, I am confused, where is which)

9.3.3 Questions about assumed knowledge**How is the tunnelling conductance dI/dV related to the spectral function?**

(GPT:)

In scanning tunnelling spectroscopy, the measured quantity is the tunnelling current between the STM tip and the sample as a function of the applied bias voltage V . A more microscopic expression for the current can be written in the tunnelling-Hamiltonian approximation as

$$I(V) = \frac{2\pi e}{\hbar} \sum_{kq} |T_{kq}|^2 [f(\epsilon_k - eV) - f(\epsilon_q)] \delta(\epsilon_k - eV - \epsilon_q),$$

where k labels states in the tip, q labels states in the sample, T_{kq} is the tunnelling matrix element, and $f(\epsilon)$ is the Fermi function. Replacing the sums over states by densities of states gives

$$I(V) = \frac{2\pi e}{\hbar} \int d\omega |T(\omega)|^2 \rho_{\text{tip}}(\omega - eV) \rho_{\text{sample}}(\omega) [f(\omega - eV) - f(\omega)].$$

For an interacting sample, the local density of states is directly related to the local retarded Green's function,

$$\rho_{\text{sample}}(\omega) = A(\omega) = -\frac{1}{\pi} \text{Im } G^R(\omega),$$

where $A(\omega)$ is the local spectral function. Therefore, more generally, the tunnelling current probes a convolution of the tip density of states, the sample spectral function, the tunnelling matrix element, and the Fermi occupation factors:

$$I(V) \propto \int d\omega |T(\omega)|^2 \rho_{\text{tip}}(\omega - eV) A(\omega) [f(\omega - eV) - f(\omega)].$$

Differentiating with respect to voltage gives

$$\frac{dI}{dV} \propto \int d\omega |T(\omega)|^2 \rho_{\text{tip}}(\omega - eV) A(\omega) \left[-\frac{\partial f(\omega - eV)}{\partial \omega} \right],$$

up to additional terms if the tunnelling matrix element or tip DOS varies significantly with energy. At zero temperature,

$$-\frac{\partial f(\omega - eV)}{\partial \omega} = \delta(\omega - eV),$$

so if the tip density of states and tunnelling matrix element are approximately constant in the relevant energy window,

$$\frac{dI}{dV}(V) \propto A(eV) = -\frac{1}{\pi} \text{Im } G^R(eV).$$

Thus, the experimentally measured differential conductance dI/dV is approximately proportional to the local spectral density of the sample. The voltage V used experimentally and the frequency variable ω used in the theoretical spectral function describe the same energy scale: in ordinary units $E = eV = \hbar\omega$, while in condensed-matter calculations one often sets $\hbar = 1$ and simply treats ω as an energy variable measured relative to the Fermi level.

When is $dI/dV(V) \propto A(eV)$ not applicable?

(GPT:)

The frequently used relation

$$\frac{dI}{dV}(V) \propto A(eV)$$

is not an exact general identity. It follows from the more general tunnelling expression

$$I(V) \propto \int d\omega |T(\omega, V)|^2 \rho_{\text{tip}}(\omega - eV) A_{\text{sample}}(\omega) [f(\omega - eV) - f(\omega)].$$

Thus, the differential conductance directly reproduces the sample spectral function only when several conditions are satisfied: the temperature is sufficiently low, the density of states of the STM tip is approximately constant in the relevant energy interval, the tunnelling matrix element is approximately independent of energy and bias, and the weak-tunnelling approximation is valid.

The simple proportionality can fail or require corrections in the following situations:

1. **Finite or high temperature.** At $T > 0$,

$$-\frac{\partial f}{\partial \omega}$$

has a finite width of order $k_B T$. Consequently,

$$\frac{dI}{dV}(V) \propto \int d\omega A_{\text{sample}}(\omega) \left[-\frac{\partial f(\omega - eV)}{\partial \omega} \right],$$

even for a featureless tip and constant tunnelling matrix element. Therefore, dI/dV is a thermally broadened version of the spectral function rather than its value at one energy.

2. **Energy-dependent density of states of the tip.** If $\rho_{\text{tip}}(\omega)$ changes appreciably over the energy window of interest, the measured conductance contains spectral structures originating from both the sample and the tip:

$$\frac{dI}{dV} \not\propto A_{\text{sample}}(eV).$$

This is particularly important when the tip itself has nontrivial electronic structure, for example for a superconducting tip.

3. **Energy- or bias-dependent tunnelling matrix element.** In general,

$$T = T(\omega, V, \mathbf{r}),$$

so different sample states can have different probabilities of tunnelling into the tip. The measured dI/dV is then a matrix-element-weighted spectral density rather than the bare local spectral density.

4. **Breakdown of the weak-tunnelling approximation.** The standard expression assumes that the tip and sample are weakly coupled and that tunnelling can be treated perturbatively. If the tip is brought sufficiently close to the sample, higher-order tunnelling and modification of the sample by the tip can become relevant, and the simple relation between dI/dV and $A(\omega)$ is no longer valid.

5. **Additional inelastic tunnelling channels.** Electrons may tunnel while exciting phonons, spin excitations, or other collective modes. Such processes can generate additional structures in dI/dV (and particularly in d^2I/dV^2) that cannot be interpreted simply as peaks of the one-electron sample spectral function.
6. **Strong voltage dependence or large-bias measurements.** At sufficiently large bias, the electronic structure, tunnelling barrier, and tunnelling matrix elements may change significantly with V . In this regime it is generally unjustified to treat the tip DOS and tunnelling matrix element as constants.

Hence, $\frac{dI}{dV}(V) \propto A(\text{eV})$ should be understood as a useful low-temperature, weak-tunnelling, featureless-tip approximation. In the general case, dI/dV is a convolution and matrix-element-weighted probe of the electronic spectral function rather than the spectral function itself.

9.3.4 Reproduction of some statements

Why does the hopping scale as d^{-5} ?

(GPT: see cited paper, there is no short derivation of this complicated statement)

In the Supplementary Material, the hopping between the David-star-centered Wannier orbitals is estimated using the standard Harrison scaling for transition-metal d orbitals,

$$t_{dd}(d) \propto d^{-5}.$$

This scaling originates from tight-binding estimates of two-center hopping matrix elements between d orbitals. In Harrison's parametrization, the d - d hopping integrals have the form

$$V_{ddm} \propto \frac{\hbar^2 r_d^3}{m d^5}, \quad m = \sigma, \pi, \delta,$$

where d is the interatomic separation and r_d characterizes the spatial extent of the atomic d orbital. Thus, changing the distance from d_0 to d gives approximately

$$r \equiv \frac{t(d)}{t(d_0)} \simeq \left(\frac{d_0}{d} \right)^5.$$

The d^{-5} dependence is therefore not derived specifically for the David-star Wannier orbitals of 1T-TaS₂; Skolimowski *et al.* adopt Harrison's d -orbital scaling as an estimate for how their hopping changes with the David-star separation.

Reference: W. A. Harrison, *Electronic Structure and the Properties of Solids: The Physics of the Chemical Bond* (Freeman, San Francisco, 1980).

Derivation of the mixed-basis kinetic Hamiltonian.

(GPT:)

The kinetic part of the Hubbard Hamiltonian is

$$H_{\text{kin}} = - \sum_{\langle i,j \rangle, \sigma} t_{ij} c_{i\sigma}^\dagger c_{j\sigma}.$$

To exploit the translation symmetry along the domain-wall direction, one introduces a partial Fourier transform along this direction,

$$c_{x,n,\sigma} = \frac{1}{\sqrt{N}} \sum_k e^{ikna} c_{x,k,\sigma},$$

where x labels the distance perpendicular to the domain wall, n labels sites along the wall, k is the corresponding quasi-momentum, and a is the inter-site distance. The triangular lattice has two kinds of nearest-neighbour hopping processes. First, hopping between the two neighbours within the same row x gives

$$-t \sum_{x,n,\sigma} (c_{x,n,\sigma}^\dagger c_{x,n+1,\sigma} + c_{x,n,\sigma}^\dagger c_{x,n-1,\sigma}).$$

After the Fourier transformation,

$$\sum_n c_{x,n}^\dagger c_{x,n\pm 1} = \sum_k e^{\pm ika} c_{x,k}^\dagger c_{x,k},$$

so that

$$e^{ika} + e^{-ika} = 2 \cos(ka)$$

and therefore this contribution becomes

$$- \sum_{x,k,\sigma} 2t \cos(ka) c_{\{x,k\},\sigma}^\dagger c_{\{x,k\},\sigma}.$$

Second, neighbouring rows x and $x+1$ are connected by two diagonal triangular-lattice bonds with longitudinal displacements $\pm a/2$ and hopping amplitudes $t_{1,x}$ and $t_{2,x}$. Under the partial Fourier transform, a longitudinal displacement Δy produces a phase factor $e^{ik\Delta y}$, so these two bonds give the effective k -dependent hopping

$$t_{1,x} e^{-ika/2} + t_{2,x} e^{ika/2}.$$

Thus the hopping from row x to row $x+1$ becomes

$$- \sum_{x,k,\sigma} (t_{1,x} e^{-ika/2} + t_{2,x} e^{ika/2}) c_{\{x+1,k\},\sigma}^\dagger c_{\{x,k\},\sigma}.$$

The reverse hopping is the Hermitian-conjugate contribution,

$$- \sum_{x,k,\sigma} (t_{1,x-1}^* e^{ika/2} + t_{2,x-1}^* e^{-ika/2}) c_{\{x-1,k\},\sigma}^\dagger c_{\{x,k\},\sigma}.$$

Combining all terms gives

$$\begin{aligned} H_{\text{kin}} = & - \sum_{x,k,\sigma} \left[2t \cos(ka) c_{\{x,k\},\sigma}^\dagger c_{\{x,k\},\sigma} \right. \\ & + (t_{1,x} e^{-ika/2} + t_{2,x} e^{ika/2}) c_{\{x+1,k\},\sigma}^\dagger c_{\{x,k\},\sigma} \\ & \left. + (t_{1,x-1}^* e^{ika/2} + t_{2,x-1}^* e^{-ika/2}) c_{\{x-1,k\},\sigma}^\dagger c_{\{x,k\},\sigma} \right], \end{aligned}$$

which is Eq. (3) of the Supplementary Material. The factor $2t \cos(ka)$ originates from the two nearest neighbours along the domain-wall direction, while the terms $t_{1,x} e^{-ika/2} + t_{2,x} e^{ika/2}$ originate from the two diagonal bonds connecting adjacent rows of the triangular lattice. In this mixed representation, the Hamiltonian becomes block diagonal in k , so that each fixed- k block describes an effective one-dimensional system in the transverse x direction. The Supplementary Material states this partial-Fourier-transform construction and the resulting Eq. (3), although it does not show the intermediate algebra explicitly.

Derivation of the boundary self-energy, Eq.

$$\Sigma_{\text{B-S}}(z, k) = \frac{z + 2t \cos(ka)}{2} \left(1 - \sqrt{1 - \frac{4|t(e^{ik\frac{a}{2}} + e^{-ik\frac{a}{2}})|^2}{(z + 2t \cos(ka))^2}} \right)$$

(SUMMARY: GPT:)

After the partial Fourier transformation along the domain-wall direction, each fixed- k block becomes an effective one-dimensional chain in the transverse x direction. Far away from the domain wall the system is homogeneous, so the hopping between neighbouring x -layers is

$$\tau_k = t(e^{ika/2} + e^{-ika/2}) = 2t \cos\left(\frac{ka}{2}\right),$$

while the motion along the domain-wall direction produces the diagonal energy shift

$$\epsilon_k = -2t \cos(ka).$$

Therefore, for a fixed k , the homogeneous semi-infinite part of the system is equivalent to a semi-infinite one-dimensional chain with on-site term ϵ_k and nearest-neighbour hopping τ_k . The Supplementary Material introduces the boundary self-energy in precisely this way, writing it in terms of the surface Green's function of a semi-infinite chain. :contentReference[oaicite:0]index=0

Let

$$g_s(z, k)$$

be the Green's function at the first site of this semi-infinite chain. Since removing the first site leaves another identical semi-infinite chain, the surface Green's function satisfies the recursion relation

$$g_s(z, k) = \frac{1}{z - \epsilon_k - |\tau_k|^2 g_s(z, k)}.$$

Using

$$\epsilon_k = -2t \cos(ka),$$

this becomes

$$g_s(z, k) = \frac{1}{z + 2t \cos(ka) - |\tau_k|^2 g_s(z, k)}.$$

Multiplying through by the denominator gives

$$|\tau_k|^2 g_s^2 - [z + 2t \cos(ka)] g_s + 1 = 0.$$

Solving this quadratic equation,

$$g_s(z, k) = \frac{z + 2t \cos(ka) \pm \sqrt{[z + 2t \cos(ka)]^2 - 4|\tau_k|^2}}{2|\tau_k|^2}.$$

The physical branch is selected by requiring

$$g_s(z, k) \sim \frac{1}{z} \quad \text{for } |z| \rightarrow \infty,$$

which selects the minus sign:

$$g_s(z, k) = \frac{z + 2t \cos(ka)}{2|\tau_k|^2} \left[1 - \sqrt{1 - \frac{4|\tau_k|^2}{[z + 2t \cos(ka)]^2}} \right].$$

The finite system couples to this semi-infinite environment through the hopping τ_k . Integrating out the semi-infinite chain therefore generates the boundary self-energy

$$\Sigma_{\text{B-S}}(z, k) = |\tau_k|^2 g_s(z, k).$$

Substituting the expression for g_s gives

$$\Sigma_{\text{B-S}}(z, k) = \frac{z + 2t \cos(ka)}{2} \left[1 - \sqrt{1 - \frac{4|\tau_k|^2}{[z + 2t \cos(ka)]^2}} \right].$$

Finally, inserting

$$\tau_k = t (e^{ika/2} + e^{-ika/2})$$

yields

$$\Sigma_{\text{B-S}}(z, k) = \frac{z + 2t \cos(ka)}{2} \left[1 - \sqrt{1 - \frac{4|t(e^{ika/2} + e^{-ika/2})|^2}{[z + 2t \cos(ka)]^2}} \right],$$

which is Eq. (4) of the Supplementary Material. Equivalently,

$$\Sigma_{\text{B-S}}(z, k) = |t(e^{ika/2} + e^{-ika/2})|^2 g_s(z + 2t \cos(ka), k).$$

Thus, Eq. (4) is simply the usual embedding self-energy

$$\Sigma = |\tau|^2 g_{\text{surface}}$$

for a semi-infinite tight-binding chain, applied separately to each quasi-momentum k block produced by the partial Fourier transformation.

10 Quantum jamming transition to a correlated electron glass in 1T – TaS₂ by Gerasimenko, Vaskivskyi, Litskevich, Ravnik, Vodeb, Diego, Kabanov, Mihailovic (2019)

Abstract

Distinct many-body states may be created under non-equilibrium conditions through different ordering paths, even when their constituents are subjected to the same fundamental interactions.

The phase-transition mechanism to such states remains poorly understood.

Here, we show that controlled optical or electromagnetic perturbations can lead to an amorphous metastable state of strongly correlated electrons in a quasi-two-dimensional dichalcogenide.

Scanning tunnelling microscopy reveals a hyperuniform pattern of localized charges, whereas multitip surface nanoscale conductivity measurements and tunnelling spectroscopy show an electronically gapless conducting state that is different from conventional Coulomb glasses and manybody localized systems.

The state is stable up to room temperature and shows no signs of either local charge order or phase separation.

The mechanism for its formation is attributed to a dynamical localization of electrons through mutual interactions.

Theoretical calculations confirm the correlations between localized charges to be crucial for the state's unusual stability.

10.1 Article

10.1.1 Article

In the search for fundamentally new forms of quantum matter through non-equilibrium transitions ^{1–6}, other options may be available beyond standard Ginzburg-Landau transitions (and the Standard Model) or the currently popular topological transitions ⁷. Perhaps the most intriguing, and possibly the "deepest and most interesting unsolved problem in condensed matter theory" is the glass transition ⁸. However, in spite of significant studies by different types of excitation in very diverse systems that exhibit such transitions, profoundly new states have proved elusive. Most commonly in complex electronic materials, short-lived transient ordering of electrons is observed that rapidly reverts to the ground state ^{9,10}. Alternatively, metastable states may form, but these are usually closely related to nearby phases in the equilibrium phase diagram ^{2,11–16}. Among candidate systems that have multiple competing interactions and rapid electronic ordering ¹⁷, a material of recent interest is the layered dichalcogenide 1T-TaS₂ (Fig. 1a). In equilibrium this well-studied dichalcogenide has an extraordinarily rich phase diagram driven by lattice strain ¹⁸, Coulomb interactions ¹⁹, a Fermi surface instability ²⁰ and orbital ordering ²¹, and includes a hightemperature metallic state and various charge-density wave states, as well as superconductivity ²² and an unusual gapless quantum spin liquid-like ground state ²³. Its phase diagram is extended by photoexcitation ¹³ and short-lived transient shifts of the electronic ordering vector have been reported under different conditions ²⁴. Here we report a study of a dense metastable glassy electronic quantum state transition that is unrelated to any of the existing states of the equilibrium or non-equilibrium phase diagram of this or any other known quantum system. It is formed by density-driven correlations of nonequilibrium electrons, which form a hyperuniform spatial charge density distribution ²⁵. Hyperuniformity is an important category of non-equilibrium many-body ordering that leads to maximally random jammed packing ^{25,26}, a state with the highest achievable packing density ²⁵. Such distributions were previously found in systems as diverse as the cosmic microwave background ²⁷, cold (Bosonic) atoms ²⁸, chicken eyes ²⁹, fairy circles ³⁰ and, theoretically so far, in spin-polarized free Fermions ³¹, but not observed experimentally in electronic states.

The commensurate (C) ground state of the system of 1 T – TaS₂ at 4.2 K from which we began our experiments is shown in the scanning tunnelling microscope (STM) image in Fig. 1c. Commonly, it is viewed either as a triple charge density wave ^{20,21} or a hexagonally packed Mott state of localized electrons-or polarons-subject to screened Coulomb interactions ^{19,22,23,32}. In the latter correlated state picture, polarons are formed by a central Ta atom with a localized electron, surrounded by 12 Ta atoms displaced towards it to form the shape of a hexagram that provides screening (Fig. 1c insets). Their characteristic signature appears in photoexcitation experiments as a peak in optical conductivity ³³. After exposure of a $d \approx 100\mu\text{m}$ diameter spot to a single 30fs, 400 or 800 nm (3 or 1.5 eV) laser pulse with fluence adjusted above a threshold value of $F \approx 3.5\text{ mJ cm}^{-2}$ (Methods, Supplementary Note 1 and Supplementary Figs. 1 and 2), the peak electronic temperature within a few hundred femtoseconds is estimated to be in excess of 4,000 K, whereas the lattice one exceeds 600 K after 15 ps (Supplementary Fig. 3). The STM image reveals a dramatic change caused by the photoexcitation (Fig. 1d,e). There is no sign of order, but the polarons now show an amorphous (A) arrangement that densely fills the entire surface. Remarkably, we saw no long-range density fluctuations, which is a signature of hyperuniformity ²⁶ rather than of randomness. A similar effect over an area $l^2 \approx 1 \times 1\mu\text{m}$ was observed when a 10 V pulse from an STM tip was passed through the sample (Methods). The amorphous structure was completely stable at 4.2 K during the scanning (Supplementary Fig. 4). Remarkably, under sequential STM scanning conditions at 77 K the system became perceptibly more amorphous with time, and showed no tendency of relaxation towards the C ground state. Measuring the polaron diffusion with consecutive scans

revealed an anomalous diffusion exponent α with the mean square displacement $\sigma_d^2 \propto \Delta t^\alpha$ and $\alpha \simeq 0.6$. Such subdiffusion processes with $\alpha < 1$ are observed in glassy systems³⁴ and commonly discussed in the context of non-ergodicity³⁵. (A detailed analysis is

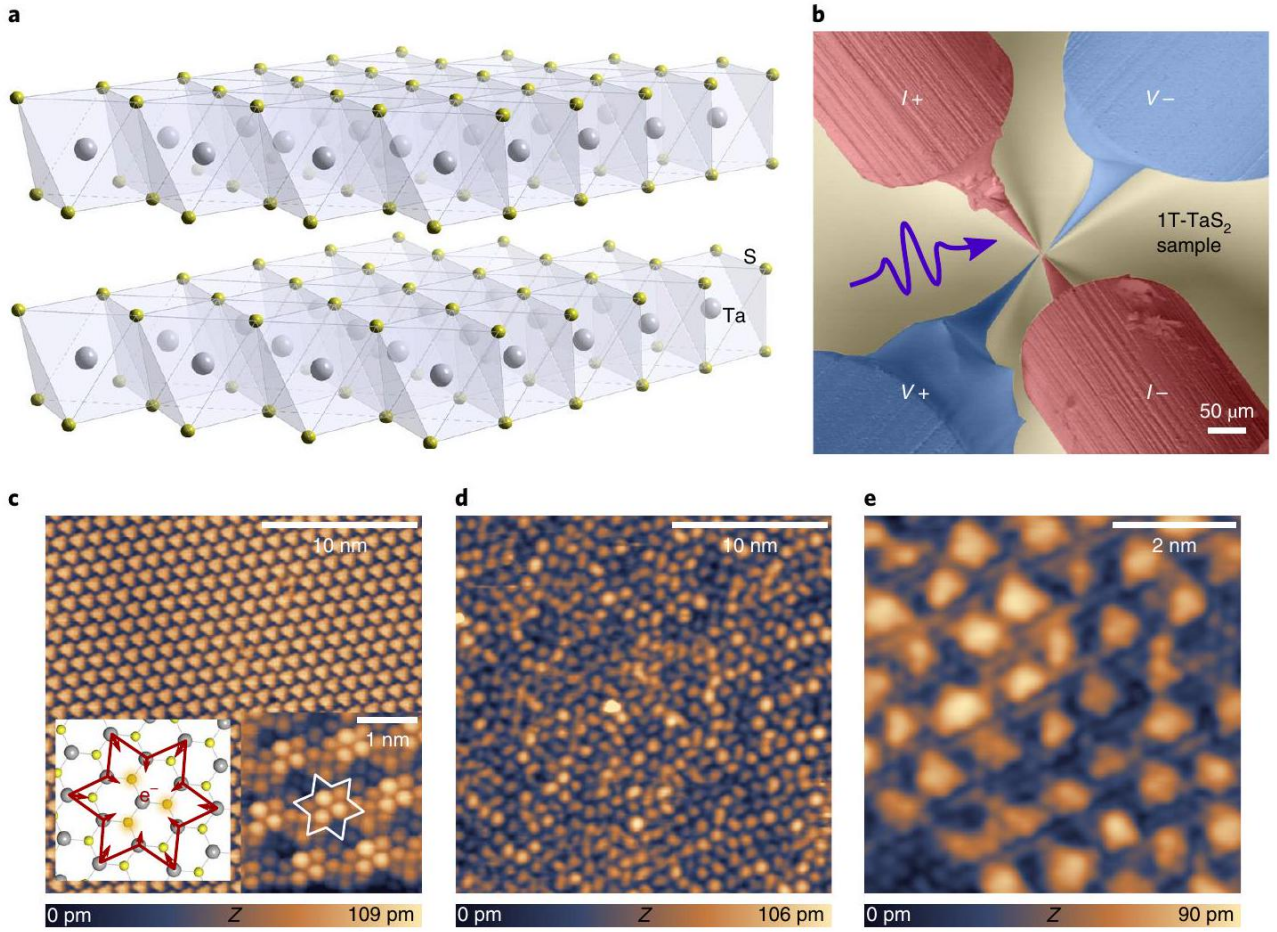


Fig. 1 | Structure, experiment and basic observation by STM of the initial and final states of polarons after excitation by a single laser pulse. **a**, Schematic view of two layers of a 1T-TaS₂ crystal. The lines represent bonds. **b**, Four-tip ultrahigh vacuum low-temperature STM combined with ultrafast laser pulse excitation. The pseudocolour image is taken in situ from above with a scanning electron microscope. The tips coloured red and blue are used for current injection and voltage sensing, respectively, in the four-probe resistivity measurements. **c**, The raw STM image of the C ground state exhibits a regular lattice of polarons. Left inset: a polaron schematic (only the top S layer is shown). Right inset: a (raw) atomic resolution STM image. A triangular pattern of S atoms on the surface around the central Ta atom is enhanced by the chosen tip bias voltage ($V_t = 100\text{mV}$ for the right inset and -800 mV for main panel). Z is the apparent height measured by STM. **d**, The raw STM image of the photoexcited state (A) formed after a single 30 fs pulse at 4.2 K shows an amorphous structure. **e**, An atomic resolution image of the A state shows localized polarons superimposed on the atomic lattice.

presented in Supplementary Note 2.) The barrier for relaxation to the C state is thus clearly quite high, which is confirmed by the fact that the unperturbed state is stable for long periods (days) up to 200 K, and even at room temperature when pinned around imperfections. However, 3 V pulses from the STM tip eventually caused local patches of C order to appear (Supplementary Fig. 8). The fluence dependence of the spectral features of the collective mode measured by coherent phonon spectroscopy reveals that the transformation was not limited to

the surface layer, but was present up to a depth of at least 20 nm (Supplementary Note 1). This is confirmed by the tip-distance dependence of resistivity in multitip transport measurements described later.

Optimizing STM contrast and tip bias allows us to identify the relative positions of localized electrons and compare their polaronic pair distribution functions (PDFs) $g_{\text{pol}}^{(2)}(r)$, which give the average probability of finding two particles separated by distance r , in the A state with the C ground state (Fig. 2a-c). Two things became apparent: (1) the A state had a much smaller nearest-neighbour distance $d(1 \pm 0.05 \text{ nm})$ than the C state and (2) there was a notable absence of any peaks at $r > 3 \text{ nm}$, which implies an absence of long-range correlations beyond three nearest neighbours. A similar PDF analysis for the atomic pattern $g_{\text{at}}^{(2)}(r)$ (Fig. 2d,e) revealed that the smaller near-est-neighbour positions found in polaronic PDFs (Fig. 2b) coincide with the fifth atomic neighbour, which demonstrates that in the A state electrons predominately cause distortions on atomic sites, which correspond to nearest-neighbour polaron-polaron distances.

Clearly, separated peaks at large distances (Fig. 2e) signify that the underlying lattice is only locally distorted without perturbation of the long-range lattice order.

The simplest picture of the amorphous polaron state is that the local hexagram maintains its original shape whereas the longrange order of the hexagrams is lost. Figure 2e supports this picture, but the absence of atomic spots in the autocorrelation image (Supplementary Fig. 9) suggests that the local hexagram structure itself is not well-defined and not always centred at the Ta site, as it is in the C state.

Plotting the polaron number variance σ_N^2 , evaluated on different spatial scales R , as $\sigma_R^2 = (\sigma_N/(R/D))^2$ versus the normalized distance (R/D), where D is the nearest-neighbour distance, we see a clear spatial decay, which is a signature of a hyperuniform distribution common in classic jammed systems²⁵. A fit (Fig. 2f) reveals a hyperuniformity exponent of $\beta = -0.60 \pm 0.03$. For comparison, random polaron packing would give $\beta = 0$ ($\sigma_R^2 = \text{constant}$) (Supplementary Method 1 gives a detailed analysis). We note that number density fluctuations in the A state are suppressed on length scales substantially larger than the estimated screening length of the electric field (Supplementary Fig. 12). Remarkably, the density of localized polarons in the A state is $\sim 23\%$ higher ($n_A = 0.98 \pm 0.02 \text{ nm}^{-2}$) than that in the hexagonally packed C ground state ($n_C = 0.80 \pm 0.02 \text{ nm}^{-2}$); a surprising fact, given that the hexagonal packing of charges in the C state is the densest possible packing of classic spheres in two dimensions (2D). The remarkable stability (to $> 200 \text{ K}$) and the absence

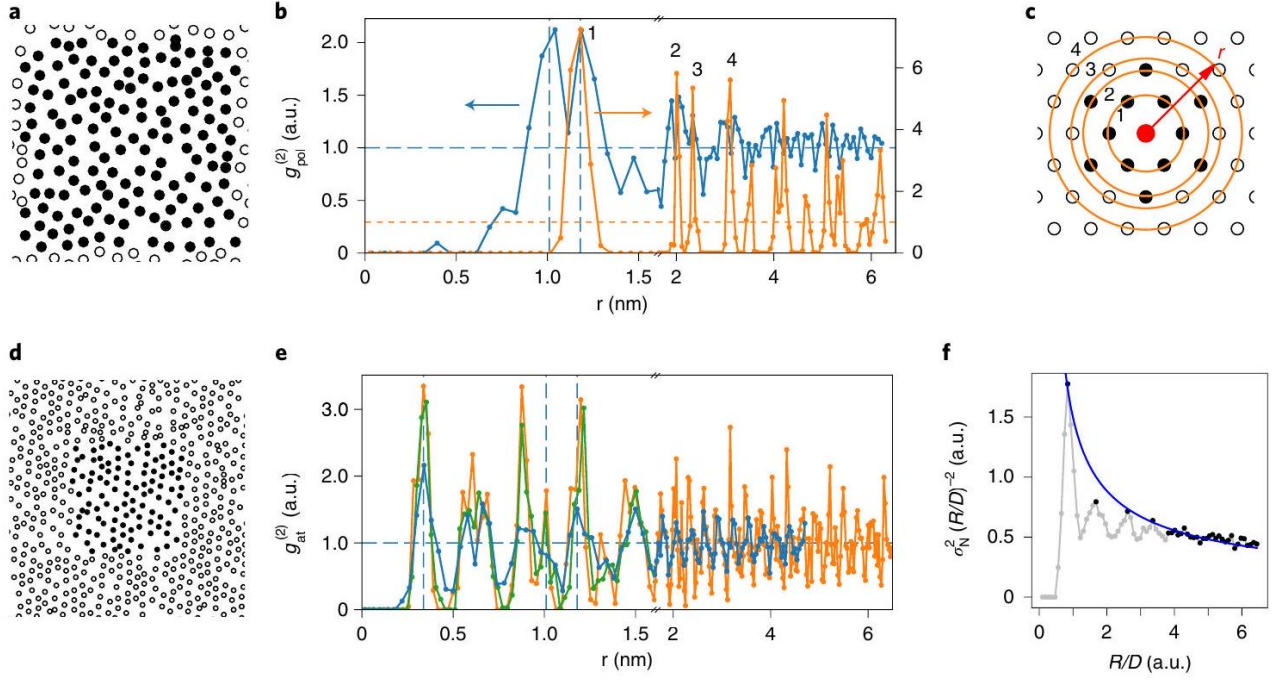


Fig. 2 | Distances in between polarons and atoms. **a**, A point pattern extracted from the experimental STM images of polarons in Fig. 1d (Methods). Filled black circles mark the particles over which the averaging was done in the calculation of the PDF. **b**, Polaron PDFs $g_{\text{pol}}^{(2)}(r)$ for the A (blue) and C (orange) states derived from **a**. Blue and orange dashed horizontal lines indicate the $g_{\text{pol}}^{(2)}(r) = 1$ levels (that is, lack of order-homogeneous particle distribution) for the A and C states. **c**, The peak assignments for the C state in terms of the nearest neighbours (coordination circles). **d**, A point pattern of atoms extracted from Fig. 1e. **e**, Atomic PDFs of the A (blue), C (orange) and simulated C (green) states. Blue dashed horizontal line indicate $g_{\text{at}}^{(2)}(r) = 1$ level. The PDF in the A state is distorted at 1 nm and 1.15 nm, which correspond to the nearest-neighbour polaron distances (blue vertical dashed lines). **f**, Radial dependence of the normalized polaron number variance $\sigma_N^2 = (\sigma_N/(R/D))^2$ (polaron density fluctuations). Here R and D are the observation window radius and characteristic polaron size. The blue line is a power law fit to σ_N^2 , which gives the hyperuniformity exponent $\beta = -0.6 \pm 0.03$ (Supplementary Method 1 gives details of the calculations and fit). a.u., arbitrary units.

of relaxation towards the C state implies that polarons are trapped in configurational space by strong mutual correlations and exhibit the kind of non-ergodicity that is expected for maximally correlated jammed states²⁶.

Investigating the electronic structure by scanning tunnelling spectroscopy reveals that the density of electronic states (DOS) derived from the logarithmic derivative of the conductance $\text{DOS} \propto (dI/dV)/(I/V)$ is convincingly gapless at all points on the surface (Fig. 3a-c) with a small V-shaped dip in the range $\pm 0.1\text{eV}$ from the Fermi energy (E_F) that can be interpreted as a signature of incipient localization by some fraction of the carriers³⁶, typical for interacting systems with disorder³⁷ (Fig. 3b shows the spot-to-spot variation of spectra). In contrast, the C state shows distinct sharp features commonly assigned to Hubbard bands^{19,38–40} and zero conductance within the gap from -0.1 V to $+0.15\text{ V}$ (Fig. 3a).

To ascertain the nature of charge transport with the evidently immobile charges in the A state we performed a four-STM-tip measurement with ohmic contacts, $\sim 2.5\mu\text{ m}$ apart (Fig. 1b and Supplementary Fig. 13). STM scans were first used to confirm the amorphous polaron structure after switching with a 30 mA pulse passed between a pair of tips (Supplementary

Method 2 gives details). The result of switching is unambiguous: the resistivity drops on $C \rightarrow A$ switching to $\rho \approx 18 \text{ m}\Omega \text{ cm}$, with a linear current-voltage characteristic (Fig. 3d). This is more than two orders of magnitude smaller than typical in-plane published values²² of the C state at 4 K or one order of magnitude smaller than the resistivity of crystals from the same growth batch⁴¹ at 20 K, as shown in Fig. 3d. The temperature dependence of resistivity by a four-probe measurement was found to be compatible with 3D variable range hopping (VRH) of the form $R_{\text{VRH}} \propto \exp(T/T_0)^\gamma$, with $\gamma \simeq -1/4$ (Fig. 3d and Supplementary Discussion 2). The 3D nature of transport is confirmed by the fact that the resistance between tips depends on the distance L between them and shows behaviour close to $R \approx 1/L$ expected for 3D (Supplementary Method 2). The implication is that the localized charges observed by STM are not responsible for transport—in fact, they do not move when a current is passed—but they are coupled to other carriers that show VRH-like transport.

Amorphous matter that is denser than the crystalline form is very rare in nature⁴², which leads to the intriguing question: what is the path that leads to such a new state in a system that already exhibits multiple and diverse orders and that does not lead to one of the existing ones? Emergent states of quantum matter may be created if—through many-body interactions—its constituents order before it reaches thermal equilibrium. The non-ergodic dynamics observed here suggest that the localization of a significant fraction of the available electrons takes place through mutual correlations.

If we consider the Coulomb repulsion as an analogue of hard-sphere interactions in classic systems, then above a certain critical density all the available space is filled by the localizing carriers and the electrons become immobilized as a result of mutual correlations following the classic density-driven jamming transition scenario. Thereafter, the band picture is no longer applicable, and we need to consider a coupled system of itinerant holes and jammed electrons, respectively, for which there is no obvious precedent. Note that the localized states occupy the same region of real space as the itinerant carriers, which can lead to quantum interference between the itinerant and localized states⁴³.

Conventional many-body electron localization may occur on a regular 2D lattice as a result of coupling to either slow spin²³ or lattice fluctuations^{44,45}, which leads to disorder and non-ergodic behaviour^{45,46}. However, so far such model discussions^{46,47} have led to single-system many-body localization with a gapped spectrum,

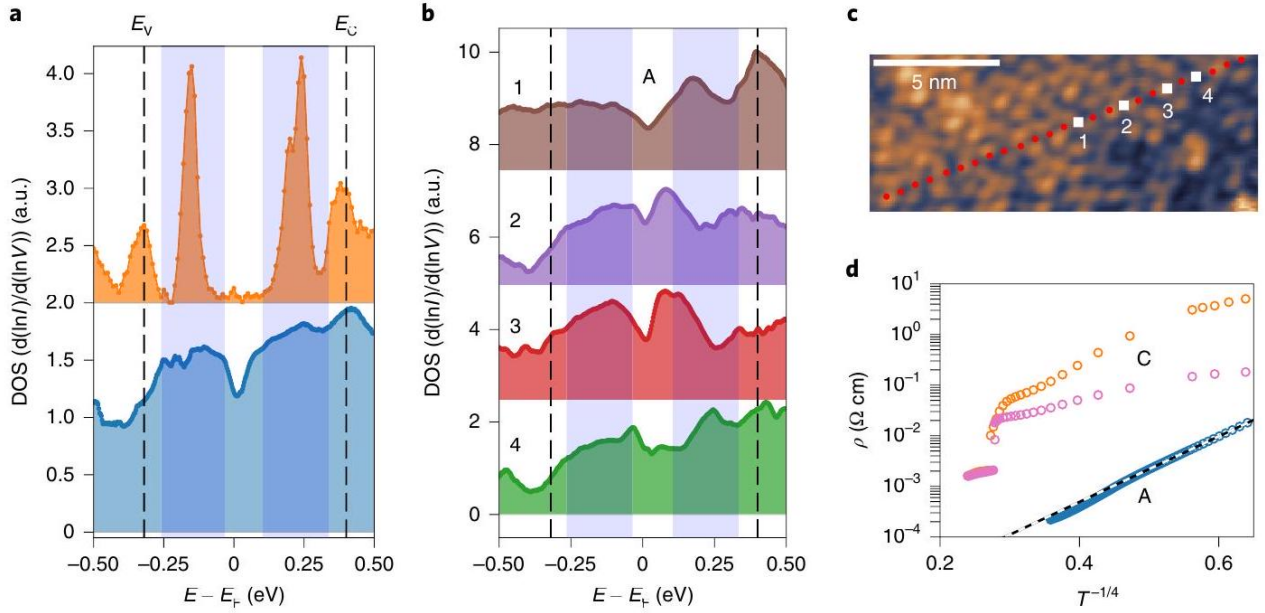


Fig. 3 | Electronic properties from tunnelling spectroscopy and transport measurements. **a**, Comparison of the DOS in the C (top) and A (bottom) states (the latter is averaged over 25 different points on the surface shown in **c**). The dashed lines indicate the C -state band edges, E_V and E_C , and the vertical grey regions indicate the position of the lower and upper Hubbard bands. The energy is shown with respect to E_F . **b**, Individual DOS curves measured at different points (white squares in **c**), which illustrate the variations of the DOS. **c**, Surface topography in the A state. Red dots indicate where the spectroscopy curves were measured for the average DOS in **a**. **d**, The four-tip resistivity in the C state and the A state measured with ohmic contacts. The C -state temperature (T) dependence is known to vary significantly from sample to sample, shown here for two extreme examples. In contrast, the T dependence of the A -state resistance is more consistent, with VRH $R \propto \exp(T/T_0)^\gamma$. The fits give $\gamma = -1/4$.

which is not compatible with gapless DOS and transport seen here. The stability of the correlation-localized electron subsystem, subject to Coulomb repulsion and lattice strain, can be investigated with the classic Hamiltonian $^{32}H = \sum_{i,j} V(i,j) (n_i - \bar{n})(n_j - \bar{n})$. Here $V(i,j)$ is an exponentially screened Coulomb potential (provided by the itinerant electron background), $n_i = 1$ if the site is occupied and 0 otherwise, and $\bar{n}$ is the average polaron density. Model Monte Carlo simulations of H on a triangular lattice using the experimental density $\nu_A = 0.094$ per unit cell as a fixed input parameter gave a configurational minimum which compares remarkably well with the experiments (Fig. 4a,b), whereas a density that corresponds to the C state ($\frac{1}{13}$) leads to a hexagonally packed ordered state (Methods and Supplementary Discussion 3 give details). The minor differences in the local packing are probably related the effects of the lattice that are not taken into account by the model, such as interaction via distortions and the fact that the polarons are not point charges but rather have a specific atomic arrangement that needs to be matched between the neighbours. Experimentally, our observation that relaxation proceeds in the direction of greater disorder (Supplementary Note 2) supports the implied notion that the A state is energetically favourable. The model also predicts a hyperuniform distribution of polarons-the PDFs (Fig. 4f) show quite good agreement with the STM data (Fig. 2b) and a comparable hyperuniformity exponent $\beta_{\text{theory}} = -0.87 \pm 0.04$ (Fig. 4g). Screened Coulomb interactions are thus apparently sufficient to obtain a hyperuniform polaron distribution even without considering spin or lattice disorder. However, as charge transport is limited by carrier diffusion within this model 32,48 , by itself it cannot explain the observed transport properties.

Although the localized carriers discussed by the polaron lattice gas model do not contribute to transport, coupled quasiparticles lead to transport that is similar to that in regular charge density waves. The major difference is that the A state is gapless, and hence the VRH behaviour and not a simple activated temperature dependence defined by a charge density wave gap. Such itinerant VRH/localized carrier duality has been observed, but not yet properly understood, in some other complex multiband systems, most notably cuprate superconductors ⁴⁹.

Generically, self-assembled glasses may be thought to result from competing interactions with different ranges. The glass-like behaviour is predicted theoretically to arise as a result of the appearance of an exponentially large number of metastable states with different effective charge density ⁵⁰. The undoped C ground state structure has an electron number density $\nu = \frac{1}{13}$ per 1T-TaS₂ elementary unit cell, but other electron-rich metastable structures with different $\nu = \frac{1}{4}, \frac{1}{7}, \frac{1}{9}, \frac{1}{12}, \frac{1}{13} \dots$ are possible; their primitive cells are shown in Fig. 4e. The observed average experimental density in the A state is $\nu = 0.094$. The effective charge q^* of each localized polaron is shown by a Voronoi cell construction shown in Fig. 4a,b for the experimental data and the model, respectively. It reveals a tiling of irregular polygons with no translational or rotational symmetry. Generally, $q^* \neq e/13$ so each electron is shared between different numbers of Ta atoms. By analysing the inter-polaron distances, we can assign polaron surroundings to the corresponding primitive cells (Fig. 4c,d), which shows a tessellation with tiles whose charge densities are between $e/9$ and $e/13$ per elementary unit cell. Significantly, there was no sign of phase separation or aggregation into any kind of regular structure, which confirms that the A structure is a local minimum of energy. Reaching this minimum requires dynamic localization that leads to a density-driven transition to the hyperuniform state.

The present experiments suggest a specific path of the quantum glass transition to a hyperuniform state of a system of thermalizing Fermions. In the present case, there are specific features of the Fermi surface that appear to be relevant, such as the dispersionless band close to the Fermi level ²⁰ (Supplementary Fig. 16), which leads to localization and jamming of some proportion of the non-equilibrium electrons. However, we may expect to find more examples of an amorphous state in 2D fermionic systems on the basis of screened Coulomb interactions on square lattices, as in transition metal oxides, for example, where competing orders are very common.

Although we have discussed the problem in terms of the polaron picture, an alternative viewpoint (discussed in Supplementary Discussion 4) invokes a description of the observed charge density in terms of coherent superpositions of electrons in the bands near

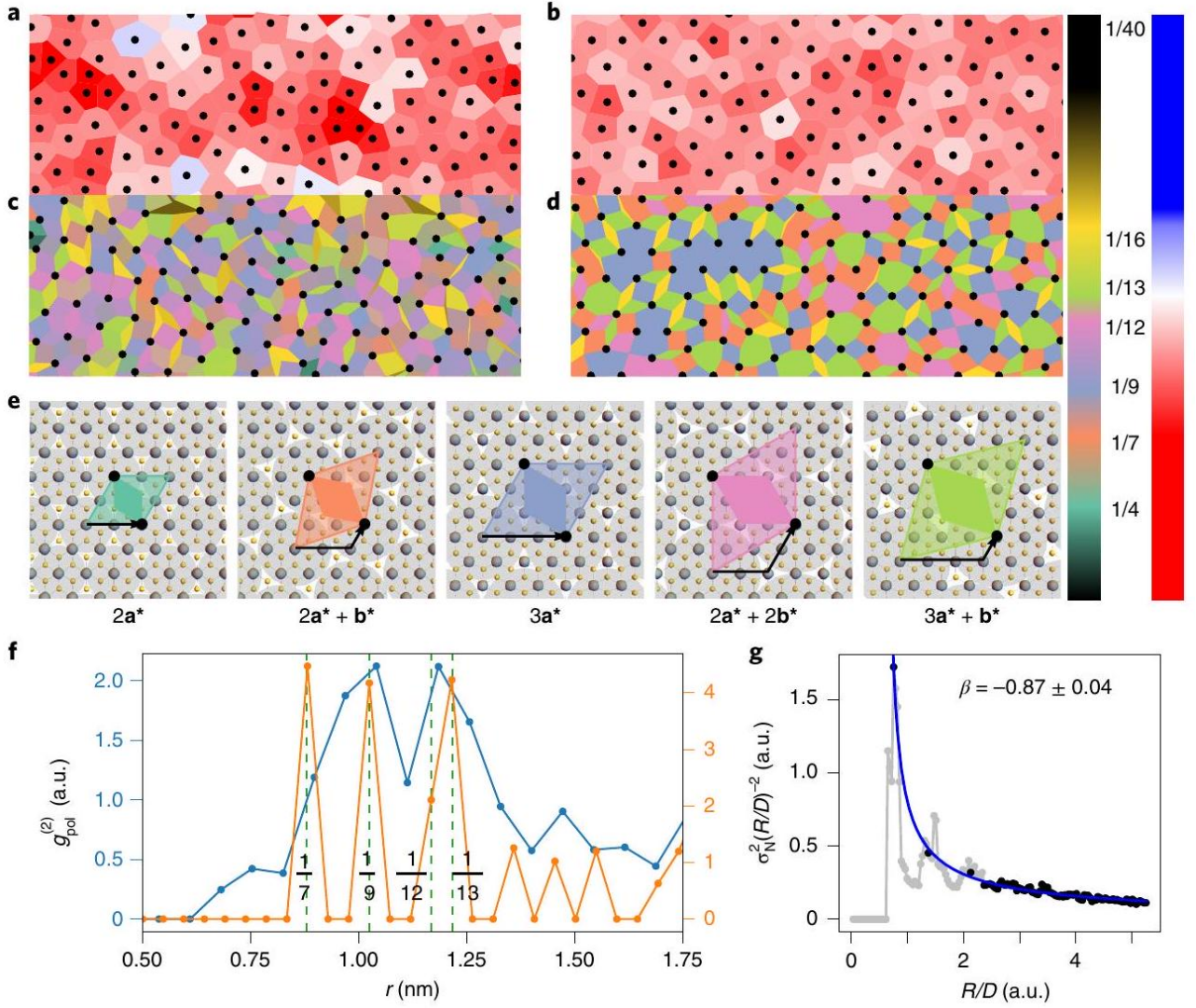


Fig. 4 | Tiling patterns formed by polarons in the A state, comparing experiment (**a, c**) and theory (**b, d**). **a, b**, The effective polaron charge for each Voronoi cell, which varies from $\frac{1}{7}$ to $\frac{1}{16}e^-$ per atomic unit cell (right vertical colour bar). **c, d**, Tiling based on the distances between the nearest neighbours in the pattern that corresponds to the characteristic superstructures on the triangular atomic lattice shown in the primitive cell (**e**). The fractions in the colour bars show the effective localized charge per atomic unit cell; the latter is defined by the basis vectors $\mathbf{a}^*$ and $\mathbf{b}^*$. **e**, Five consecutive commensurate superstructures, from left to right, $\frac{1}{4}$, $\frac{1}{7}$, $\frac{1}{9}$, $\frac{1}{12}$ and $\frac{1}{13}$ (grey circles) on the triangular atomic lattice and their primitive cells (coloured polygons). The black arrows show the respective atomic periods. **f**, Experimental (blue) and theoretical (orange) polaron PDFs. The dashed vertical lines show the positions of the peaks that correspond to specific superstructures (**e**). **g**, Normalized polaron number variance $(\sigma_N/(R/D))^{-2}$ versus R/D from theory (grey curve) and power law fit (blue curve). The fitted value of the hyperuniformity exponent is $\beta_{\text{theory}} = -0.87 \pm 0.04$.

the Fermi level, akin to laser speckle³¹. However, without Coulomb interactions it is not clear how to explain the origin of metastability purely in terms of such a wave picture. We note that the demonstrated resistance switching by charge injection and room-temperature stability provides a new correlation-driven mechanism for an ultrafast all-electronic resistance-switching memory device.

10.1.2 Methods

Switching to the A state. Measurements were done with a customized Omicron Nanoprobe ultrahigh-vacuum low-temperature microscope with four independent STM scanners and equipped with the optical input for an ultrafast laser and scanning electron microscope located on top of the STM chamber (Fig. 1b)¹⁶. Optical switching was done at 4.2 K with a single 800 nm or 400 nm 30 fs pulse the latter obtained by a second harmonic generation from the 800 nm Ti:sapphire ultrafast laser and focused to a $100\mu\text{m}$ spot on the sample. The exposure was repeated several times with a 10 s interval. Electrical switching with an STM tip was done by approaching at a gap voltage of +10 V and a setpoint current of 200 nA. The tip was then retracted back and returned to its normal scanning conditions. The switching was done at a temperature of 4.2 K. Two/four-tip switching details are described in Supplementary Method 2. There is no qualitative difference between the resulting topography or electronic properties of the A state obtained by either optical or electrical switching, but in the former case much larger areas are switched, and the image appears flatter.

STM image analysis. To take into account the non-ideal scanner calibration, raw STM images were corrected for the atomic structure to match the ideal triangular lattice using the standard Fourier transform affine algorithm in SPIP software. Affine coefficients were several percent for all the images. The respective values varied within the error due to Fourier peak width and did not affect the results of the PDF analysis and the conclusions of the paper. Sample tilt was subtracted in all the images. Polaronic and atomic features in the STM images were detected using a maximum filter or Laplacian of Gaussian algorithm (Supplementary Fig. 17 gives details).

Monte Carlo simulations. Monte Carlo simulations of the Markov chain dynamics for the Hamiltonian $H = \sum_{i,j} V(i,j) (n_i - \bar{n})(n_j - \bar{n})$ on a triangular lattice were performed using the standard Metropolis algorithm⁵¹. The proposed successive state in the chain consists of setting $n_i = 0$ at an occupied site and $n_j = 1$ at a randomly selected unoccupied site⁵². The simulations were performed with a fixed number of charged particles on the lattice of the size of $L \times W$ ($L = 84, W = 78$) with periodic boundary conditions and with the lattice period a . The amorphous configuration was also confirmed as the number of particles varied within 5%. The interaction potential $V(i,j)$ in the simulations shown in the paper has a Yukawa form with the screening radius $r_s = 4.5a$ and was cut at distances larger than $24a$. Note that the screening length is larger than the polaron radius in the C state. Various screening radiuses ($1 \div 50a$) were checked to give the amorphous configuration. The annealing simulations were performed by decreasing the temperature from 10^{-2} to 10^{-3} with a step of 10^{-5} with 1.4×10^6 Monte Carlo steps at each temperature point. The temperature was measured in the units of $e^2/k_B\epsilon_0a$, where e is the electron charge and ϵ_0 is the static dielectric constant of the material in the C state.

For rigorous confirmation that the A state is, indeed, an energetically favourable low-temperature polaron configuration, we also employed a parallel tempering Monte Carlo algorithm⁵³. Here M replicas are simulated in parallel using standard Monte Carlo procedures, where replica m is assigned a fixed temperature T_m . In our simulations we always used $M = 32$ replicas. With this relatively large number of replicas it was sufficient to distribute the temperatures in regular intervals ($T_m = T_1 + \frac{T_M - T_1}{M}m$). For simulations of a single replica we used the Metropolis algorithm as described above. This was done for ten Monte Carlo sweeps between two successive replica exchanges. The proposed exchange was between the nearest- and next-nearest-neighbour replicas. In a single equilibration simulation, a total of 1,000 replica exchanges was typically superfluous to achieve convergence.

10.1.3 SM 1

SM Note 1: Signatures of the A state in the time-resolved optical reflectivity

We have performed three pulse destruction-pump-probe (D-P-Pr) measurements on 1T-TaS₂ at $T = 160$ K using the method previously reported¹ to monitor the coherent phonon behaviour upon switching to the A state. A low repetition rate (1 kHz) pulsed laser was used¹ to allow the sample cool down between the pulses. To minimally disturb the sample, P and Pr fluences were set to very low values (0.2 and 0.05 mJ/cm² respectively). D pulse fluence was varied to observe switching to different states. The D pulse arrives 50 ps before the P pulse, which allows us to measure the switched sample. Suppl. Fig. 2a,b shows P-Pr traces and their respective Fourier transform spectra for different fluences of D pulse. For low fluences practically no changes to the spectrum are observed. For fluences above 1 mJ/cm² the phonon frequency shifts from 2.36 to 2.22 THz, which can be seen as an increase of oscillations period in Suppl. Fig. 2a, and as a shift of the peak in Suppl. Fig. 2b. This corresponds to the switching from the C to the H (idden) state (frequencies of C and H peaks are shown with vertical dashed lines), and is in agreement with previous measurements¹. Further fluence increase strongly damps oscillations (Suppl. Fig. 2a), which results in the H state peak becoming less and less prominent (Suppl. Fig. 2b). The area under the H state peak (the shaded part on Suppl. Fig. 2b) shows rapid decrease above certain fluence. We attribute this to switching of more and more layers of the crystal to the A state (the penetration depth at 800 nm is 20 ~ 30 nm at this temperature²). Due to amorphous nature of the A state, we expect destructive spatial interference of phonons and thus less pronounced phonon oscillations, which is clearly seen at highest used fluences.

SM Note 2: Stability of the A state at various temperatures. Anomalous diffusion.

The A state at 4.2 K is extremely stable without any visible signs of relaxation (change of polaron positions) within 10 hours of scanning at $V_g = -800$ mV, $I_t = 300$ pA (Suppl. Fig. 4a,b). At 77 K it becomes more malleable: from scan to scan polaron positions fluctuate less than the nearest neighbor distances (< 1 nm), but global pattern does not change with time (Suppl. Fig. 4c,d). Remarkably, even at 150 K during scanning (Suppl. Fig. 4e,f) there are changes in relaxation compared to 77 K. Interestingly, there is no polaron exchange between ordered and amorphous parts of the sample in the studied temperatures region (4.2 – 150 K) (Suppl. Fig. 4), signifying the qualitative difference between these states. This is an unusual situation from the perspective of the dynamics of phase transitions. In particular, an inhomogeneous mixture of two phases tends to evolve towards a formation and growth of domains with time because of diffusion and surface tension - the so-called Lifshitz-Allen-Cahn growth^{3,4}. Deviation from such behavior indicates that system does not relax thermally up to 150 K. Remarkably, azimuthal cross-sections of Fourier transform (FT) (Suppl. Fig. 5) of the initial and final images in the consecutive scans series at 77 K readily reveals that the FT weight in between the peaks (i.e. random part) increases towards the end of the series. This is equivalent to the system becoming effectively more random with time and suggests non-ergodic behavior. See Supplementary Discussion 1 below for the details of the A state in reciprocal space.

To investigate non-ergodic properties, we track changes in the polaron positions with time by comparing consecutive STM scans of the same area at 77 K. To cancel thermal drift effects, observation area was linked to three defect sites seen in every scan in the set. The polaron positions detected in five frames are shown in Suppl. Fig. 6a. Histogram in Suppl. Fig. 6b shows the distribution of polaron displacements with respect to the initial position at different times since the first frame. The histogram is averaged over all the directions and cut off above the nearest neighbor distance. Variance as a function of time, plotted in Suppl. Fig. 6c, has a

nonlinear form $\sigma_d^2 \propto t^\alpha$ with $\alpha \approx 0.6$ consistent with anomalous diffusion and being an evidence for non-ergodicity⁵. Detailed proof of non-ergodicity is generally difficult and would require an analysis of temporal correlation functions, which goes far beyond the scope of the present paper.

SM Discussion 1: The A state in reciprocal space

Reciprocal space analysis is a simple approach to the angular correlations in the particle positions, which can shed some light on the path from the C to the A state. Suppl. Fig. 7a shows the Fourier transform (FT) of the STM image of the C state. It consists of six sharp peaks, which form hexagonal unit cell of a regular triangular lattice of polarons. The unit cell is determined by 3 inequivalent vectors Q_C . They are rotated by 13.9° from the reciprocal atomic unit cell vectors (a^*, b^*) , and has the length $Q_C/a^* = 0.277$, as follows from the commensurability condition $Q_C = \frac{1}{13}(3a^* + b^*)$. Together they form $\sqrt{13} \times \sqrt{13}$ star of David reconstruction, with the "3 + 1" atomic units periodicity of the polaron lattice⁶. In contrast, in the A state the Fourier density becomes circular with six-fold diffuse peaks on top. The latter is seen in more details in the azimuthal cross-section (Suppl. Fig. 7b): the A state has non-vanishing intensity at all angles; it is the largest in the atomic vector direction (a^*) and is the smallest in between. No prominent peak is observed at the Q_C direction. Diffuse angular FT intensity is consistent with loss of directional long-range order of polaronic lattice with respect to the atomic one. Suppl. Fig. 7c shows 2D projection of FT intensity in the A state on angular and radial axes with respect to the atomic lattice. The latter is well-defined as can be seen from the size of the respective peak. Fourier intensity from polarons is mostly spread into $\pm 13.9^\circ$ range around the atomic lattice direction. The simultaneous presence of both negative and positive deviations is not observed either in the C state (i.e. no double peak structure symmetrical to atomic direction) or any other state in the 1 T – TaS₂. The peak along a^* is clearly split, with at least two values Q' and Q'' identified (Suppl. Fig. 7d), consistent with the splitting observed in the polaronic PDF (Fig. 2b in the main text). It signifies the loss of the long-range translational order in the polaronic lattice. The split peaks are located at $Q'/a^* = 0.286$ and $Q''/a^* = 0.306$. The former is close to the Q_C ("3 + 1" period) by length, but the direction coincides with that of the atomic Bragg peak. Such a vector is known to appear in the equilibrium incommensurate charge density wave phase at high temperatures⁶. The second peak, Q'' , is not observed in any equilibrium state in 1 T – TaS₂ and most likely corresponds to the 3 atomic units distance between polarons seen in the polaronic PDF (Fig. 2b in the main text).

SM Method 1: Analysis of particle number fluctuations and hyperuniformity in the A state

To investigate the hidden order (hyperuniformity⁷) that might be present in the amorphous state created by an electric or ultrafast laser pulse, we perform a statistical analysis of the point pattern deduced from the coordinates of the centers of polarons (see Suppl. Fig. 10a). We are particularly interested in the variance in the number of points within the circular observation window of a radius R , $\sigma_N^2(R)$ ⁷. In the beginning, we separate the square image with side L with point pattern into the array of circles of radius R centered at the points of the pattern. To avoid edge effects, we restrict the number of points to those lying inside the square with the side $(L - 2R)$. Then, we count the number of points within each of the circles and build a histogram. Finally, we calculate the number variance, $\sigma_N^2 = \langle N^2 \rangle - \langle N \rangle^2$, where averaging is done over all circles. The procedure is then repeated for another R . In Suppl. Fig. 10b one can clearly see that the width of number distribution increases with R , hence variance also increases (Suppl. Fig. 10c). For a 2D disordered point pattern variance is known to grow as

fast as the area of the observation window, $\sigma_N^2(R) \propto R^2$. For a 2D periodic lattice it grows as a surface area instead, $\sigma_N^2(R) \propto R$. Intermediate behavior means that number fluctuations will decay on large scale and system will actually become long-range ordered on these scales. More strictly, quadratic term must become zero at $R \rightarrow \infty$. Such systems are called hyperuniform⁷.

The straightforward way to check whether the system is hyperuniform is to plot $\sigma_N^2(R)/R^2$ as a function of R . If it decays with R rather than being constant, then system is hyperuniform. The corresponding plot is shown in Suppl. Fig. 10d and clearly demonstrates normalized variance decay at large R .

The oscillations at small R correspond to short-range order present in the system, as seen in pair distribution function. The variance has a local maximum for radii lying in between the nearest neighbors. The exponent of decay can be extracted in two ways. One way is to fit the overall dependence. Another one is to choose only peak values in the oscillating part, which actually represent the degree of local disorder in the system. Both curves show power law decay, the respective exponents are extracted from the slope of the linear fit in double-logarithmic coordinates and are somewhat different: -0.34 (green) and -0.60 (blue). Similar values were obtained for another dataset. Structure factor $S(k) = 1 + \rho h(k)$ also shows decay $S(k) \rightarrow 0$ when $k \rightarrow 0$ (Suppl. Fig. 11b), as expected for the hyperuniform pattern. Here $h(k)$ is the Fourier transform of the generalized PDF, $g^{(2)}(r) - 1$.

It should be noted, that generally point patterns are analyzed for monodisperse systems⁸. In contrast, we are dealing with particles of different sizes and, more importantly, shapes. For polydisperse system, analysis of point pattern can give false negative⁹, which is not the case here.

The alternative approach in the polydisperse case is to analyze the variance of the local volume fraction⁸. However, this approach relies strongly on the way the volume fraction is calculated, and for real images reconstruction is necessary to estimate it correctly⁹. In the current case we do not perform such reconstruction and corresponding analysis, since jammed polaronic distortions on the discrete atomic lattice give volume fraction quite different from that for soft-spheres due to significant shape variation.

SM Method 2: Multi-tip experiment - in situ switching and characterizing the A state

A four-tip experiments were performed to switch part of the sample into the A state with a short electric pulse and measure the resistance of the new state. Resistance measurements were done in the standard four-probe configuration with tips positioned in a line. All the tips were made from chemically etched W wire and cleaned in situ at UHV conditions to strip the oxide layer and obtain high imaging resolution. Low aspect ratio tips were used for current leads for switching to avoid melting from high currents, high aspect ratio tips were used otherwise to achieve precise positioning (see Fig. 1b in main text). All the operations were done at 4.2 K base temperature, where the bulk C state resistance is high. Positioning was done using SEM (Suppl. Fig. 13b): the beam at 25 keV was focused on the sample and the image was taken with the backscattered electrons detector. Typical current values with the 100 μm aperture used were $\sim 1\text{nA}$. It was checked in advance that with such parameters SEM scanning leaves the A state intact.

To avoid sample damage, tips were approached in such a way that ballistic contact was established. High sample resistance was taken into account when choosing setpoint (30 mV and 100 nA were used as the reference). Tip-sample separation for the current leads was further adjusted to achieve proper linearity of the two-tip I-V curve and low resistance. In the present case values of 10 kOhm for a tip separation of 2 – 5 μm were achieved.

Switching and measurements were done using a Keithley 6221 current source and 2182A nanovoltmeter (Suppl. Fig. 13a). In the typical STM measurement configuration, the sample

is grounded, so that tips can be approached independently at their own potential (Suppl. Fig. 13a). The current source and voltmeter were used in the floating mode, with one of the current leads grounded and the sample ungrounded. Proper grounding was used to avoid transient pulsed during interconnections. Two and four-tip I-V curves were taken before and after the switching (Suppl. Fig. 13c,d). The switching was routinely done with a single 10 – 30 mA pulse of 30 ms duration. All four tips remained in contact with the surface even after switching. Resistance has dropped after the single pulse. To confirm that the switched state is indeed amorphous the surface around and in between the contacts were imaged at -800 mV and 100 pA. Resistivity was estimated using the tip geometry seen in SEM (Fig. 1b) by assuming finite penetration depth of current due to factor of 10 inter/intralayer resistance anisotropy in the C state, which gave $\rho_A \approx 18 \text{ m}\Omega \cdot \text{cm}$ (after thermally cycling the sample to 60 K). In addition, resistivity in the A state was extracted by scaling the tip separation in the linear four-probe configuration¹⁰. Lower boundary obtained by setting the geometric factor $\equiv 1$ is $\rho_A \approx 3 \text{ m}\Omega \cdot \text{cm}$ (Suppl. Fig. 13e).

The temperature dependence was measured with the help of the commercially available FTV sample holder. It has the sample stage resting on four thin posts providing weak thermal link to the cryostat. The stage has its own large-area meander Pt heater ($\sim 30 \Omega$ at 4.2 K) and Si-diode thermometer connected with manganin wires to contact posts kept at the base temperature (Suppl. Fig. 13b). To avoid loosing the contact between the leads and the sample, the former were lowered additionally by 5 nm. To avoid large thermal drift, heating was limited to 60 K. Temperature was ramped at 0.3 K/min to allow for proper thermalisation. $R(T)$ curves were measured on cooling with a DC current of alternating polarity in a four-probe configuration.

10.1.4 SM 2

SM Discussion 2: $R(T)$ in the A state

The insulating temperature dependence of resistance in the A state clearly does not follow the Arrhenius activation law, slowing down at low temperatures (Suppl. Fig. 14a). To estimate the type conductivity, we have analysed the function $F(T) = -d \ln R / d \ln T$, plotted as $\ln F$ vs $\ln T$ (Suppl. Fig. 14b). Such choice of axes allows to extract the exponent of T and distinguish between various regimes of hopping transport¹¹. The plot clearly shows $-1/4$ exponent at low temperatures, consistent with 3D Mott variable-range hopping¹¹. At higher temperatures, the exponent changes to ≈ -1 . Fitting the slope in latter temperature range on Arrhenius plot gives activation energy of ≈ 64 K.

In the limited temperature range we cannot clearly distinguish exponential and power-law behavior. The exponent in the latter case can be extracted by analysing the derivative of conductivity, $G(T) = d(1/R)/dT$ plotted on the double-logarithmic scale (Suppl. Fig. 14c). The slope is 0.92, which gives $\sim T^2$ behavior of conductivity. It can indeed stem from the V-shaped dip at the Fermi level observed in the density of states, given the mobility is temperature independent in this range. However, the latter is known to be strongly temperature dependent in the ground C state¹², which makes this interpretation less plausible. Further experimental investigations are necessary to clarify this issue.

SM Discussion 3: Details of the Monte Carlo modeling of the A and C states

As it was stated in the main text, the key difference between the models for the C and A states is the polaron density ν . Experimental results show that in the C state $\nu = 1/13$ and in the A state $\nu \approx 1/10.56$. In our simulations we fixed ν to the experimental values and were able to reproduce the experimentally observed polaron patterns for both cases. This was shown

in the main text.

Lattice Coulomb gas model was explored in details for various values of ν by Vodeb et al.¹³. Magic densities were found at which a hexagonal polaron lattice is commensurate with the underlying atomic lattice ($1/3, 1/4, 1/7, 1/9, 1/12, 1/13, 1/16, 1/19, 1/21, \dots$). This explains the C state as a $1/13$ magic density case. Results from Karpov et al.¹⁴ show that if the polaron density is perturbed slightly from a magic density, a magic density lattice with domain walls emerges. However, the density of the A state is far from being only slightly perturbed. It lies approximately in the middle between the magic densities $1/9$ and $1/12$ ($\sim 15\%$ underdoped $1/9$ or $\sim 14\%$ overdoped $1/12$). Vodeb et al.¹³ show that the polaron lattices overlayed on top of a hexagonal atomic lattice at densities far from the magic densities cannot be hexagonal due to the frustration between the repulsive interaction and the atomic lattice. This results in a large near degeneracy of different long range ordered polaron arrangements which causes glassy features in the system and a glassy transition. In contrast, each magic density case exhibits a clear first order order-disorder crystallization transition. Therefore, there is a narrow range of densities around each magic density in which crystallization occurs (with domain walls). In between these narrow ranges one obtains a much wider range of densities where a glassy transition is present to an amorphous state.

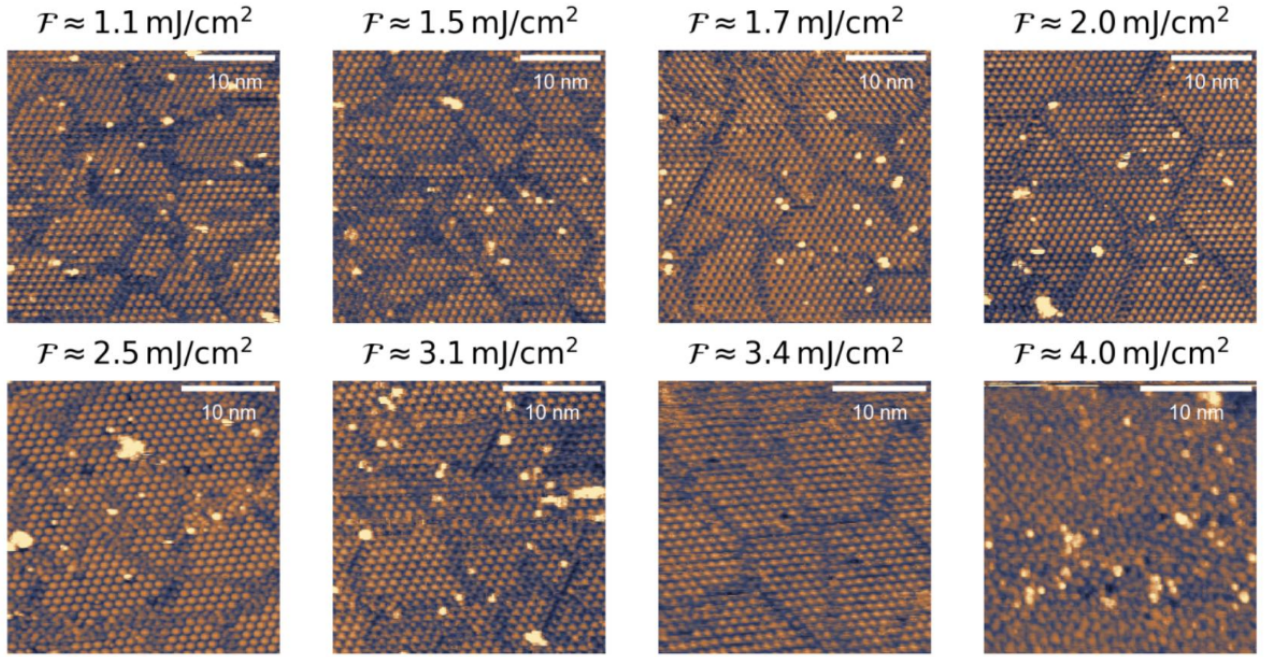
In order to rigorously confirm the fact that the model for C state indeed exhibits crystallization and that the model for A state shows an energetically favorable disordered polaronic pattern at low temperatures we performed MC simulations using the parallel tempering method. The parallel tempering method was employed in an even wider temperature range and confirms the presence of the A state down to temperatures as low as $k_B T = 0.001 V_0$, where $V_0 = e^2/\epsilon_0 a$, where e is the electron charge, ϵ_0 the static dielectric constant of the material and a the lattice constant. The acceptance ratio between nearest neighbor replicas $A_{i,i+1}$, defined as the ratio between accepted swaps and the total number of proposed swaps, can be used for detecting a phase transition in a system^{15–17}. Phase transitions are detected as pronounced suppressions of $A_{i,i+1}$ at the critical temperature. Suppl. Fig. 15 shows the dependence of $A_{i,i+1}$ versus temperature. It is clear that there is a first order phase transition in the case of $1/13$ or C state. Meanwhile, there is a glassy transition present in the case of $1/10.56$ or A state. There is a suppression of $A_{i,i+1}$ present at a lower temperature but it is not as pronounced as in the case of C state. We interpret the temperature at which the suppression is present as the temperature of the glassy transition, where the entropy of the many low lying energy states dominates the thermodynamics down to very low temperatures (as low as MC allows). It is clear that no ordering occurs in the case of A state based on our calculations.

It is unusual that the disordered A state is more energetically favorable than multiple phase separated ordered states. Pokrovsky and Uimin¹⁸ have shown for frustrated triangular lattices that multiple almost degenerate minima are present between $1/9$ and $1/12$ as well as other magic fillings, in consistency with the current conclusions. Interestingly, similar results stemming from frustration were also found on a square lattice^{19,20}.

SM Discussion 4: Quantum interference between jammed electrons

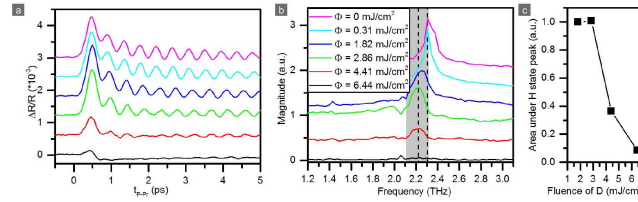
CDWs are often considered as standing waves formed from counterpropagating electrons with opposite momenta²¹, so we may consider the A state as an interference between waves with pseudo-random wavevectors of similar magnitude. Such a distribution is known to lead to hyperuniform patterns, the well-known laser speckle pattern being a good example^{22,23}. For this to work, the de-Broglie wavelength between carriers λ_{dB} needs to exceed the interparticle distance. Initially, at ~ 4000 K, $\lambda_{dB} = \hbar/\sqrt{2mk_B T_e} \sim 0.1$ nm is too short for coherent interference on the 1 nm scale. Estimating the time-evolution of with a customary two-temperature model (Suppl. Fig. 3), after 20 – 30ps the electrons equilibrate with the lattice, and $T_e \sim T_L = 600 \sim 700$ K. At this point λ_{dB} exceeds the inter-particle distance (

$\lambda_{dB} \gg 1 \text{ nm}$), and electrons can interfere constructively to provide a hyperuniform fermionic speckle pattern^{23,24} in a similar way as the IC state can be considered as a quantum interference of nested electrons²¹. Within this quantum interference picture, the relaxation bottleneck in the region of the 'Fermi ridge' defines the wavevectors and energy of the participating electrons. The bottleneck thus provides a k -space analogue to jamming that localizes electrons in the Fermi ridge (FR), providing the necessary slow, long wavelength electrons with a wide distribution of k -vectors, but closely spaced in energy. A crucial property of the A state is metastability. Within the CDW picture, in order to achieve the observed metastability, e-h recombination needs to be suppressed such that the excess electron density is stabilized. This is not provided by the above scenario, which has the weakness that Coulomb interactions are neglected, so the picture is incomplete as such.

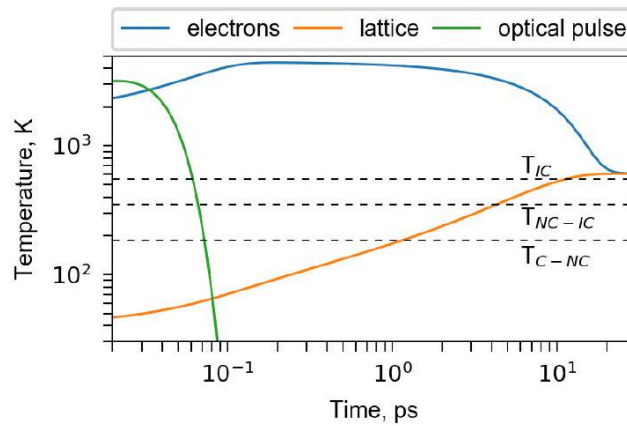


Supplementary Figure 1: Evolution of the polaronic patterns with fluence: set of STM images taken at $T = 6 \text{ K}$ at increasing optical fluence, $\mathcal{F}$, in the range $1 \sim 4 \text{ mJ/cm}^2$. The threshold switching to the A state is clearly seen on crossing the threshold of $\gtrsim 3.5 \text{ mJ/cm}^2$. Below the threshold, the domain textured "hidden" (H) state is observed. The density of domain walls is not correlated with the fluence in the H state. These data conclusively shows the A and H states to be distinct, and negates the notion of a continuous transformation between them. Comparison of electronic properties is provided below in Suppl. Fig. 18.

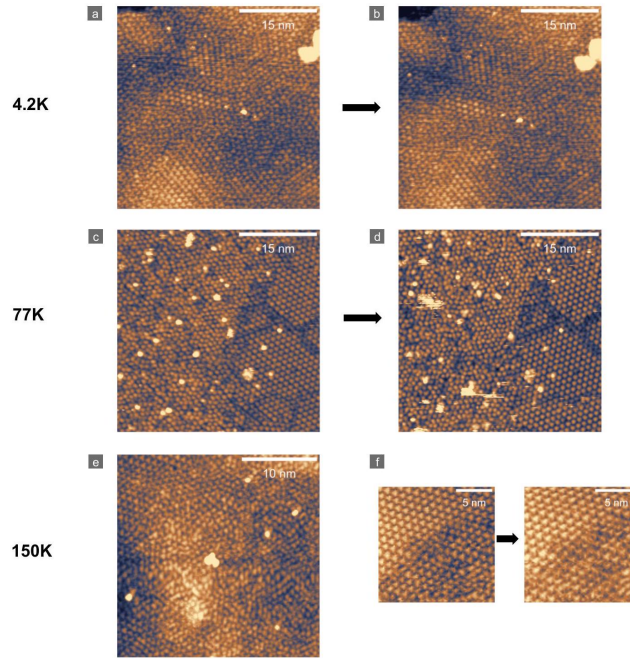
To avoid ambiguity in experimental conditions, the switching was done with a single optical (800 nm) pulse with the peak fluence above the threshold, and the whole dataset was measured within the area exposed to a laser spot. The gaussian spatial profile of the fluence in the spot was characterized outside and inside the UHV STM chamber. Scanning electron microscope was used for the precise in situ STM tip positioning within the spot.



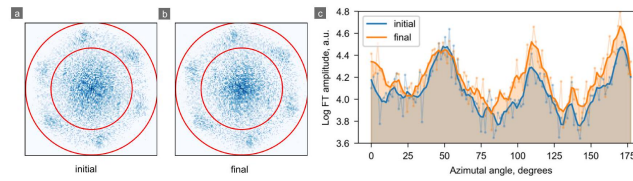
Supplementary Figure 2: Three-pulse optical pump-probe reflectivity measurements to detect the A state: **a**, **b**, time traces of the normalized transient reflectivity (a) and their Fourier transform (b) for a set of switching pulse (D) fluences in a range of 0 – 6.44 mJ/cm². **c**, normalized FT spectral weight in the frequency range of the H peak in FT (b) as a function of fluence.



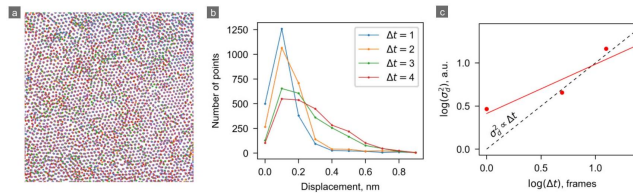
Supplementary Figure 3: Estimation of the electron and lattice heating by a single ultrafast pulse with the twotemperature model: Time dependence of the electron and lattice temperatures calculated within the two-temperature model for 1T-TaS^{2,26} for the optical pulse fluence of 4.25 mJ/cm² applied at $T = 10$ K. The fluence is slightly above the threshold for the optical switching to the A state, as can be seen from Suppl. Fig. 2. Dashed horizontal lines show equilibrium transition temperatures in 1T-TaS₂ upon heating. C— commensurate, NC— nearly commensurate, IC— incommensurate charge density wave states. Triclinic phase to NC is a crossover rather than a transition, so it is not shown explicitly. Optical pulse shape is shown with the green line, amplitude is plotted in arbitrary units.



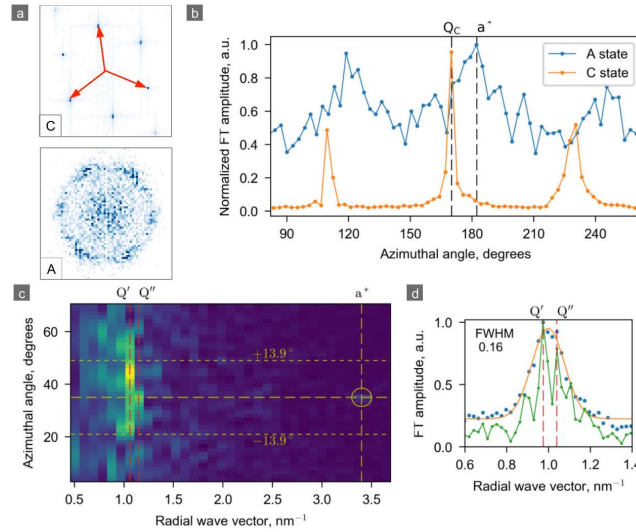
Supplementary Figure 4: Stability of the **A** state at various temperatures: stability of the A state at various temperatures: a-b, 4.2 K, 10 hours scanning; c-d, 77 K, 2.5 hours; e-f, 150 K - single large scale image (e) and series (f), 1.5 hours. Nonlinearities in the panel (f) are due to large thermal drift.



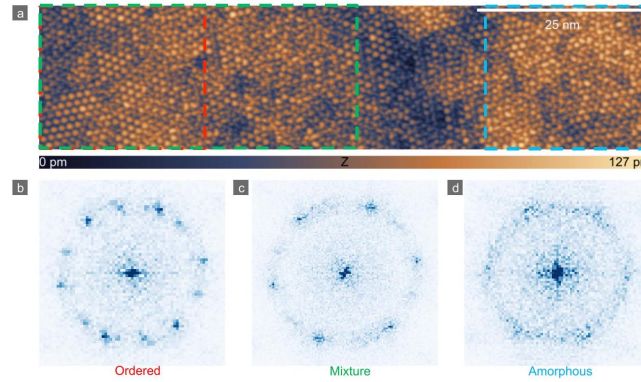
Supplementary Figure 5: Evolution of the **A** state image Fourier transform with time: azimuthal cross-sections of the FT (see also Suppl. Fig. 7b for conventions) of the A state in the initial and final images in the consecutive series (2.5 hours) taken at 77 K.



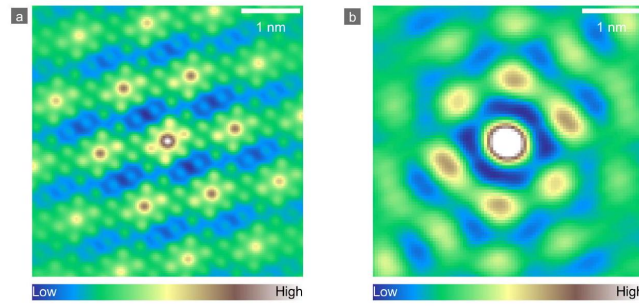
Supplementary Figure 6: Anomalous polaron diffusion in A state at **77 K**: a, polaronic point patterns for five consecutive scans (blue, orange, green, red, purple) overlaid on top of each other; b, histogram showing the distribution of jumps in polaron positions with respect to the initial ones in the first scan; c, double-logarithmic plot of the variance of the distribution of jumps (in b) as a function of time showing $\sigma^2 \propto (\Delta t)^{0.6}$ dependence; black dotted line shows the slope expected for the conventional diffusion $\sigma^2 \propto \Delta t$



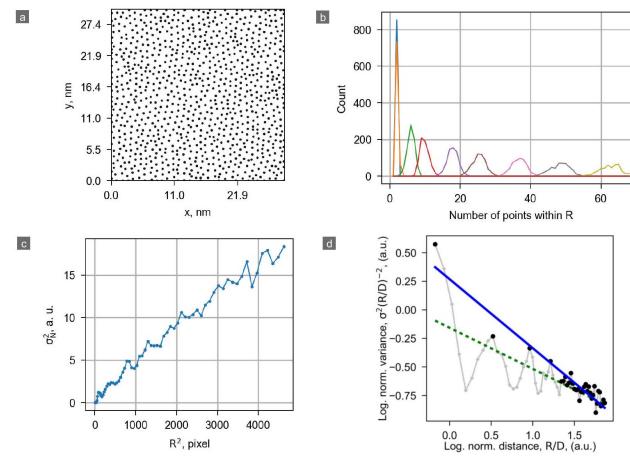
Supplementary Figure 7: Reciprocal space analysis of the A state: a, 2D Fourier transforms of STM topographic data in Fig. 1c,d in the main text. b, 180 degrees azimuthal cross-section of FTs in (a) averaged over 10-pixel ring centered at CDW peaks. c, Radial cross-section of the FT of atomically-resolved STM image of the A state (Fig. 1e in the main text) shows the distribution of polaron positions with respect to the atomic lattice a^* (the corresponding peak is marked with the yellow circle). Polaron peak groups are marked with Q' and Q'' . The lines at $\pm 13.9^\circ$ show the expected C state angles. d, 35-degree average (blue dots) of the one of the radial cross-section curves (green) from high reciprocal resolution FT. Orange curve shows Gaussian fit of the averaged data with the spread of wave vectors length about 16% (compared to resolution of $\sim 2\%$). Peaks are located at $Q'/a^* = 0.286$ and $Q''/a^* = 0.306$.



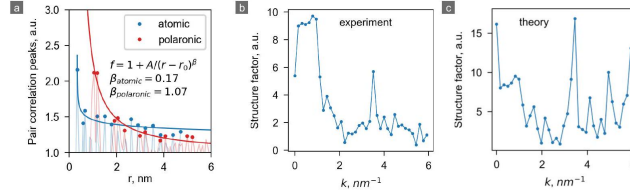
Supplementary Figure 8: Pulse-induced relaxation from A to C states: a, STM image of the A state after a small voltage pulse (3 V; measured current $\sim 30 - 60\text{ nA}$) was applied on the left side. Red, green and blue squares show relaxed (ordered), mixed and amorphous parts respectively. The relaxation can be understood as local injection of charge with smaller concentration than the one present during the creation of the A state. The direction of relaxation is thus towards the C state with 1/13 reconstructions (smaller polaron density) rather than 1/12 or 1/9 (larger polaron density). b-d, Fourier transforms of the ordered, mixed and amorphous parts shown by squares in (a).



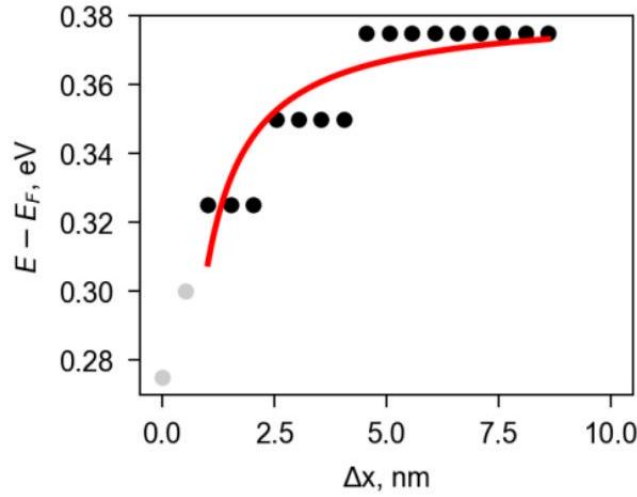
Supplementary Figure 9: Autocorrelation of the atomically resolved images of the **C** and **A** states: a, *C* state, hexagram reconstruction characteristic of sulfur atoms is seen; b, *A* state, no universal reconstruction pattern is found, emphasizing multiple polaron shapes, rather than the single hexagram pattern.



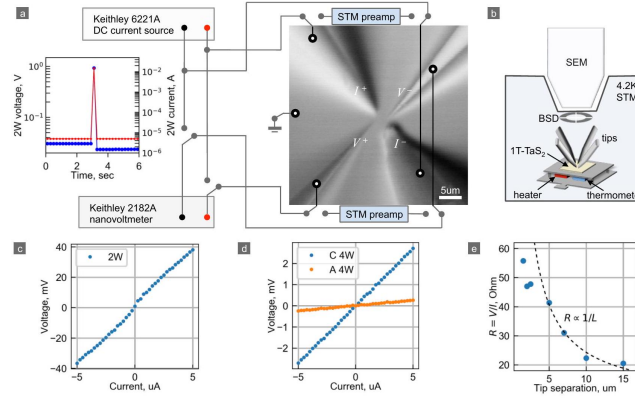
Supplementary Figure 10: Analysis of polaronic pattern for hyperuniformity: a, point pattern derived from detected polaron centers. b, histograms showing the number of points within the circular observation window of radius R (increases from blue to yellow curve). c, variance (the width of histograms in (b)) as a function of window radius R . d, double-logarithmic plot of the variance normalized by area of observation window as a function of its radius (gray curve). Solid blue and dashed green curves show power law decay fit of peak only (black) and all experimental points respectively.



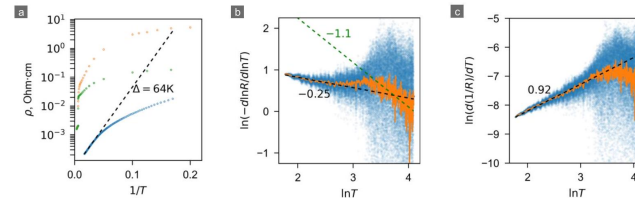
Supplementary Figure 11: Properties of the polaronic and atomic patterns: a, power law fits of atomic and polaronic pair correlation peaks (dots), full PDF is shown by semi-transparent solid lines. Based on the decay rate, we can ascribe polaronic distribution to short-range ordered, while the atomic one - to quasi-long-range ordered. b, structure factor of the experimental polaronic pattern clearly shows decay for $k \rightarrow 0$, as expected in case of hyperuniformity. c, structure factor of the theoretical (MC) polaronic pattern also decays for $k \rightarrow 0$. Large value $S(k = 0)$ is due to PDF average being different from 1, which is related to the finite size of the image in MC simulations.



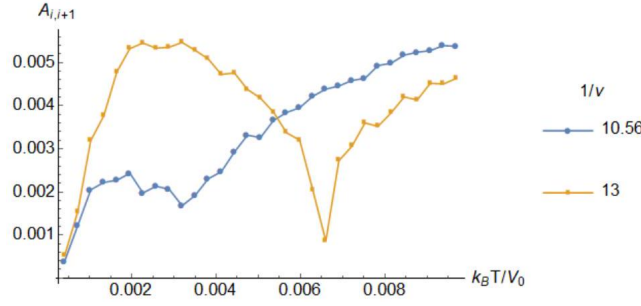
Supplementary Figure 12: Estimation of the screening length: the data points show band edge bending as a function of distance caused by an isolated domain wall in the C state (numerical data is adapted from the tunneling spectra in Fig. 1d in Ref. ²⁷). $\Delta x = 0$ corresponds to the domain wall center, black (gray) dots correspond to the outside (inside) the domain wall. 1T-TaS₂, as a layered 2D system, is expected to be screened on the scales larger than the thickness of the stack ²⁸ (~ 10 nm in this case). The fit (red) with Debye screening $\exp(-\Delta x/a)/\Delta x$ outside the wall gives screening length $a \sim 1.7$ nm in the C state. The conductivity in the A state is almost two orders of magnitude higher than in the C state, hence the screening length will be even smaller.



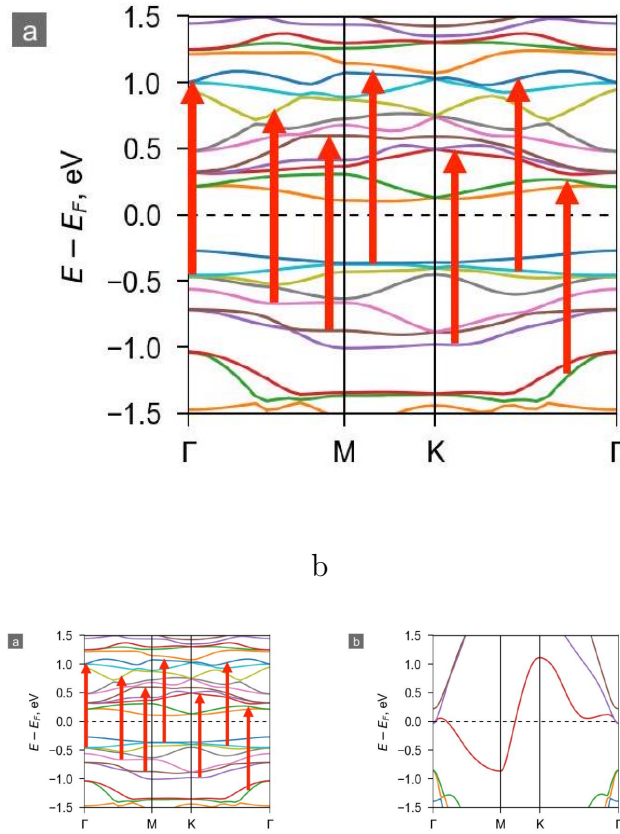
Supplementary Figure 13: The multi-tip experiment - in situ switching and characterizing the **A** state: a, schematic circuit diagram for switching and 2-probe (2W) or 4-probe (4W) resistance measurements. SEM image shows tips configuration used for switching. Plot on the left shows time trace of 2W current and voltage upon switching (thermal EMF subtracted). b, schematic view of the system: SEM - scanning electron microscope, BSD - backscattered electrons detector. c, I-V curve between two current leads before switching (C state). d, four probe I-V curve before (C state) and after switching (A state); resistance values: $R_C = 542\text{Ohm}$ and $R_A = 50\text{Ohm}$. e, scaling of the four probe resistance with tip separation in the A state is consistent with $R \propto 1/L$ (black dashed line) 3D transport. Lower bound for resistivity $\rho_A \approx 3\text{mOhm} \cdot \text{cm}$ can be extracted, if geometric factor is set $\equiv 1$.



Supplementary Figure 14: $R(T)$ in the A state: a, Arrhenius plot of the temperature dependencies of resistivity in the A (blue) and C states (orange, green - different samples). High-temperature part can be fit (dashed black line) to an activation law. b, double-logarithmic plot of the logarithmic derivative of $R(T)$ used for estimating possible T -exponent in the hopping transport: pale blue dots are raw data, orange curve - smoothed data, black and green dashed lines - linear fits of the low and high-temperature parts respectively. c, double-logarithmic plot of the derivative of conductance $1/R(T)$ used for estimating possible power-law behavior: pale blue dots are raw data, orange curve - smoothed data, black dashed line - linear fit of the low-temperature part.

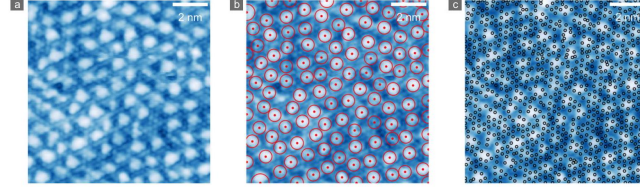


Supplementary Figure 15: Acceptance ratio $A_{i,i+1}$ dependence versus dimensionless temperature $k_B T / V_0$: The legend on the right of the image shows the corresponding filling of the system ν . In the case $1/\nu = 13$ it is clear from the pronounced suppression of $A_{i,i+1}$ at $k_B T = 0.007V_0$ that there is a first order phase transition present. The suppression of $A_{i,i+1}$ at the filling $1/\nu = 10.56$ is much less pronounced and broadened out, which is the consequence of the glass transition present in this case.

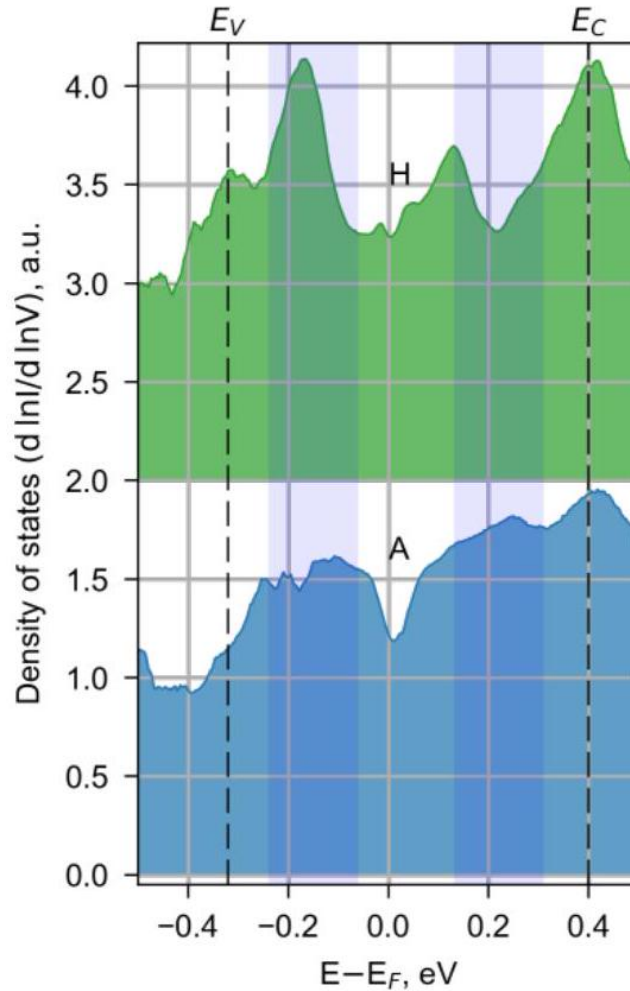


Supplementary Figure 16: Schematic of optical transitions within the initial **C** state bands and the resulting high-temperature band structure after photoexcitation: a, low-temperature **C** state below $T = 190$ K calculated by LDA for a single TaS₂ layer (Jernej Mravlje, private communication). The arrows show possible photoexcitation transitions at 1.5 eV (800 nm) photon energy. The low- T band structure has multiple bands due to Brillouin zone folding caused by the $\sqrt{13} \times \sqrt{13}$ unit cell reconstruction in the **C** state. This provides multiple excitation paths for a large set of energies, rather than a single dominant transition. b, The high-temperature metallic state band structure above $T_{IC} = 550$ K after photoexcitation with 3.5 mJ/cm² pulses. is dominated by a single band crossing Fermi level, with a 'Fermi ridge' along the $K - \Gamma$ direc-

tion. (The estimated electron temperatures are shown in Suppl. Fig. 3)



Supplementary Figure 17: Atomic and polaronic features detection in STM images: a, atomically-resolved image of the A-state; b, the same image (a) with detected polaron centers, marked with red dots, and red circles of various radii reflecting Gaussian width for each polaronic feature found by the LoG algorithm²⁹; c, the same image (a) with detected atoms black circles of almost the same radii found by the LoG algorithm. Detection fails at the centers of polarons, as the protracting orbitals smear out topographic features of the top layer S atoms. The parameters used for atomic (polaronic) detection are: maximum Gaussian width = 1 (7) pixels, minimum Gaussian width = 0 (5) pixels; overlap threshold for neighboring Gaussians = 1%. Image size is 203 pixels.



Supplementary Figure 18: Comparison of the A state with the photoinduced "hidden" state in 1T-TaS₂: The C state can be switched with a single shot laser pulse of the fluence $\sim 0.8 - 3 \text{ mJ/cm}^2$ into a long-range ordered domain textured phase²⁵ called "hidden" state² (see also Suppl. Fig. 1). Here we compare the spatially averaged spectra in the A and hidden states taken on the same sample and with the same tip. Dashed lines and shaded lines show the position of CDW and Hubbard band in the C state respectively. Absence of the CDW peaks and explicit Hubbard bands clearly show that the A state is qualitatively different from the hidden state. This result, along with the threshold switching to the A state, allows one to dismiss the notion that one can smoothly vary the fluence to increase the domain wall density

in the hidden state to obtain the A state.

11 Interplay of electron-electron and electron-phonon interactions in the low temperature phase of 1T-TaS₂ by Cho et al.

Doohee Cho Yong-Heum Cho Sang-Wook Cheong Ki-Seok Kim Han Woong Yeom

Abstract

We investigate the interplay of the electron-electron and electron-phonon interactions in the electronic structure of an exotic insulating state in the layered dichalcogenide 1T-TaS₂, where the charge-density-wave (CDW) order coexists with a Mott correlation gap. Scanning tunneling microscopy and spectroscopy measurements with high spatial and energy resolution determine unambiguously the CDW and the Mott gap as 0.20 – 0.24 eV and 0.32 eV, respectively, through the real space electron phases measured across the multiply formed energy gaps. An unusual local reduction of the Mott gap is observed on the defect site, which indicates the renormalization of the on-site Coulomb interaction by the electron-phonon coupling as predicted by the Hubbard-Holstein model. The Mott-gap renormalization provides new insight into the disorder-induced quasi-metallic phases of 1T-TaS₂.

Metal-insulator transitions in low dimensional condensed matter systems are driven by various interactions between relevant degrees of freedom, such as spin, charge, orbital, and lattice. For example, charge density waves (CDW) [21] and Mott insulators [2] are paradigmatic examples of electron-phonon (*e-ph*) and electron-electron (*e-e*) couplings, respectively. These couplings are often entangled to yield exotic states of electrons as recently discussed for high-temperature superconductors [3]. On the other hand, the interplay of *e-ph* and *e-e* couplings has been discussed for a while for the CDW transition [14] in a layered transition metal dichalcogenide of 1T-TaS₂ [16]. Upon decreasing temperature, it undergoes a series of transitions from a metallic phase through incommensurate and nearly commensurate CDW to commensurate (C)-CDW [14]. The ordered CDW superstructures could be directly observed using scanning tunneling microscopy (STM) in real space [9, 22]. The C-CDW superstructure splits the broad metallic band into a manifold of narrow subbands but cannot account for the most important gap opening at the Fermi level (E_F) with one half-filled band left [7]. The insulating gap was then explained by introducing the on-site Coulomb repulsion, which is enhanced by the substantial narrowing of the band width due to the CDW formation [16]. Thus, the multiple gap structure in this system itself is a hallmark of the interplay between *e-ph* and *e-e* couplings.

However, while this material has been investigated for a long time, the multiple gap structure is not fully characterized yet by experiments. The gap structure was investigated by angle resolved photoemission spectroscopy (ARPES) [26], inverse-ARPES [10] and scanning tunneling spectroscopy (STS) [22] below the critical temperature ($T_c \sim 180$ K). ARPES probed only the occupied part of the gap and inverse-ARPES for the empty part did not provide proper energy resolution. The previous STS study only focused on the gap at E_F without any clear information on the multiple gaps. Moreover, these spectroscopic works reported substantially larger gaps than those measured by optical and transport measurements [11, 12, 13]. Considering the fact that the multiple gap structure is crucially important to understand not only the ground state but also the statically or dynamically excited states with the anomalous metallic property and the superconductivity of this system [7, 11, 12, 31, 8], the experimental establishment of the energy gap structure in its ground state is imperative. It is also important to trace how the

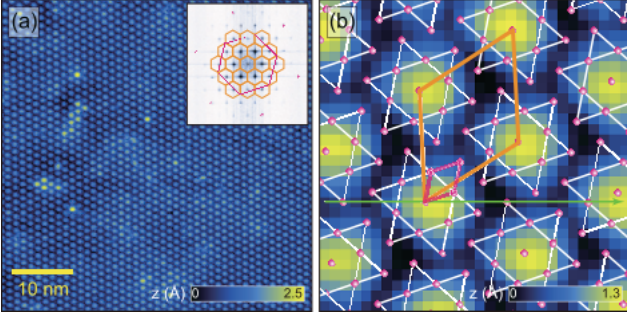


Figure 11.1: (color online) (a) STM image (tunneling current $I_t=100$ pA, sample bias $V_s=+0.2$ V and 50×50 nm²) of 1T-TaS₂ at 78 K displaying long range ordered CDWs. The inset shows its corresponding 2D Fourier transform. Orange and purple hexagons (parallelograms in Fig. 27.1(b)) indicate the 1st Brillouin zone (unit cells in real space) of $p(\sqrt{13}\times\sqrt{13})R13.9^\circ$ C-CDW and 1×1 normal states, respectively. (b) STM image (3.5×3.5 nm² and 30×30 pixel) acquired during dI/dV measurements ($I_t=100$ pA and $V_s=-1.20$ V). The superimposed sketches highlight the units of the CDW.

Mott or CDW gap changes upon external perturbations or internal fluctuations in this respect. Moreover, generally speaking, beyond the gap structure, little is known about the physical consequences of the coupled $e-e$ and $e-ph$ interactions in this interesting system.

In this Letter, we report the STS results with substantially improved resolution, which identifies and quantifies clearly the multiple gaps. The origins of different gaps are unambiguously determined by the real space phases of relevant electrons. Furthermore, we unveil for the first time the local reduction of the Mott gap at the defect site, which is presumably renormalized by the local variation of the $e-ph$ coupling. This manifests the interplay of $e-ph$ and $e-e$ couplings within the Hubbard-Holstein model and has important implications for the emergence of intriguing metallic C-CDW phases with intrinsic or extrinsic disorders [19, 31].

We performed STM and STS measurements with an ultrahigh vacuum cryogenic STM (Unisoku, Japan) at 78 K. The real space electron density as a function of energy was acquired via spatially resolved (SR) differential conductance (dI/dV) measurements; the normalized tunneling conductance $[(dI/dV)/(I/V)]$ is proportional to the local density of states (LDOS) [20]. The lock-in technique with a bias modulation of $V_{rms}=20$ mV, $f=1$ kHz was applied to acquire dI/dV. 1T-TaS₂ single crystals were grown by the chemical vapor transport method with iodine as a transport agent. The crystals were cleaved in high vacuum before cooling down.

Below the transition temperature of ~ 180 K, the CDW forms a long-range ordered superstructure [22, 26] as shown in the STM topographic image of Fig. 27.1(a). Its Fourier transformation [the inset of Fig. 27.1(a)] shows strong peaks and their higher orders with a wavelength of $\sqrt{13}a_0\sim 12.1$ Å, which are rotated clockwise by 13.9° with respect to the 1×1 lattice of 1T-TaS₂. The zoom-in image of Fig. 27.1(b) shows how the CDW maxima match with the underlying Ta lattice. The lattice is distorted into the unit of 13 Ta atoms with 12 atoms in the shape of a star of David displaced toward the center atom.

In order to detail the electronic structure of the C-CDW phase, SR-STs measurements were performed simultaneously with the topographic imaging of Fig. 27.1(b). A particular line scan along the green arrow in Fig. 27.1(b) is shown in Fig. S2(a) and a few typical normalized conductance curves in Fig. S2(b). The opening of the energy gap close to E_F is clearly resolved. A gap size is unambiguously determined by the LDOS peaks at $+0.22$ and -0.10 eV as 0.32 eV. They would correspond to the coherent peaks of upper and lower Hubbard states [U(L)HS]. More clear evidence of the Mott gap will be discussed below. Depending on samples and tip conditions, the positions of coherent peaks vary within a few tens of meV [22]. This can be related with the spatial inhomogeneity of the doping level induced by intrinsic impurities.

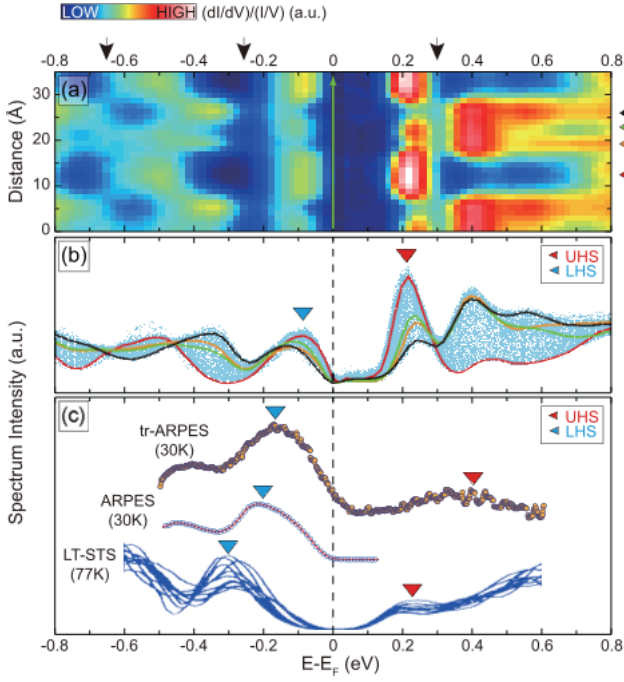


Figure 11.2: (color online)(a) Normalized dI/dV spectrum acquired along the green arrow in Fig. 1(b). (b) A collection of 900 normalized dI/dV spectra over the area shown in Fig. 27.1(b). The highlighted spectra (red, orange, green, and black) are obtained at the marked positions in Fig. S2(a). (c) Previously reported spectra, acquired by STS [22], ARPES and tr-ARPES [35] for the C-CDW phase. The red (blue) triangle indicates the U(L)HS.

However, the size of the correlation gap is consistent with 320 meV and E_F is always closer to the LHS. In addition to the gap at E_F , three other gap-like features are identified around +0.30, -0.25 and -0.65 eV (marked by arrows in Fig. S2), which divide the measured spectra into five subbands.

The previous spectroscopic results summarized in Fig. S2(c) consistently indicated the insulating property of the C-CDW phase of 1T-TaS₂ [22, 35]. However, the estimated gap size ranges from 500 to 600 meV, which is substantially larger than the present result. This variation can stem largely from experimental limitations in the energy range or the resolution. Considering the broad line shape and the limited resolution, the ARPES results [10, 26, 35] seem roughly consistent with the present results for the LHS. The even more limited resolution and sensitivity are likely to prevent properly identifying the UHS in the inverse-ARPES [10] and time-resolved ARPES works [35]. The line shape of the very early STS measurement suggests that it could not resolve the first and the second peak of filled states in our STS spectra [22]. The suppression of the spectral intensity near E_F , especially for the LHS peak, is noticeable in the previous measurement, which is highly possible for a low conductance tip condition. Furthermore, this pioneering work did not address the multiple gap structure discussed in the following. On the other hand the optical conductivity works measured a much smaller band gap of 100 – 200 meV [11, 13]. If one considers the finite spectral width of the U(L)HS peak in STS, the present measurement agrees very well with this measurement, establishing firmly the standard for the Mott gap of this material. The quantitative calculations taking into account of the correlation effect consistently reproduced the gap size of about 200 meV with the on-site Coulomb energy of 2 – 4 eV [23, 18].

As mentioned above, in addition to the Mott gap at E_F , we found a few other gaps and their distinct characteristics can be shown clearly through the real space phase of relevant electrons. The phase of the 2D real space electron density was analyzed as referenced by that

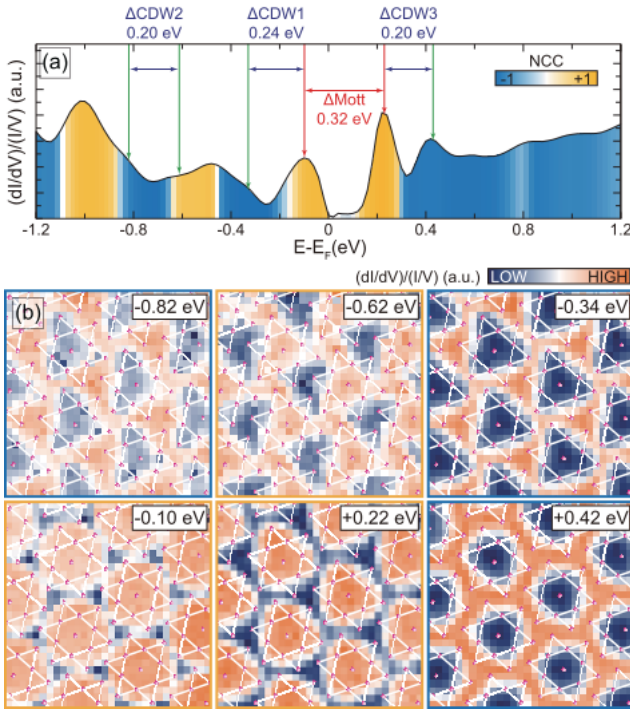


Figure 11.3: (color online)(a) Spatially averaged STS spectrum. The color scale indicates the normalized correlation coefficient (NCC) as referenced by the image at $+0.22$ eV. The green arrows denote the onset of the subband manifolds. (b) LDOS maps of the states marked with arrows in Fig. 3(a) on a 3.5×3.5 nm² area. The frame colors of the maps represent their NCC.

of the UHS [the $(dI/dV)/(I/V)$ map at $+0.22$ eV shown in Fig. 27.3(b)]. The apparent phase difference can be noticed immediately in the maps taken at different biases in the figure; while the map for UHS has bright maxima at the centers of stars of David, the maps at -0.82 , -0.34 , and $+0.42$ eV have dark minima. In order to quantify the phase difference, for example, between two states α_{ij} and β_{ij} , we use the normalized correlation coefficient (NCC) between two corresponding images, $NCC = \langle (\alpha_{ij} - \mu_\alpha)(\beta_{ij} - \mu_\beta) \rangle / (\sigma_\alpha \sigma_\beta)$, where μ and σ are averages and standard deviations of the images [25]. The spatially averaged STS spectrum in Fig. 27.3(a) was colored with the value of NCC obtained, showing how the relative real space phase changes for different electronic states. In particular, we notice that the phase completely flips at energies around -1.10 , -0.85 , -0.65 , -0.45 , -0.18 , and $+0.30$ eV, which are obviously associated with the multiple spectral gaps as given in the figure. This is in clear contrast with the gap at E_F , crossing which the electron are apparently in-phase in real space. That is, the present result makes clear the distinction of the gap at and away from E_F experimentally.

The phase flip of the real space electron density is naturally expected for any band gap formed by a periodic lattice distortion and thus can straightforwardly be related to the CDW in the present system [26]. From the onsets of the subbands identified by the detailed inspection of the spatially resolved STS spectra shown in Fig. S2, we can quantify the gap sizes as 0.22 ± 0.02 eV; three CDW gaps, two in the occupied and the other in the unoccupied states, have a similar size. This manifests further the common origin of these gaps, the periodic potential provided by CDW and the lattice distortion. Note that the CDW gap positions in the energy agree well with the previous band structure calculations [7, 3] and the ARPES measurements [10, 26, 28]. The reported gap sizes of 100–150 meV and 100–200 meV (only the occupied state gaps), respectively, are in reasonable agreement with the present quantification.

Beyond the distinct character of the Mott and CDW gaps, the real space electron densities of UHS and LHS show the clear particle-hole asymmetry; the former is more localized at the center Ta atom than the latter [Fig. 27.3(b)]. This wave function characteristics seems consistent with

the STS spectra where the UHS has a narrower band width (larger spectral peak intensity) than the LHS. This asymmetry in 1T-TaS₂ has not been reported so far in this system and its origin is not clear at this point.

For disordered 1T-TaS₂, intriguing metallic behaviors were reported previously [10, 29]. This metallic state was explained by the screening of the e - e Coulomb interaction through charge carriers of the discommensurations induced by the defects. This sounds similar to the nearly-commensurate CDW phase found at higher temperatures. Note that the effect of disorders on the conductivity of a correlated system can also be influenced by the aforementioned particle-hole asymmetry in theory [30]. More importantly, no direct and clear spectroscopic information is available how a defect affects the Mott and CDW gaps in the present system. We thus focus on the most popular point defect in this system; the brighter CDW maxima in the STM image of Fig. 27.1(a). Figures 27.4(a) and 27.4(b) ($I_t=100$ pA and $V_s=\mp 0.20$ eV) show a reduced and enhanced contrast with respect to the normal CDW maximum on this defect at filled and empty state images, respectively. Within a defect concentration of our sample, they do not destroy the long or short range CDW ordering at all. The SR-STs measurement across this defect shows unexpectedly that the Mott gap is reduced considerably from 320 to 180 meV only on this site while the CDW gaps are preserved. The asymmetric U(L)HS peak becomes symmetric. Considering the change of the E_F position into the center of the gap compared to the surrounding, this defect is thought to be slightly negatively charged. The local reduction of the Mott gap has never been reported previously and is sharply contrasting with the known behavior of charged impurities in a conventional Mott insulator; the spectral weight of the U(L)HS is transferred partially to a adjacent gap state [31, 32, 33]. Since the CDW order and the CDW gap are preserved, the local change of the Mott gap cannot be explained in relation to CDW.

However, the reduction of the gap size can be explained by the other aspect of the interplay between e - e and e - ph couplings within the Hubbard-Holstein model. In this model, the effective e - e coupling is renormalized by the interaction between electrons and optical phonons as given by $U_{eff} = U_{e-e} - 2g^2/\omega_0$ (ω_0 denotes the optical phonon frequency and g the e - ph coupling constant) [34]. The previous optical conductance measurements evidenced the optical phonons at the relevant energy range of 25 meV, which also exhibit the temperature-dependent softening [13]. This strongly suggests that the optical phonons can also be tuned by the local structural deformations. Our scenario is that the defect-induced local structural deformation reduces the optical phonon frequency and in turn leads to the reduced effective interaction U_{eff} . The reduced U_{eff} would make the Mott gap smaller and the finite width of the U(L)HS drives the system marginally metallic as shown in Fig. 27.4. This result bears important implications for the appearance of the quasi-metallic behavior in the C-CDW phase of disordered 1T-TaS₂ [19, 31].

In summary, we have demonstrated the interplay between e - ph and e - e coupling in the electronic structure of the low temperature ground state of 1T-TaS₂ using spatially resolved scanning tunneling spectroscopy. The multiple gap structure consisting of Mott and CDW gaps, the primary hallmark of the interplay, is well quantified and their distinct origins are unambiguously visualized through the real space phases of the relevant electrons. The impurity-induced local reduction of the Mott gap is revealed and interpreted to reflect the effect of the local e - ph interaction within the Hubbard-Holstein model, which is another hallmark of the interplay.

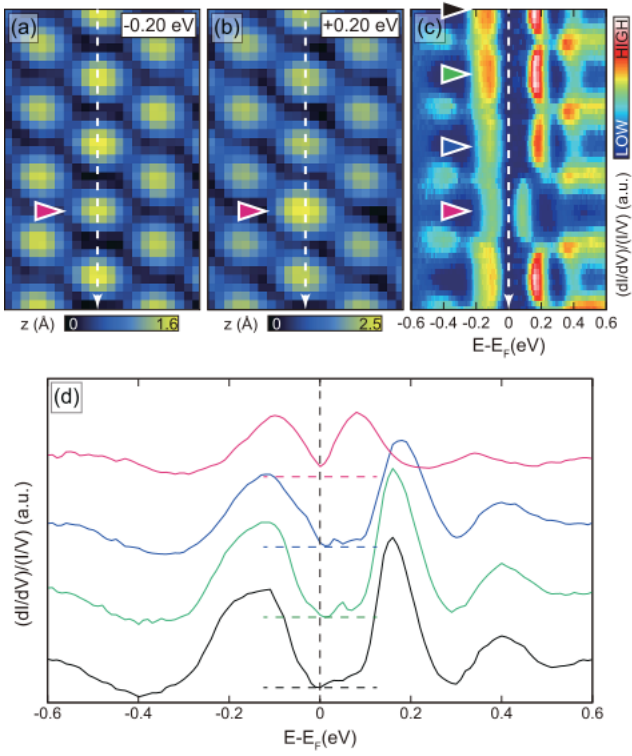


Figure 11.4: (color online) Filled (a) and empty (b) state STM images ($I_t=100$ pA, $V_s=\mp 0.20$ eV and 3.5×5.5 nm²) of an impurity on the $1T\text{-TaS}_2$ surface, marked by the triangles. (c) Normalized differential conductance map measured along the white dashed arrow in Fig. 27.4(a) and (b). (d) Representative normalized dI/dV spectra acquired at the CDW crests denoted by triangles in Fig. 27.4(c).

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12 Modeling of networks and globules of charged domain walls observed in pump and pulse induced states by Karpov, Brazovskii (2017)

Abstract

Experiments on optical and STM injection of carriers in layered MX_2 materials revealed the formation of nanoscale patterns with networks and globules of domain walls. This is thought to be responsible for the metallization transition of the Mott insulator and for stabilization of a “hidden” state. In response, here we present studies of the classical charged lattice gas model emulating the superlattice of polarons ubiquitous to the material of choice $1T - \text{TaS}_2$. The injection pulse was simulated by introducing a small random concentration of voids which subsequent evolution was followed by means of Monte Carlo cooling. Below the detected phase transition, the voids gradually coalesce into domain walls forming locally connected globules and then the global network leading to a mosaic fragmentation into domains with different degenerate ground states. The obtained patterns closely resemble the experimental STM visualizations. The surprising aggregation of charged voids is understood by fractionalization of their charges across the walls’ lines.

12.1 Introduction

Major anticipations for the post-silicon electronics are related to materials which demonstrate a layered structure with a possibility for exfoliation down to a few and even a single atomic layer, akin to the graphene. The latest attention was paid to oxides and particularly di-halcogenides of transition metals MX_2 with $M = \text{Nb, Ta, Ti}$ and $X = \text{S, Se}$, see e.g. [1, 2] for reviews.

These materials show a very rich phase diagram spanning from unconventional insulators of the so called Peierls and Mott types to the superconductivity [3]. The transformations among these phases involve formation of superstructures like several types of so called charge density waves (CDW) and/or of hierarchical polaronic crystals. Recent studies of these materials fruitfully overlapped with another new wave in solid state physics. This is the science of controlled transformations of electronic states or even of whole phases by impacts of strong electric fields and/or the fast optical pumping. A super goal is to attend “hidden” states which are inaccessible and even unknown under equilibrium conditions. In relation to this article subjects, the success came recently from observations of ultrafast (at the scale of picoseconds) switching by means of optical [4, 7] and voltage [5, 6] pulses, as well by local manipulations [8, 9]. The registered ultrafast switching is already discussed as a way for new types of RAM design, see [10] and rfs. therein.

Most challenging and inspiring observations have been done in studies by the scanning tunneling microscopy (STM) and spectrometry (STS) [8, 9, 11, 7]. They have shown that the switching from an insulating to a conducting state proceeds via creation of local globules or extended networks of domain walls enforcing fragmentation of the insulating electronic crystal into a conducting mosaics of domains with different multiply degenerate ground states.

Most important observations have been done upon very popular nowadays layered material $1T - \text{TaS}_2$ which is a still enigmatic “polaronic Wigner-crystalline Mott insulator”. The rich phase diagram of $1T - \text{TaS}_2$ includes such states as incommensurate, nearly commensurate, and commensurate CDWs which unusually support also the Mott insulator state for a subset of electrons. Recently, new long-lived metastable phases have been discovered: a “hidden” state created by laser [4, 7] or voltage [5] pulses, and a most probably related “metallic mosaic” state created locally by STM pulses [8, 9].

$1T - \text{TaS}_2$ is a narrow-gap Mott insulator existing unusually on the background formed by a sequence of CDW transitions which have gaped most of the Fermi surface of the high temperature metallic (with 1 electron per Ta site) parent phase [2]. Incomplete nesting leaves each 13-th electron ungaped which in a typical CDW would give rise to a pocket of carriers. Here, each excess carrier is self-trapped by inwards displacements of the surrounding atomic hexagon (forming the “David star” unit) which gives rise to the intragap local level accommodating this electron. Exciting the self-trapped electron from the intragap level deprives the deformations from reasons of existence, the David star levels out in favor of a void in the crystal of polarons. The charged voids are expected to arrange themselves into a Wigner crystal subjected to constraints of commensurability and packing with respect to the underlying structure.

A major question arises: why and how the repulsive voids aggregate into the net of walls leaving micro-crystalline domains in-between? In this paper, we answer this and related questions by modeling the superlattice of polarons upon the 2D triangular basic lattice of all Ta atoms by a classical charged lattice gas with a screened repulsive Coulomb interaction among the particles. The external pulse injecting the voids was simulated by introducing a small random concentration of voids reducing the particles concentration ν below the equilibrium $\nu_0 = 1/13$ (some other experimentally relevant concentrations are briefly described in the Supplementary Material, Sec. III). The subsequent evolution of the system, including the passage through the thermodynamic first order phase transition, was studied by means of the Monte Carlo simulation. Surprisingly, this minimalistic model is already able to capture the formation of domain walls in a close visual resemblance with experimental observations and also to explain the effect qualitatively as an intriguing result of the charge fragmentation.

12.2 The model

We model the system of polarons by a lattice gas of charged particles on a triangular lattice. Each particle represents the self-trapped electron in the middle of the David star, thus the effective charge is $-e$, which is compensated by the static uniform positive background.

The external pulse is simulated by a small concentration of randomly seeded voids reducing the particles’ concentration below the equilibrium: $\nu = \nu_0 - \delta\nu$. The interaction of polarons located at sites i, j is described by an effective Hamiltonian $H = \sum_{i,j} U_{ij} n_i n_j$ with repulsive interactions U_{ij} . Here the sum is over all pairs of sites $i \neq j$; $n_i = 1$ (or 0) when particle is present (or absent) at the site i , and we choose U_{ij} as the screened Coulomb potential

$$U_{ij} = \frac{U_0 a}{|\mathbf{r}_i - \mathbf{r}_j|} \exp\left(-\frac{r - a}{l_s}\right), \quad (12.1)$$

where $U_0 = e^2 \exp(-a/l_s)/a$ is the Coulomb energy of interaction of particles at neighboring sites in the Wigner crystal state with the distance $a = \sqrt{13}b$ between them (b is the lattice

spacing of the underlying triangular lattice, Fig. 12.1a), l_s is the screening length. We keep in mind also the background uniform neutralizing positive charge.

12.3 Superlattice and its charged defects.

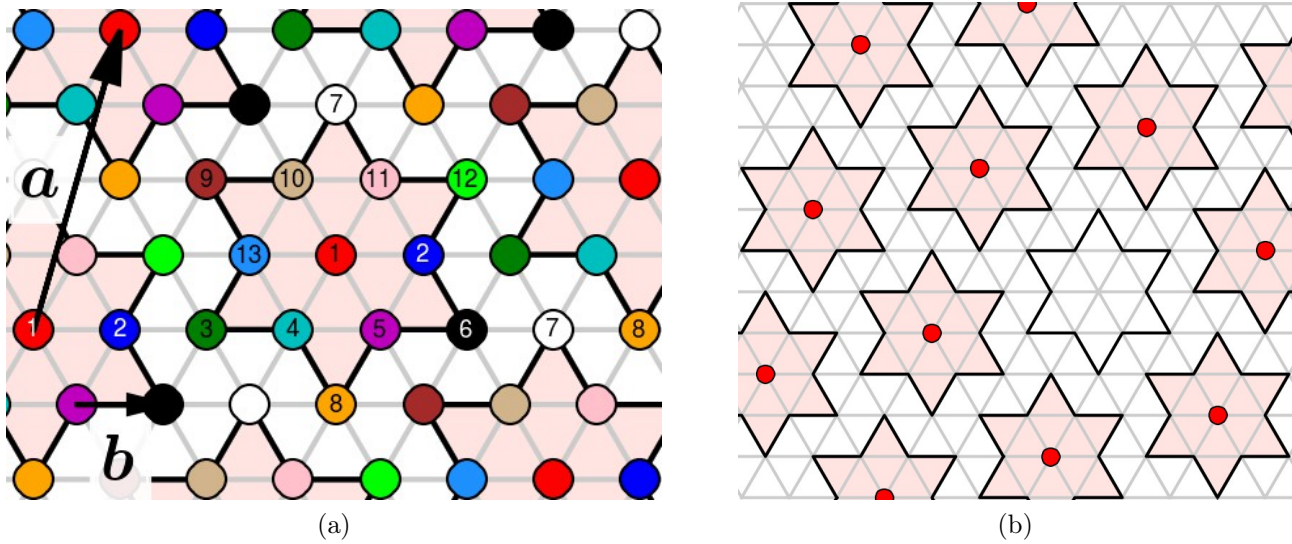


Figure 12.1: (a) Underlying triangular lattice (with the period b) of all Ta-atoms and the coloring scheme showing its 13 sublattices; in the ground state only one sublattice (with the period a) is occupied. (b) Lattice with $\nu = 1/13$ concentration of polarons at presence of one void (the emptied "David star"). The occupied polaronic sites, marked by red circles, are surrounded by filled "David stars" which perimeters pass through neighbors which positions are actually displaced inwards (not shown here).

In the ground state, all particles living on the triangular lattice tempt to arrange themselves in also the triangular superlattice, which is close-packed and most energetically favorable in 2D [12] (with some notable exceptions for more exotic potentials [13]). Since the concentration of particles is $1/13$, then the ground state is 13-fold degenerate with respect to translations (Fig. 12.1a). An additional mirror symmetry makes the ground state to be in total 26-fold degenerate. But since within a given sample two mirror-symmetric phases do not coexist both in the experiment [14] and in the modeling for the sufficiently slow cooling rates (because of the high energy of the corresponding twinning wall), then we consider only one of them.

The simplest lattice defect is a void or a "polaronic hole" (Fig. 12.1b) which is formed when the electron from the intragap level is taken away or excited to the conduction band and soon the associated lattice distortions vanish. The single void has the relative charge $+e$ (keeping in mind the background neutralizing charge) and the Coulomb self-energy of the order $E_{\text{void}} \simeq e^2/a$. While the void is a particular manifestation of a general notion of vacancies in crystals, in our case there can be also a specific topologically nontrivial defect – the domain wall separating domains with a different 13-fold positional degeneracy of the ground state (Fig. 12.2). The domain wall cross-section resembles the discommensuration known in CDW systems [15].

Experimentally, the lattice defects can be introduced via external pulses, by impurity doping or by the field effect. For example, a laser or STM pulse can excite the Mott-band electrons residing in the centers of the David star clusters, creating an ensemble of voids. Since the voids are charged objects, then at first sight they should repel each other and form a Wigner crystal themselves. But our modeling consistent with the experiment shows that the voids

rather attract one another at short distances and their ensemble is unstable towards formation of domain walls' net. Qualitatively, this instability can be understood from the following argument. Compare energies of the isolated void and of the domain wall segment carrying the same charge. The minimal charge of domain wall per the translation vector $\mathbf{a}_1$ is $+e/13$ (Fig. 12.2a), and the energy of the wall's segment carrying the charge $+e$ can be estimated as for a uniformly charged line:

$$E_{wall} \simeq 13 \times \frac{(e/13)^2}{a} \ln(l_s/a), \quad (12.2)$$

For moderate screening lengths l_s , it is lower than the void's self-energy E_{void} , making energetically favorable to decompose the voids into fractionally-charged domain walls. The local effects beyond our model can also favor domain walls with other charges: for the single-step $+1e/13$ domain wall there are anomalous sites where David stars intersect (Fig. 12.2a) which raises its energy and can make the double-step $+2e/13$ domain walls (Fig. 12.2b) to be energetically favorable.

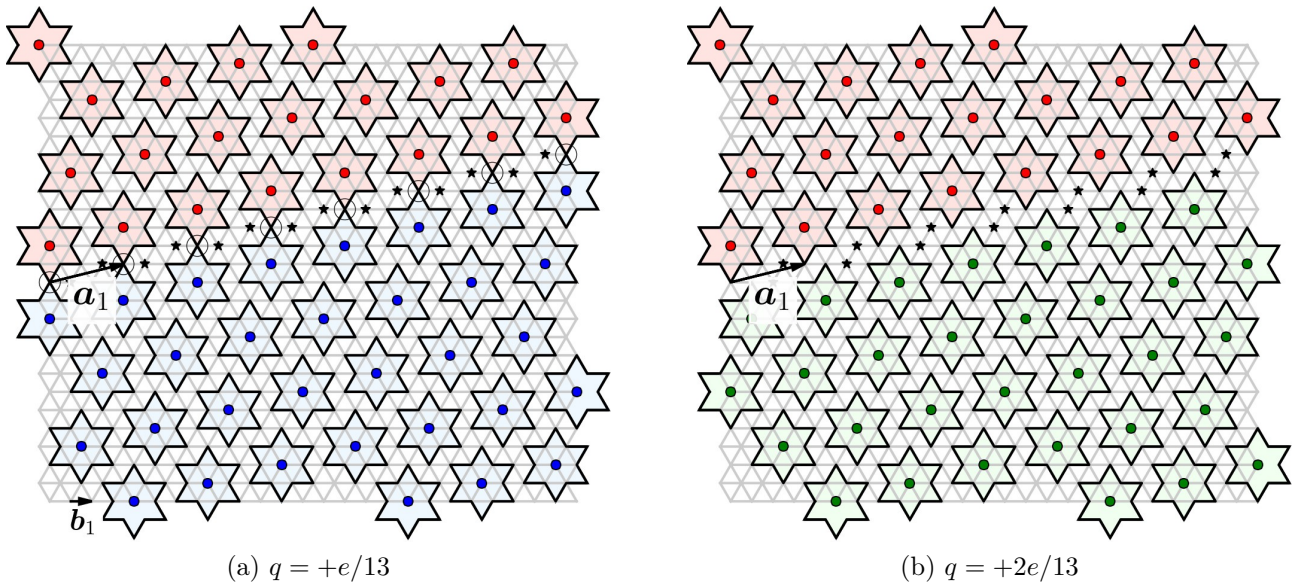


Figure 12.2: Positively charged domain walls with charges per unit cell length $\mathbf{a}$: (a) $+e/13$; (b) $+2e/13$. The whole sequence of domain walls can be obtained by consecutive displacements of the blue domain by the vector $\mathbf{b}_1$ as indicated in (a). In (a), the sites are encircled where David stars within the wall share the corners. Black asterisks designate the sites not belonging to any star.

12.4 Numerical modeling

We simulated the cooling evolution of the classical lattice gas with the interaction potential (12.1) via Metropolis Monte Carlo algorithm (see Methods). We perform slow cooling from $T = 0.07U_0$, which is above the detected ordering phase transition (see below), down to $T = 0.01U_0$ with a step $\Delta T = -0.0002U_0$, reaching either a ground state or a very close in energy metastable state. Below we, first, consider undoped systems (where particles concentration ν is exactly $\nu_0 = 1/13$), and then systems doped by voids (with $\nu = \nu_0 - \delta\nu \equiv \nu_0(1 - \nu_{voids})$, where $\nu_{voids} = \delta\nu/\nu_0$ is the voids' concentration). Results for another sign of doping are briefly presented in the Supplementary Material, Sec. III.

12.4.1 Undoped system.

As a reference system we chose the sample with 91×104 sites with the total a number of particles $N_p = 728$, which corresponds to the concentration $\nu_0 = 1/13$.

On cooling, the order-disorder phase transition takes place at $T_c \approx 0.056U_0$, below which the triangular superlattice is formed confirming the expectations for the Wigner crystal. Temperature dependencies of the order parameter $M = \sqrt{\sum (m_i - 1/13)^2 / 13 \cdot 12}$, where m_i is the fraction of particles at i -th sublattice (Fig. 12.3a) and of the mean value of energy per particle (Fig. 12.3b) indicate that the transition is of the first order. The insets in the Fig. 12.3a show a plenty of defects just above T_c , while only two displaced positions are left just below T_c .

On heating, the order-disorder phase transition takes place at $T \approx 0.063U_0$, which agrees with our mean field analysis (see Supplementary Sec. II). With increasing l_s the temperature hysteresis and the tendency to overcooling become more pronounced. An overcooling or even freezing into in a glass state feature is known for electronic systems with either a frozen disorder or a Coulomb frustrations [16]; however in the present model these both factors are absent – the effect is presumably due to only the long-range Coulomb interactions under the lattice constraints.

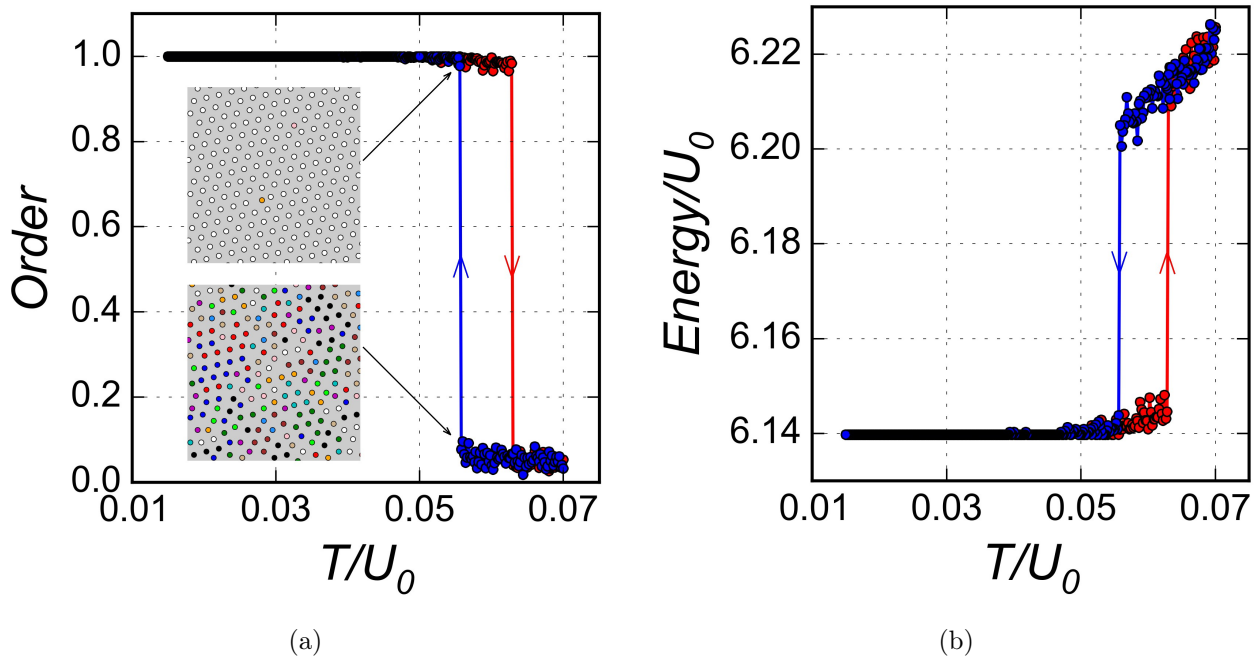


Figure 12.3: Temperature dependencies of integrated characteristics for the undoped system. (a) The order parameter; the insets show snapshots of configurations of the system just above and below the phase transition; (b) mean energy per particle. Blue symbols are for cooling and red symbols are for heating simulations.

12.4.2 Doped system.

We emulate the doping (the charge injection) by seeding voids at random places and following the subsequent evolution. By global characterizations like those in Fig. 12.3, the order-disorder transition is preserved, while at a lower temperature. But locally the new mosaic ground state with the net of domain walls is formed as we will demonstrate below.

Seeding at $T < T_c$ a small number of voids, down to two defects per sample, we observe that the single-void states are unstable with respect to their binding and progressive aggregation.

Seeding more voids initiates their gradual coalescence into a globule of interconnected segments of domain walls. The resulting globule performs slowly a random diffusion over the sample while keeping closely its optimal shape and the structure of connections (the Supplementary Video of the system evolution under cooling and its description are presented in Supplementary Sec. I).

Figure 12.4a shows the low- T configuration of system 130×156 system, where initially $N_p = 1544$ of particles (with the corresponding concentration of voids $\nu_{voids} \approx 1.0\%$) were randomly seeded and then the system was slowly cooled from $T = 0.07U_0 > T_c$ down to $T = 0.01U_0$. In spite of the initial random distribution of particles over the whole sample, finally the voids aggregate into a single globule immersed into a connected volume of the unperturbed crystal. We compare the results of our modeling in Fig. 12.4a with the experimental picture in Fig. 12.4b [8]. Similar patterns have been observed also in other experiments: [5] (Fig. 3 of the supplement) and [9] (Fig. 1).

With a further increase of doping, the globule size grows over the whole sample, and finally the branched net of domain walls divides the system into the mosaics of randomly shaped domains (Fig. 12.5a,c). The comparison of the modeling with the experiment on injection by the STM pulses is shown between panels (a) and (b) in Fig. 12.4, between panels (a) and (b), (c) and (d) in Fig. 12.5. The figures visualize a spectacular resemblance of our modeling with results from several STM experiments exploiting either the optical switching to the hidden state [7] or the pulses from the STM tip [8, 9]. Note that similar “irregular honeycomb network” structures were predicted for incommensurate phase of krypton on graphite with $\nu_0 \approx 1/3$ and short-range interaction [4], but with less topological restrictions here.

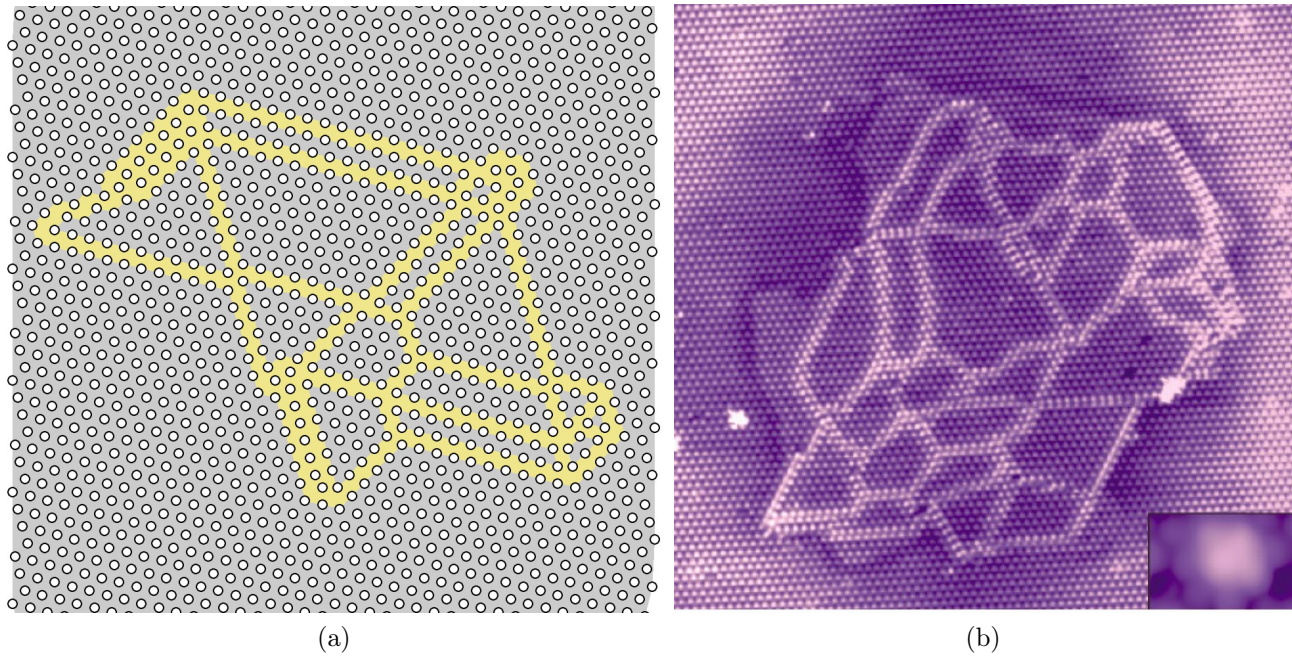


Figure 12.4: Globule structures. (a) The present modeling for $\nu_{voids} \approx 1.0\%$ in the domain walls representation, $T = 0.01U_0$; (b) from experiments in [8].

12.5 Discussion and Conclusions

Our simulations have shown an apparently surprising behavior: some effective attraction of voids develops from the purely repulsive Coulomb interactions. The coalescence of single voids starts already at their small concentration. For several voids seeded, we observe a gradual

fusion of point defects into the globule of the domain walls. Increasingly branched net develops with augmenting of the voids concentration.

That can be understood indeed by noticing that the walls formation is not just gluing of voids but their fractionalization. The domain wall is fractionally ($q = \nu_0 e$) charged per its crystal-unit length, thus reducing the Coulomb self-energy in comparison with the integer-charged single void. Being the charged objects, the domain walls repel each other, but as topological objects they can terminate only at branching points, thus forming in-plane globules. Their repulsion at adjacent layers meets no constraints, hence the experimentally observed alternation of the walls' patterns among the neighboring layers [7, 8, 9].

A similar while simpler doping induced phase transition to the state patterned by charged domain walls was predicted for quasi-1D polyacetylene-like systems with 2-fold degeneracy, see [18].

Our modeling can be straightforwardly extended to other values of concentration ν_0 : like $\nu_0 = 1/3$ which is the minimal value where the pattern formation appears with qualitatively similar to the presented here results (see Supplementary Sec. III) and corresponding, for example, to the $\sqrt{3} \times \sqrt{3}$ surface CDW observed in the lead coated germanium crystal [1]. For another experimentally known case of $2H - \text{TaSe}_2$ where $\nu_0 = 1/9$ the modeling results are quite different: in some doping range we see a "stripe" phase (see Supplementary Sec. III), which indeed was experimentally observed in this material [3]. The exception of the case $\nu_0 = 1/9$ is rather natural, because here the basis vectors of the superlattice and of the underlying triangular lattice are parallel to each other, which allows for the existence of neutral elementary domain walls.

It is also possible to study the doping by electrons by seeding the interstitials rather than voids; here the new David stars substantially overlap with their neighbors giving rise to stronger lattice deformations, which may require for a more complicated model. The fragmentation with formation of walls is always confirmed while details of patterns can differ (see Supplementary Fig. 7).

The encouraging visual correspondence of our pictures with experimentally obtained patterns in different regimes of concentrations ensures a dominant role of the universal model.

Methods

For numerical simulation of the classical lattice gas with interaction potential (12.1) we employed the Metropolis Monte Carlo method. We used the screening parameter $l_s = 4.5b \approx 1.25a$ and truncated the interactions to zero for sufficiently large interparticle distances (outside the hexagon with the side $24b$). At each temperature we performed $\sim 10 - 40$ millions of Monte Carlo steps depending on the numerical experiment. Temperature was linearly lowered from $T = 0.07U_0$ down to $T = 0.01U_0$ with a step $\Delta T = -0.0002U_0$. The following system sizes and numbers of particles were chosen: size 91×104 and $N_p = 728$ for undoped system; size 130×156 and $N_p = 1544$, $\nu_{\text{voids}} \approx 1.0\%$ for the globule system (Fig. 12.4a); size 142×164 and $N_p = 1758$, $\nu_{\text{voids}} \approx 1.9\%$ for the net system (Fig. 12.5a,c). Periodic boundary conditions were imposed.

Acknowledgements

The authors are grateful to D. Mihailovich, Y.A. Gerasimenko, E. Tosatti and H.W. Yeom for helpful discussions. We acknowledge the financial support of the Ministry of Education and Science of the Russian Federation in the framework of Increase Competitiveness Program of NUST MISiS (N K3-2017-033). SB acknowledges funding from the ERC AdG "Trajectory". Image source for Figs. 12.4(b), 12.5(b),(d) is [8]; use permitted under the [Creative Commons Attribution License CC BY 4.0](#); the images were cropped and rotated.

Author contributions

S.B. and P.K. together formulated the theoretical concept, designed the model, analyzed results, and wrote the paper; P.K. performed the numerical computations. Correspondence and requests for materials should be addressed to P.K.

Additional information

The authors declare no competing financial interests.

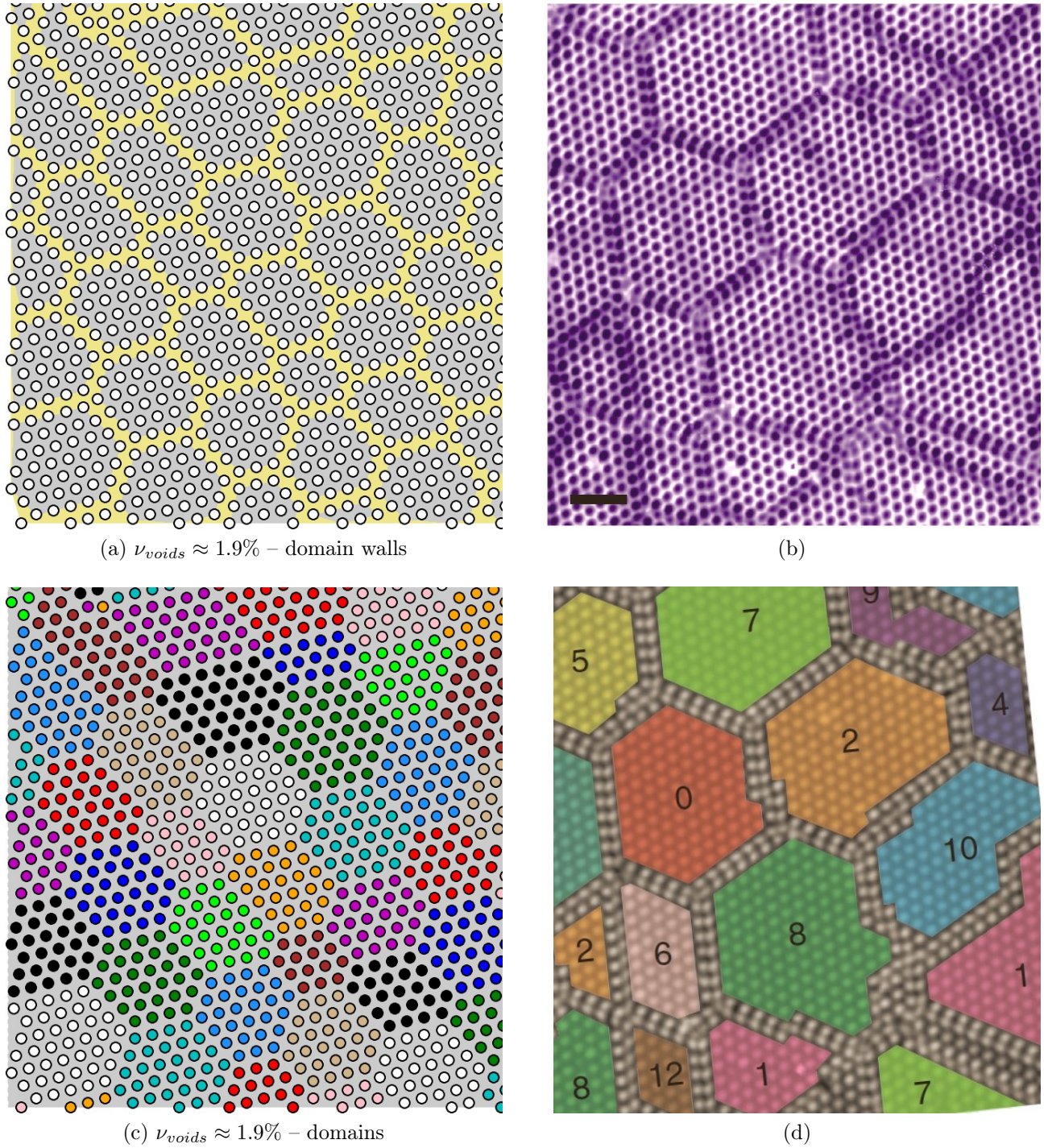


Figure 12.5: The modeling for a high doping (a,c) vs experiments (b,d). Maps of domain walls (a,b) and of domains (c,d). Figs. (a,c) show the present modeling with $\nu_{voids} = 1.9\%$ of voids at low temperature $T = 0.01U_0$, the coloring scheme for domains is indicated in Fig. 12.1. Figs. (b,d) are adapted from [8], numbers in Fig. (d) show the corresponding coloring scheme for domains. Figs.(a,c) show only a part of the system, full images can be found in Supplementary Fig. 6.

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12.6 Movie: coalescence of voids and cluster diffusion

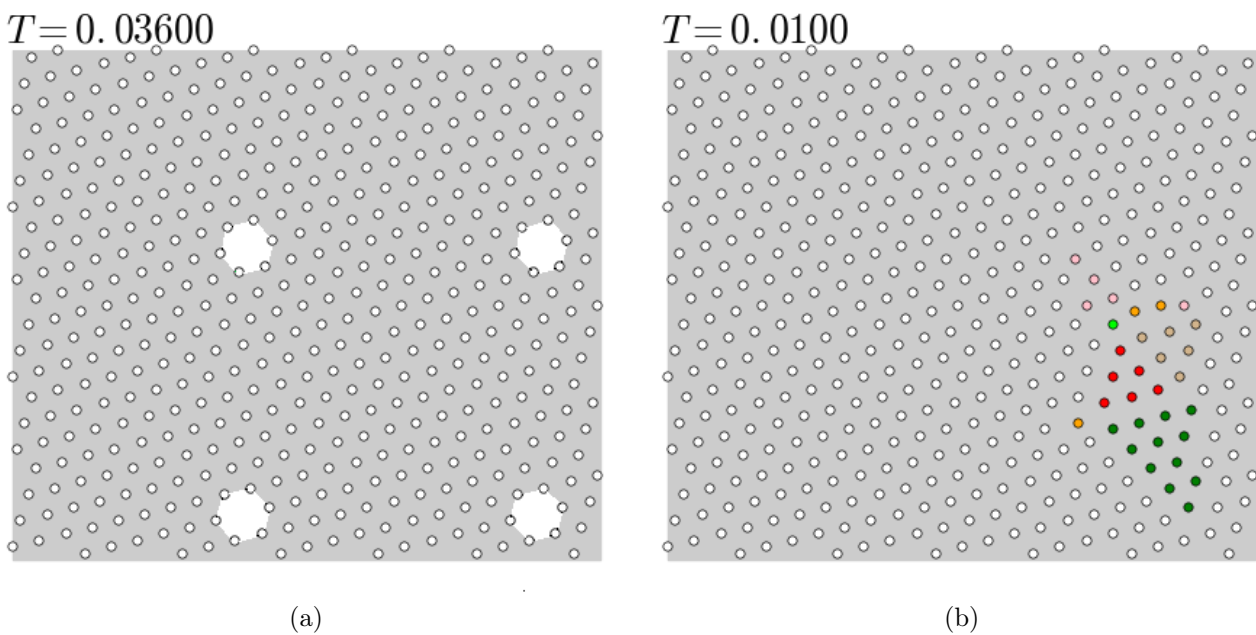


Figure 12.6: (a) The initial position of the simulation at $T = 0.036U_0$, holes' locations are highlighted by white background; (b) the final position of the simulation at $T = 0.010U_0$.

The movie (<https://www.dropbox.com/s/wv1ebnjys3bm0da/suppl-movie.mp4>) reflects the process of Monte Carlo (MC) cooling of the system, after several voids have been added to the ordered state below the transition temperature. This procedure differs from the one exploited to obtain the final states reported in the main text. There we always started from a random disordered state at $T > T_c$ in order to reach a better equilibration. The movie demonstrates two regimes in the course of the cooling: (1) merging of voids into a single big cluster seen as the globule of domain walls; (2) random diffusion of the cluster.

We start the simulation from the ordered system where 4 voids have been seeded by hands. (Fig. 12.6a shows the initial position) and cool it from $T = 0.036U_0$ down to $T = 0.010U_0$ with step $\Delta T = -0.0001U_0$, making at each temperature 10000 MC steps for higher temperatures ($T \geq 0.0310U_0$) or 50000 MC steps for lower temperatures ($T < 0.0310U_0$).

First, each of 4 voids very quickly disintegrates into a small cluster (“1-cluster”), and then begins a random diffusion (note, that periodical boundary conditions are imposed). Being the charged objects, the 1-clusters are repelled from each other. Nevertheless, if two 1-clusters overcome a potential barrier, they merge into a stable 2-cluster, this which lowers the system energy (the qualitative explanation of this counterintuitive effect is given in the main body of

the paper). The first event of two 1-clusters merging happens at $T = 0.03548U_0$ after ~ 52000 MC steps (5-th second of the video).

After several collisions and unsuccessful coalescence attempts, the 2-cluster merges with a 1-cluster at $T = 0.03407U_0$ (after ~ 193000 MC steps, 19-th second of the video). Final merging to a single cluster happens shortly after that at $T = 0.03378U_0$.

Afterwards, the resultant big cluster performs a random diffusion through the sample. After the 50-th second, the video is speeded up by the factor of 50. Figure 12.6b shows the final position of the simulation.

We conclude that it is indeed energetically favourable and dynamically sustainable for separate holes to merge into a single cluster.

12.7 Order-disorder phase transition: mean field theory

In this section we present the mean field theory for the order-disorder phase transition for an undoped system. Since the interactions are of the long-range nature and many particles affect the given one, we expect mean-field theory to be a good approximation.

At $T = 0$, perfectly ordered state is observed, where all particles occupy the same sublattice (one of the 13 equivalent sublattices, not counting for the mirror symmetry, as discussed in the main text). With gradually increasing the temperature, at some critical temperature $T = T_c$ order momentarily breaks.

In order to determine T_c we consider a simplified version of the model, dividing the whole system into closely packed David stars, and allowing for each particle to occupy only one of 13 sites of its David star (Fig. 12.7). This simplification will lead to a slight overestimation for T_c .

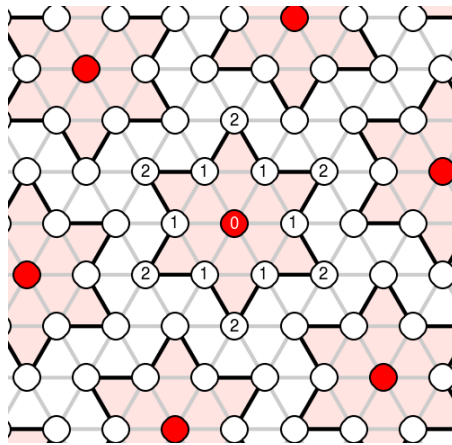


Figure 12.7: One of the ground states of the system, where particles (red circles) occupy the same sublattice. 1-st, and 2-nd coordination spheres for a given particle (“0”) are shown.

Since the energy Δ_1 (“gap”) to excite a particle from its regular position in the David star center to the first coordination sphere is several times less than the analogous energy for the second coordination sphere Δ_2 (for example, for the studied in the main text case $l_s = 4.5b$ we have found $\Delta_1 \approx 0.442U_0$, $\Delta_2 \approx 1.993U_0$). Then taking into account only 1-st coordination sphere seems to be a reasonable first approximation and we arrive at a simpler model with only 7 possible states for each particle.

Consider a particle in the mean field of other particles. Let (s_0, s_1) be the occupation numbers of the 0-th and the 1-st coordination spheres respectively. In the ground state we have $s_0 = 1$, $s_1 = 0$; in the excited state $s_0 = 0$, $s_1 = 1$. Introduce the order parameter

$$m = \frac{7}{6} \langle s_0 - \frac{1}{7} \rangle, \quad (12.3)$$

so in the ordered phase $m = 1$, in the disordered phase $m = 0$. Since on average only those particles that occupy the given sublattice try to keep the particle in the same sublattice, we use the following “temperature-dependent gap” $\Delta(T) = \Delta_1 \cdot m(T)$. The one-particle mean-field Hamiltonian $H = s_1 \Delta_1 m(T)$, gives rise to the partition function $Z(T) = 1 + 6e^{-\Delta_1 m/T}$. From the self-consistency condition (12.3), we get $m = (1 - \frac{7}{6}e^{-\Delta_1 m/T})/Z$ or

$$m = \frac{1 - e^{-m\Delta_1/T}}{1 + 6e^{-m\Delta_1/T}} \quad (12.4)$$

Expanding RHS of (12.4) to the first order in m we get $m = m\Delta_1/7T + o(m)$, which yields to the critical temperature

$$T_c = \frac{\Delta_1}{7}. \quad (12.5)$$

For $l_s = 4.5b$ we have $\Delta_1 \approx 0.442U_0$, and formula (12.5) gives us $T_c \approx 0.0631U_0$, which is very successfully compared with the Monte Carlo simulation result on heating: $T_c \approx 0.0630U_0$.

We conclude that the mean field theory is in a very good agreement (within 0.5%) with the results of the simulation. This is rather natural because for the screened Coulomb long-range interaction many coordination spheres of particle’s neighbors contribute to the mean field for a given particle (this fact is incorporated into the definition of the excitation energy Δ_1).

12.8 Results for different values of concentration ν_0

First we give the classification of filling factors on a triangular lattice, and then analyze some representative cases. Figure 12.8 shows ordinal numbers of neighbors for a given particle (black) – 1 corresponds to the nearest neighbor, 2 to the next-nearest neighbor etc. Knowledge of where the particle’s nearest neighbor sits determines the whole superstructure. Table I presents the correspondence between the number of the occupied sublattice and the concentration of the particles. The third column of the table shows, whether the superlattice possesses only charged domain walls or not: this is connected to the fact, whether the basis vectors of the superlattice are parallel to the basis vectors of the underlying triangular lattice. This is the key factor, determining the domain walls’ patterns in doped systems. The forth column shows, whether the superlattice possesses two different sectors of ground states, which can not be obtained one from another by only a translation – in this case the mirror symmetry is also needed.

In the further subsections we briefly discuss several experimentally accessible cases, with the concentrations $\nu_0 = 1/3$, $1/9$, or $1/13$.

Table 7: Classification of commensurate filling factors on a triangular lattice

# of neighbor	concentration ν_0	only charged domain walls?	two mirror symmetric sectors?
2	1/3	yes	no
3	1/4	no	no
4	1/7	yes	yes
5	1/9	no	no
6	1/12	yes	no
7	1/13	yes	yes
8	1/16	no	no
9	1/19	yes	yes
10	1/21	yes	yes

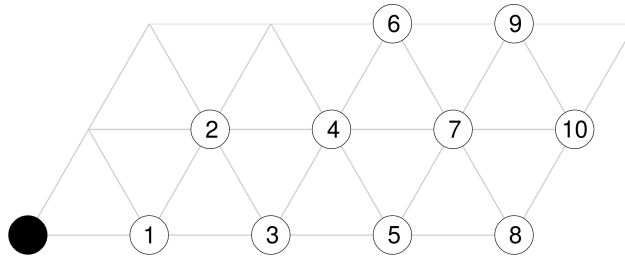


Figure 12.8: Neighbors of a given site (black) with successively increasing distances from it.

12.8.1 $\nu_0 = 1/3$

Concentration $\nu_0 = 1/3$ is the minimal case, where we observe qualitatively similar patterns as for $\nu_0 = 1/13$. There is, however, an important distinction: single holes are much more stable here and some threshold holes concentration is necessary for the first globule creation. This case corresponds, for example, to Pb on Ge surface charge density wave [1].

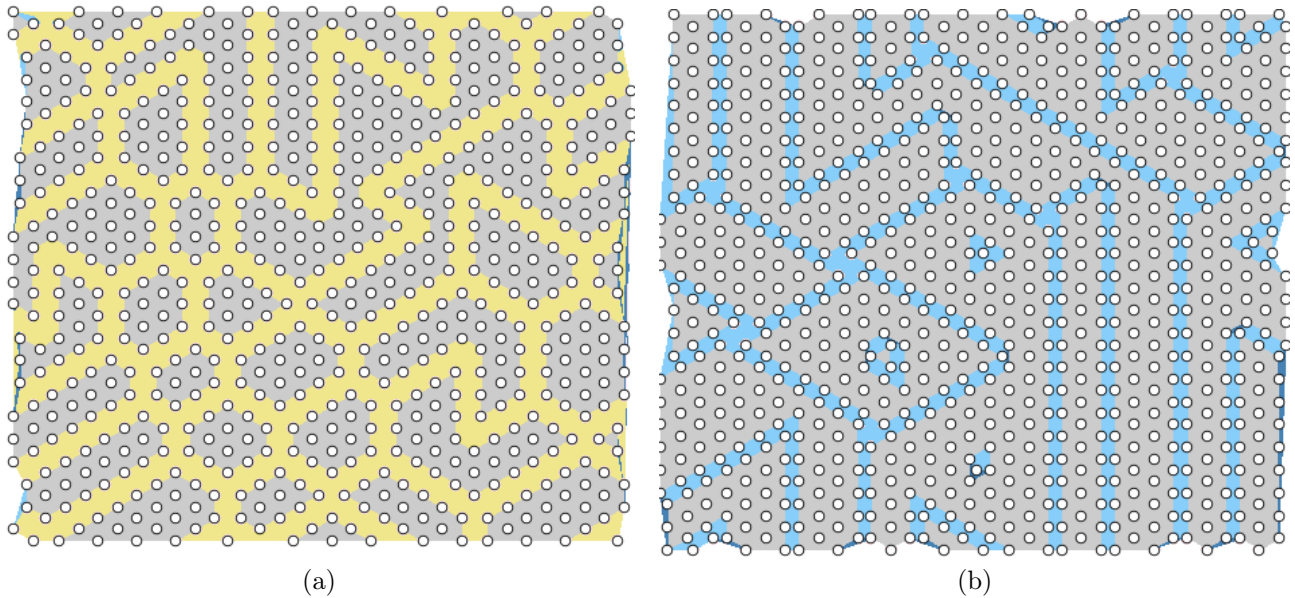


Figure 12.9: $\nu_0 = 1/3$: domain wall representation for (a) positive doping; (b) negative doping.

12.8.2 $\nu_0 = 1/9$

In the case $\nu_0 = 1/9$ the minimal domain walls are neutral, because unit vectors of the superlattice and of the underlying triangular lattice are parallel to each other for this concentration, so the results are qualitatively different from $1/3$ and $1/13$ cases. Which connectivity is more favorable (stripe or network) depends on the sign of wall-crossing energy [2]. Interestingly the “stripe” phase is experimentally observed on heating of $\nu_0 = 1/9$ commensurate charge density wave in $2H - \text{TaSe}_2$, see [3].

12.8.3 $\nu_0 = 1/13$

The case of positive doping was considered in the main text; Fig. 12.11a,b shows the full-size version of Fig. 5a,c of the main text.

Here we also extend the results of the main text to the case of the electrons’ doping which accumulate into interstitials rather than voids (Fig. 12.12). For negative doping we still observe

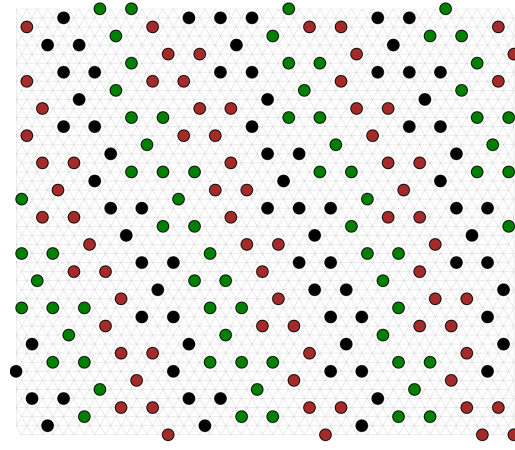


Figure 12.10: $\nu_0 = 1/9$: domain representation for the “stripe” phase for with positive doping. Here we use 9-coloring scheme (only 3 of them appear on the figure), analogous to 13-coloring scheme used in the main text.

the charge fractionalization phenomena and qualitatively similar to the case of positive doping structures. The wall crossings are still favorable (thus no “stripe phase”), but connection of 4 walls is also favorable as of 3 walls, which is presumably governed by the short-range physics. Because of this, visually the pictures look differently.

For higher l_s , the long-range part of the Coulomb interaction will become progressively more important and will favor walls’ 3-crossings, with 120° angle between them because of their repulsion, at least for sparse walls’ networks (when the walls’ structure characteristic period is $\gg l_s$). Thus we expect that the metastable states with the lowest lying energies will represent the “irregular honeycomb network” [4] as observed for the positive doping.

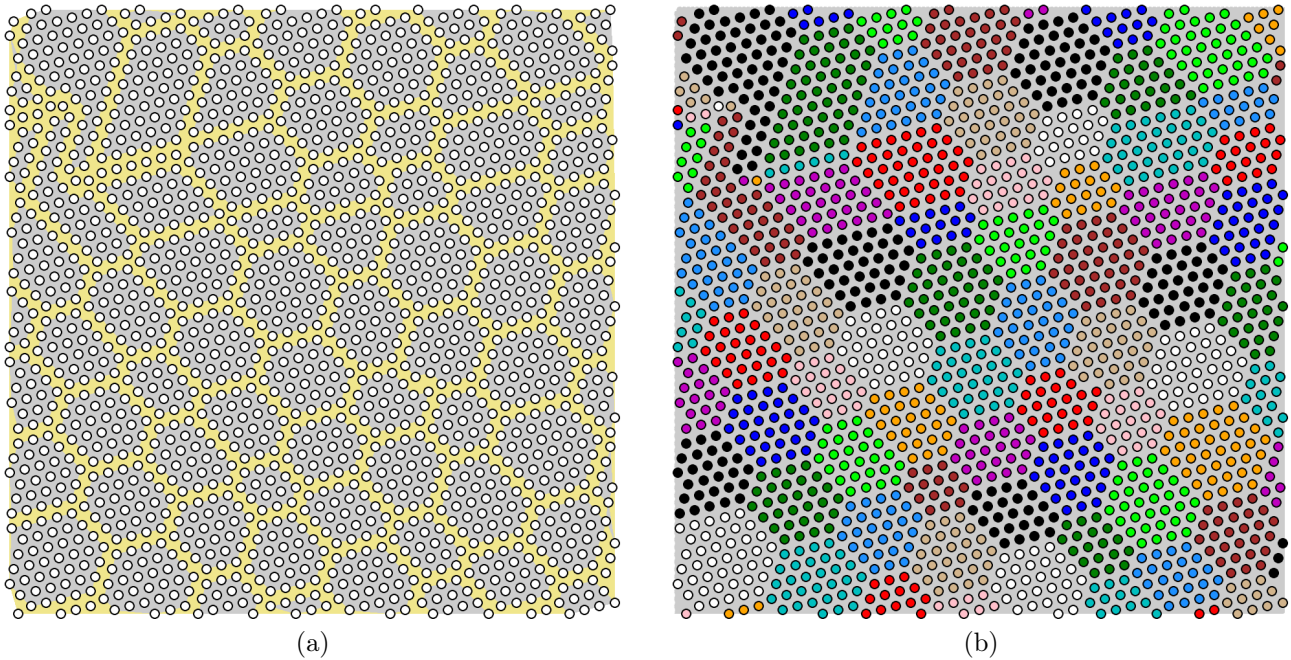


Figure 12.11: $\nu_0 = 1/13$: net structure for positive doping: full-sized version of Figure 5 from the main text. (a) Domain wall representation; (b) domain representation

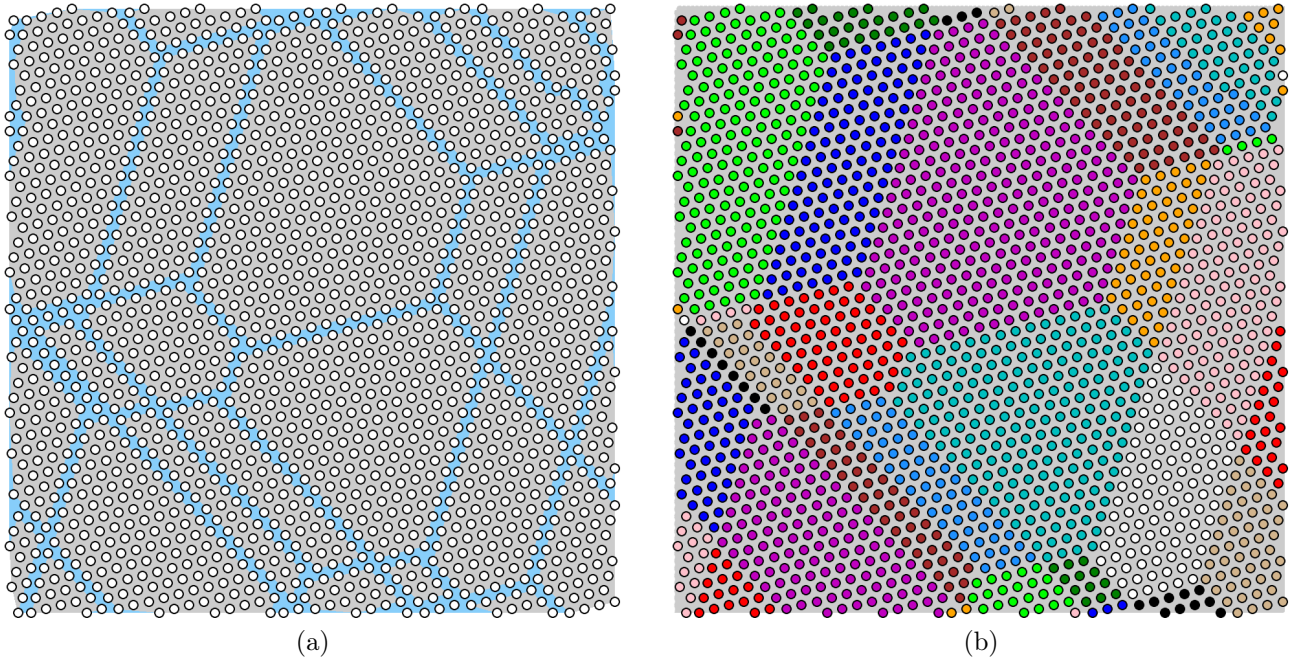


Figure 12.12: $\nu_0 = 1/13$: net structure for negative doping, $\nu_{interst} \approx 1.8\%$, $l_s = 4.5b$, $T = 0.01U_0$: (a) domain wall representation; (b) domain representation.

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13 Band structures of the layer compounds 1T- TaS_2 and 2H - TaSe_2 in the presence of commensurate charge-density waves by Smith, Kevan, DiSalvo

(Jaka said that here is the derivation of TB parameters. However, there is a link to the 1950th paper, which is maybe more important)

To cite this article: N V Smith et al 1985 J. Phys. C: Solid State Phys. 183175

Abstract

Angle-resolved photoemission spectroscopy (arpes) measurements of the $E(k)$ band structure are reported for 1 T - TaS_2 and 2H - TaSe_2 at temperatures where commensurate CDWS are well developed. Empirical tight-binding calculations of the band structure in

the presence of the experimentally known CDW superlattice are also reported. In the case of the $\sqrt{13} \times \sqrt{13}$ CDW in 1T-TaS₂, experiment and theory both reveal a gross distortion of the band structure, in which the Ta-derived d band collapses into three sub-band manifolds separated by gaps. The thirteenth electron is predicted to reside in a conduction band only 50 meV wide, where it is susceptible to a Mott-Anderson transition. In the case of 2H – TaSe, additional peaks are seen in the ARPES data in the presence of the CDW, but the effects are too weak to distinguish between a band-structure distortion and weak Umklapp associated with the 3×3 superlattice. Calculated densities of states, decomposed according to the inequivalent atomic sites, are presented.

13.1 1. Introduction

Work on layer compounds occupies a special place in the history of angle-resolved photoemission spectroscopy (arpes), since it was on such materials that the utility of ARPES in the direct mapping of band structures was first demonstrated (Smith et al 1974, Smith and Traum 1975). In the intervening decade, there have been substantial improvements in the ARPES technique in both energy and momentum resolution (see e.g. Himpsel 1983). The motivation of the present work was to return to the layer compounds and, using a superior arpes instrument, to study the effects on the band structure of charge-density waves (CDWs) in these materials.

In this paper we report experiments and calculations on the layer compound 1TTaS₂, which displays a strong CDW, and on 2H – TaSe₂, which by way of contrast displays a weak CDW. The superlattice in the case of 1 T – TaS₂ has a $\sqrt{13} \times \sqrt{13}$ unit cell rotated $13^\circ 54'$ with respect to the unreconstructed (or 1×1) unit cell. The superlattice in the case of 2H – TaSe₂ has a 3×3 unit cell aligned along the same axes as the 1×1 unit cell.

To assist in the interpretation we have devised simple tight-binding or linear combination of atomic orbitals (LCAO) models. These start by fitting the unreconstructed band structures using a minimal basis set of Ta d orbitals. The band structures in the presence of a CDW are then simulated by selective strengthenings and weakenings of hopping integrals between neighbouring atoms in the superlattice unit cell. The arpes data as elucidated by the LCAO calculations offer insight into the effects of CDWS on the electronic structure, as well as providing some estimate of the amplitudes of CDWs themselves.

13.2 2. Experimental procedure

Our arpes experiments were performed using a new instrument designed for high resolution in both energy and momentum (Kevan 1983). The source was a resonance lamp providing both HeI ($\hbar\omega = 21.22\text{eV}$) and NeI ($\hbar\omega = 16.85\text{eV}$) photons.

Single-crystal samples were attached using Ag-filled epoxy cement to a sample holder/manipulator which could be cooled to liquid nitrogen temperature. The samples were cleaved in an ultrahigh-vacuum ($3 \times 10^{-10}\text{Torr}$) preparation chamber and checked with low-energy electron diffraction (LEED) for orientation and satisfactory CDW formation. Some difficulty was experienced in getting cooled samples of 1T-TaS₂ to undergo the transformation into the commensurate CDW state. This is attributed to the inhibiting effects of the strains induced by attempting to hold the samples rigorously flat using epoxy cement. Our best results on 1T- TaS₂ were obtained on a sample which may have worked itself partially loose, thereby relieving the inhibiting strains, but leaving some doubt as to whether we have really achieved good flatness and the very high angular resolution of which our instrument is, in principle, capable.

Figure 1 compares two normal emission spectra taken on different samples of 1TTaS₂ at lowered temperature. In one case the commensurate CDW is well developed and it is seen, in

basic agreement with previous observations by Pollak et al (1981), that this is accompanied by a strong enhancement of the spectral structure and a downward shift of the peak just below the Fermi level E_F by 0.08 eV. There are three structures in the Ta d-derived region, and these are discernible in both of the spectra of figure 1, and even in room-temperature data (not shown). As we shall discuss below, the existence of more

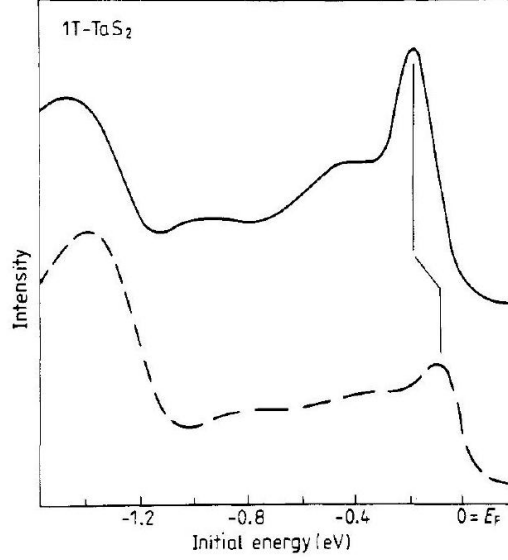


Figure 1. The full (broken) curves show angle-resolved photoemission spectra taken on 1TTaS₂ in the Ta d-band region in the presence (absence) of a commensurate CDW ($\hbar\omega = 21.2\text{eV}$, $\theta = 0^\circ$).

than one peak in the Ta d-band region is a consequence of the CDW distortion. It is therefore interesting to note that this multiplicity of d-band structures exists irrespective of whether the CDW is commensurate or incommensurate.

13.3 3. LCAO band calculations

To interpret the data we have developed simple linear combination of atomic orbitals (LCAO) models. Since we are dealing with superlattices having a large number of atoms per unit cell (39 in the case of 1T-TaS₂), ab initio band calculations would be extraordinarily expensive, and this presumably accounts for the absence of such calculations in the literature. Our approach has been to set up the simplest LCAO models which still retain the important features of the known 1×1 band structures. We have striven to keep the number of basis orbitals and the number of free parameters within manageable bounds.

In the case of 1T-TaS₂, we follow Mattheiss (1973) and set up an effective Hamiltonian involving only Ta d orbitals. It is assumed that the parametrisation is capable of absorbing the indirect Ta-ligand-Ta interactions. We make the additional assumptions of strict two-dimensionality (i.e. no interlayer interactions) and nearest-neighbour interactions within the two-centre approximation. The resulting Hamiltonian (Miasek 1957) is listed in table 1 in terms of $\xi (= k_x a/2)$ and $\eta (= \sqrt{3}k_y a/2)$, where a is the lattice parameter. There are only six parameters, the nearest-neighbour hopping integrals $dd\sigma$, $dd\pi$ and $dd\delta$, and the diagonal energies d_{z^2} , d_{xy} and d_{yz} of the $3z^2 - r^2$, $xy/x^2 - y^2$ and yz/zx orbitals respectively. Note that at this level of approximation, the yz and zx orbitals are decoupled from the other three. Since they reside at energies well above E_F , we can drop them from the basis set and discard the associated parameter d_{yz} .

Table 1. Slater-Koster matrix elements for a two-dimensional hexagonal structure in the two-centre approximation (Miasek 1957). Only non-vanishing elements are listed.

$(3z^2 - r^2/3z^2 - r^2)$	$d_{z^2} + \frac{1}{2}(\text{dd}\sigma + 3\text{dd}\delta)(2\cos\xi\cos\eta + \cos 2\xi)$
$(x^2 - y^2/x^2 - y^2)$	$d_{xy} + \frac{1}{4}(3\text{dd}\sigma + 12\text{dd}\pi + \text{dd}\delta)\cos\xi\cos\eta + \frac{1}{2}(3\text{dd}\sigma + \text{dd}\delta)\cos 2\xi$
(xy/xy)	$d_{xy} + \frac{1}{4}(9\text{dd}\sigma + 4\text{dd}\pi + 3\text{dd}\delta)\cos\xi\cos\eta + 2\text{dd}\pi\cos 2\xi$
(yz/yz)	$d_{yz} + (3\text{dd}\pi + \text{dd}\delta)\cos\xi\cos\eta + 2\text{dd}\delta\cos 2\xi$
(zx/zx)	$d_{yz} + (\text{dd}\pi + 3\text{dd}\delta)\cos\xi\cos\eta + 2\text{dd}\pi\cos 2\xi$
$(3z^2 - r^2/x^2 - y^2)$	$\frac{1}{2}\sqrt{3}(\text{dd}\sigma - \text{dd}\delta)(\cos\xi\cos\eta - \cos 2\xi)$
$(3z^2 - r^2/xy)$	$\frac{3}{2}(\text{dd}\sigma - \text{dd}\delta)\sin\xi\sin\eta$
$(x^2 - y^2/xy)$	$\frac{1}{4}\sqrt{3}(3\text{dd}\sigma - 4\text{dd}\pi + \text{dd}\delta)\sin\xi\sin\eta$
(yz/zx)	$-\sqrt{3}(\text{dd}\pi - \text{dd}\delta)\sin\xi\sin\eta$

For 1 T – TaS₂ a reasonable simulation of the first-principles bands in the vicinity of E_F is obtained by setting the five free parameters as follows: $\text{dd}\sigma = -0.05483$, $\text{dd}\pi = 0.01769$, $\text{dd}\delta = 0.00802$, $d_{z^2} = 0.4698$ and $d_{xy} = 0.4653$; energies are expressed in Rydbergs, and E_F occurs at 0.3753 Ryd. The bands are shown in figure 2(a).

In the case of 2H – TaSe₂ our abbreviated Hamiltonian is not sufficiently flexible to reproduce the precise shape of the occupied d band. This difficulty does not occur in LCAO models with the full three-centre parametrisation (Mattheiss 1973) or a basis set including the ligand orbitals (Doran and Woolley 1981). Rather than go to these lengths, we have moved in the opposite direction, towards further simplification. The average energy of the $xy/x^2 - y^2$ manifold relative to the $3z^2 - r^2$ band lies higher in the 2 H polytype with respect to the 1T polytype (Mattheiss 1973). We therefore seek a model based on the $3z^2 - r^2$ orbital alone. Such a model, having sufficient fitting flexibility, can be set up, provided one includes second and third neighbours. The band energy is given by

$$E_{z^2} = d_{z^2} + d_1(2\cos\xi\cos\eta + \cos 2\xi) + d_2(2\cos 3\xi\cos\eta + \cos 2\eta) + d_3(2\cos 2\xi\cos 2\eta + \cos 4\xi). \quad (1)$$

The coefficients d_n are equal to $\frac{1}{2}(\text{dd}\sigma_n + 3\text{dd}\delta_n)$ where the index $n = 1, 2, 3$ runs over first-, second- and third-nearest neighbours respectively. It would be more appropriate, however, to regard d_1 , d_2 and d_3 as adjuncts of the fitting scheme, rather than imbuing them with any literal physical significance.

A reasonable simulation of the band structure of 2H – TaSe₂ obtained by setting d_1 , d_2 and d_3 equal to 0.1900, 0.4700 and 0.0322 eV respectively is shown in figure 2(b). These parameters were obtained by first fitting the first-principles results and then stretching the band by about a factor of 2 in order to produce an occupied d-band width ($\sim 0.5\text{eV}$) in closer agreement with the photoemission data. Note particularly the excursion of the band below E_F midway along the ΓK symmetry line. It is this feature which cannot be reproduced by the Hamiltonian of table 1, but is important because it occurs in all first principles calculations, and is observable experimentally.

To simulate the effects of cDws on the band structure, the Hamiltonian of table 1 or of equation (1) is opened out (unfolded?) into the larger unit cell of the superlattice. X-ray diffraction work by Brouwer and Jellinek (1980) indicates that the atomic displacements associated with the CDW can be pictured in terms of 7 -atom or 13-atom Ta clusters. The effects on the band structure are calculated by assuming that the interatomic hopping integrals $\text{dd}\sigma$, $\text{dd}\pi$ and $\text{dd}\delta$ scale as D^{-5} , where D is the appropriate Ta-Ta interatomic distance. Our method is the same

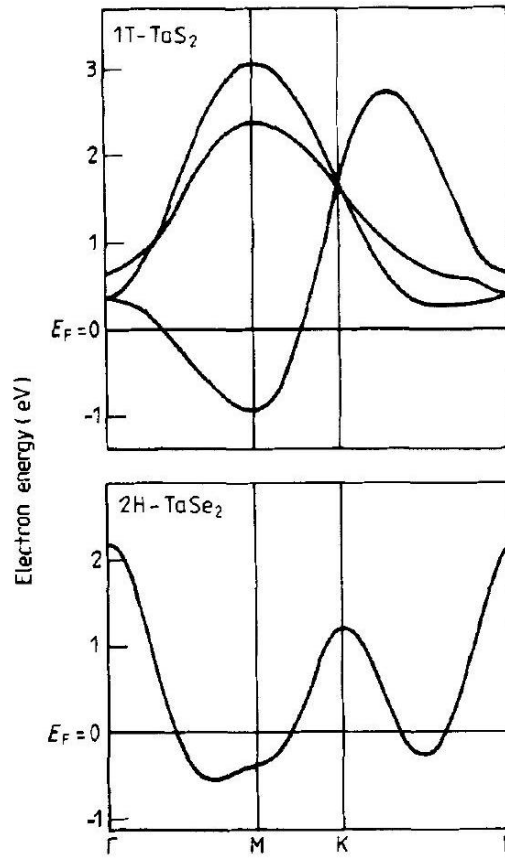


Figure 2. Empirical band structures of 1 T – TaS₂ and 2H – TaSe₂ in the unreconstructed state.

as that used by Doran and Woolley (1981), but it has been stripped to its barest essentials. By restricting the number of basis orbitals, the superlattice Hamiltonian matrix can be kept conveniently small, being 39×39 for 1TTaS₂ and 9×9 for 2H – TaSe₂. Figure 3 provides a foretaste, in the case of 1 T – TaS₂, of how the density of states is modified in the presence of a commensurate CDW .

13.4 4. 1T- TaS₂ : results and discussion

13.4.1 4.1. ARPES data

Photoemission spectra taken on 1 T – TaS₂ in the Γ M azimuth as a function of angle of emission θ with respect to the surface normal are shown in figure 4. Three structures are seen in the Ta d-band region at approximately -0.2eV , -0.5eV and -1.0eV relative to E_F . (The peak seen at -1.4eV for $\theta = 0^\circ$ is associated with the S -derived p band, and will not be discussed in this paper.) The main intensity shifts between the three d features, but there is little energy dispersion compared with the separation of the peaks.

The observation of three d peaks is in flat contradiction with the expectations of the unreconstructed band structure of figure 2(a), which permits only one occupied d band. Our spectra along the Γ K azimuth (not shown) are rather similar to those along Γ M,

which is also in contradiction with the prediction of the unreconstructed band structure. A number of authors have noted the existence of forbidden d emission along the Γ K azimuth (Smith and Traum 1975, Mamy et al 1981).

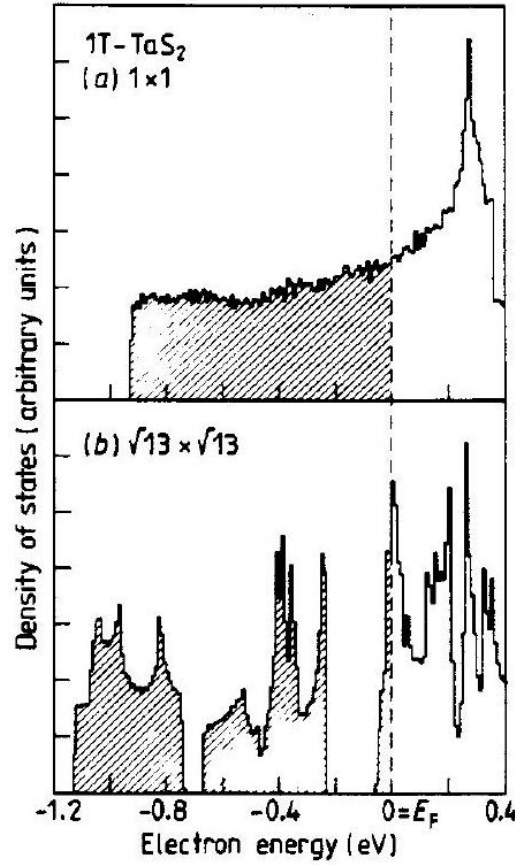


Figure 3. Calculated Ta d-band density of states: (a) in the absence, (b) in the presence of a commensurate CDW .

13.4.2 4.2. cow Structure

The $\sqrt{13} \times \sqrt{13}$ unit cell of 1 T – TaS₂ in the presence of a commensurate CDW is shown in figure 5. There are three types of inequivalent atoms designated a, b and c in the numerical proportion 1 : 6 : 6. The atomic displacements are characterised as a contraction of the seven-atom cluster comprising an atom of type *a* and its surrounding *b* atoms (Brouwer and Jellinek 1980). The *ab* distance decreases by 6.4%. The *c* atoms also move towards the nearest *a* atom—the *bc* distance decreases by 3.2%—so that we may speak of 13 -atom 'Star-of-David' clusters. We have used only the simplest representation of this structure. In particular, we have ignored the slight non-radial movements of atoms *b* and *c* with respect to the cluster. We have also ignored interlayer interactions which can also remove the strict equivalence within the *b* and *c* atom subsets (Naito et al 1983).

Figure 5 shows the Brillouin zones for both the 1×1 and $\sqrt{13} \times \sqrt{13}$ structures. In this paper we shall present results exclusively in terms of the 1×1 Brillouin zone since this corresponds more closely to our experimental procedure.

13.4.3 4.3. Comparison between experiment and theory

We first investigate whether the ARPES data could be understood in terms of Umklapp, i.e. weak Bragg diffraction through reciprocal-lattice vectors of the CDW superlattice. For example, if we have set the sample and analyser so as to scan along ΓM we are simultaneously scanning along the $\Gamma M'$ shown in figure 5(b). Electrons optically excited on this line can scatter into our line of sight by diffraction through the vector $-g$.

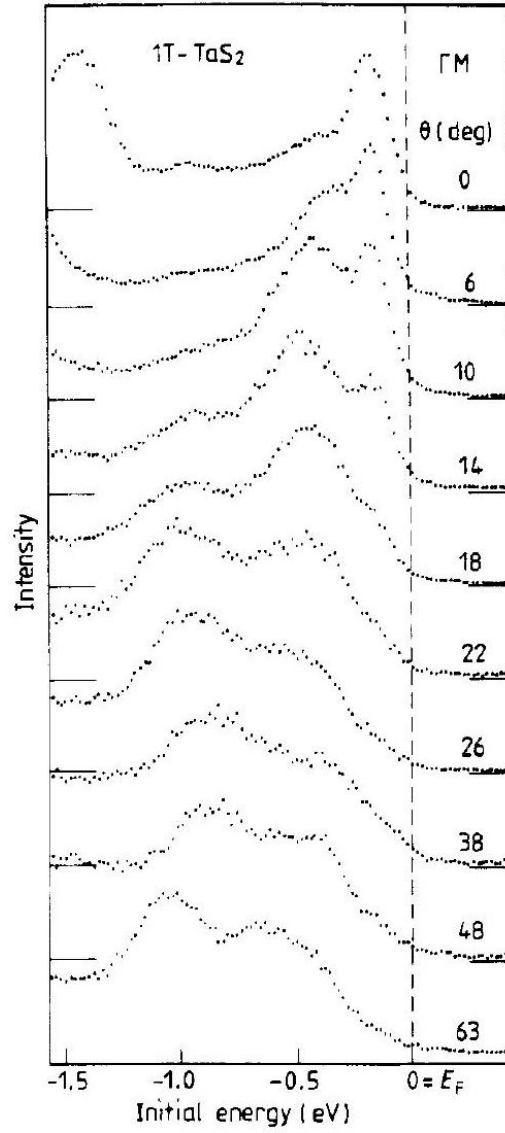


Figure 4. Angle-resolved photoemission spectra on 1 T-TaS₂ in the presence of a commensurate CDW taken as a function of polar angle of emission θ ($\hbar\omega = 21.22$ eV, Γ M azimuth).

Figure 6(a) shows (broken curves) the superposition of all additional bands derived from such Umklapp process. It should be evident that weak Umklapp is unable to explain even the qualitative features of the ARPES data.

Inclusion of the CDW atomic displacements has the effect of removing many of the band crossings, and the consequences of the D^{-5} law are shown in figure 6(b). There is a gross distortion of the original band structure. In the occupied region the bands collapse into three sub-manifolds separated by gaps: (1) a narrow (50 meV wide) manifold immediately below E_F ; (2) a middle three-band manifold in the range -0.23 to -0.67 eV ; (3) a lower three-band manifold in the range -0.74 to 1.13 eV . The lower and middle manifolds are completely occupied containing six electrons each. The remaining (thirteenth) Ta d electron populates the upper manifold, placing E_F only 50 meV above the bottom of the conduction band.

The positions of the peaks in the experimental ARPES data have been superimposed on figure 6(b). The two lower peaks in the data can be immediately identified with the lower and middle manifolds in the theoretical calculations. The mean energy positions and the extent of the energy dispersion are in good agreement. There are differences in the shape of the dispersion which we attribute to the main weight of the observed peak passing back and forth between

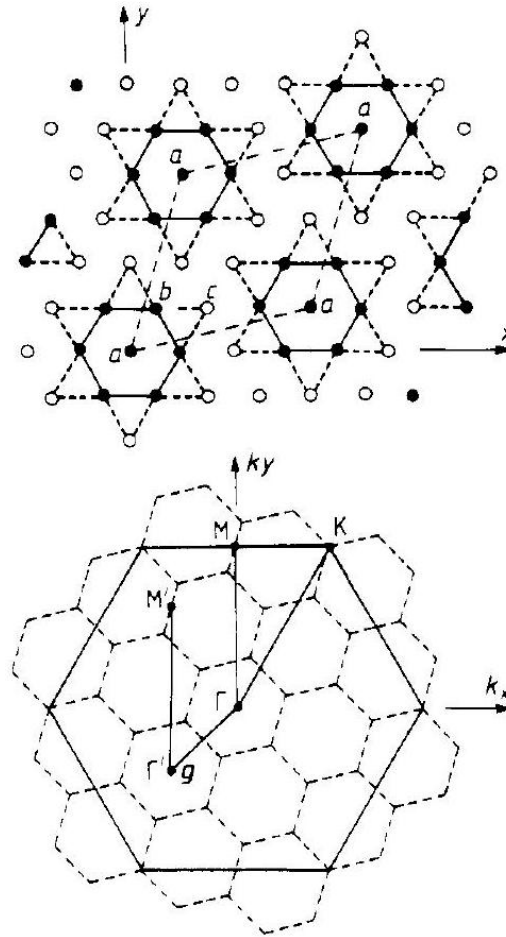


Figure 5. Real-space unit cell and Brillouin zone for the $\sqrt{13} \times \sqrt{13}$ superlattice in 1 T – TaS₂.

the three bands within each manifold.

There are two choices for the assignment of the uppermost experimental peak. First, if we identify it with the narrow uppermost theoretical manifold, we need to explain why it moves so far from E_F when the CDW is fully developed. Following Fazekas and Tosatti (1980) we may conjecture that the reconstructed system is unstable against a Mott or Anderson transition which opens up an additional gap at E_F . As emphasised by Fazekas and Tosatti, it is not the Mott transition which drives the reconstruction; rather, it is the reconstruction which brings about favourable conditions for the Mott transition to take place.

In the second and alternative assignment, we identify the uppermost experimental peak as part of the middle manifold whose upper edge lies only 0.1 eV lower (not a major discrepancy given the crudity of the theoretical calculations). We would then have to propose that there exists an as yet undetected narrow 'metallic' peak at E_F . There is a very suggestive similarity here with the situation on the 7×7 reconstructed surface of Si(111). That system has a metallic surface state which has been associated recently with a very narrow band which dominates the low-frequency behaviour (Demuth et al 1983). At present we cannot distinguish between these alternative interpretations on the basis of ARPES data. The long established semiconducting behaviour of 1 T – TaS₂ at low temperatures clearly favours the Mott-Anderson interpretation.

We conclude that the band theory with inclusion of CDW distortions is quite successful. It accounts nicely for the principal, and previously unexplained, experimental result that the d band collapses into a number of sub-manifolds separated by gaps. Note that the CDW distorted bands are relatively isotropic, also in agreement with experiment. Some discrepancies remain, which is perhaps not too surprising in view of the lack of sophistication in the theory.

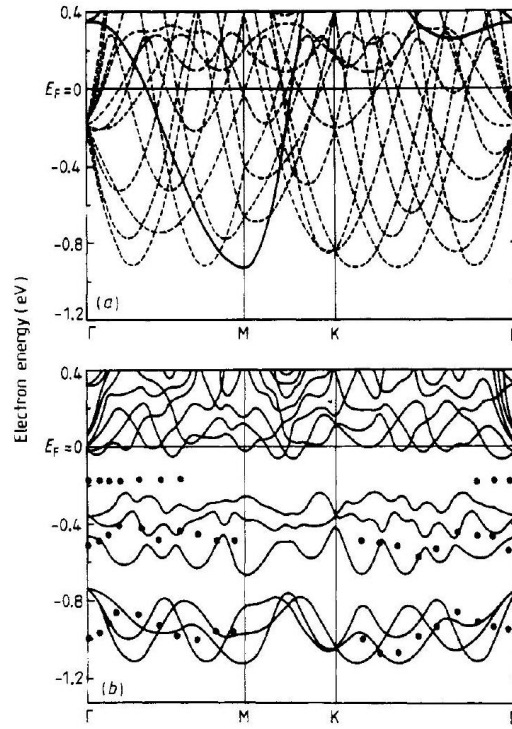


Figure 6. $E(k_i)$ dispersion relations for 1 T – TaS₂ : (a) band structure of the unreconstructed crystal (full curves), and superlattice Umklapp bands (broken curves) derived by translation through reciprocal-lattice vectors of the $\sqrt{13} \times \sqrt{13}$ unit cell; (b) experimental bandstructure results (full circles) are compared with calculated bands (full curves) which incorporate effects due to CDW atomic displacements. Γ M and MK Γ correspond to symmetry directions in the Brillouin zone of the unreconstructed crystal.

Calculations using more powerful techniques would be welcome.

13.4.4 4.4. Densities of states

The density of states (DOS) calculated in both the presence and absence of the CDW distortions has been shown above in figure 3 . In the presence of the CDW, E_F falls close to the maximum of a sharp peak in the dos. This, combined with the narrow width (50meV) of the occupied region and low electron density in the conduction band (one electron per 13 Ta atoms), lends support to the notion of a Mott transition.

The atom-by-atom decomposition of the dos is shown in figure 7. For electrons in the lower manifold, the DOS is largest for atoms of type a, whereas in the middle manifold it is largest for atoms of type b. The total numbers of occupied electrons per atom on atoms of type a, b and c are $n_a = 1.455$, $n_b = 1.311$ and $n_c = 0.611$. These numbers should not be interpreted literally, since self-consistent first-principles calculations would be required for that. Some semiquantitative conclusions can be drawn.

First, the charge transfers involve a substantial fraction of an electron per atom. The ARPES data therefore support those who propose that the CDW has a relatively large amplitude (Wilson 1978).

Secondly we find that $(n_a - n_b) < (n_b - n_c)$, implying that the CDW has a fairly uniform amplitude within the seven-atom cluster. This result serves to explain the failure to resolve a separate a-atom feature in Mössbauer data (Pfeiffer et al 1984) and corelevel x-ray photoemission spectra (Wertheim et al 1975 , Hughes and Pollak 1976, Pollak et al 1981). In the x-ray

photoemission data of Pollak et al (1981) on 1T-TaS₂ in the presence of the commensurate CDW, two 4f core-level peaks are observed showing a separation of 0.73 eV which is interpreted as the chemical shift between atoms of types b and c. Taking the ratio between $(n_a - n_b)$ and $(n_b - n_c)$ literally, we estimate that the chemical shift between atoms a and b should be 0.15 eV towards lower binding energy which is smaller than the 0.25 eV core linewidth. NMR measurements on 1 T - TaS₂ reveal more than three inequivalent Ta sites, suggesting that the sixfold b and c sets should be further subdivided in the ratio 2 : 2 : 2 (Naito et al 1983). Such distinctions appear to be beyond the sensitivity of current ARPES and core-level XPS experiments.

Our results, that n_a and n_b are very close, are inconsistent with a purely sinusoidal

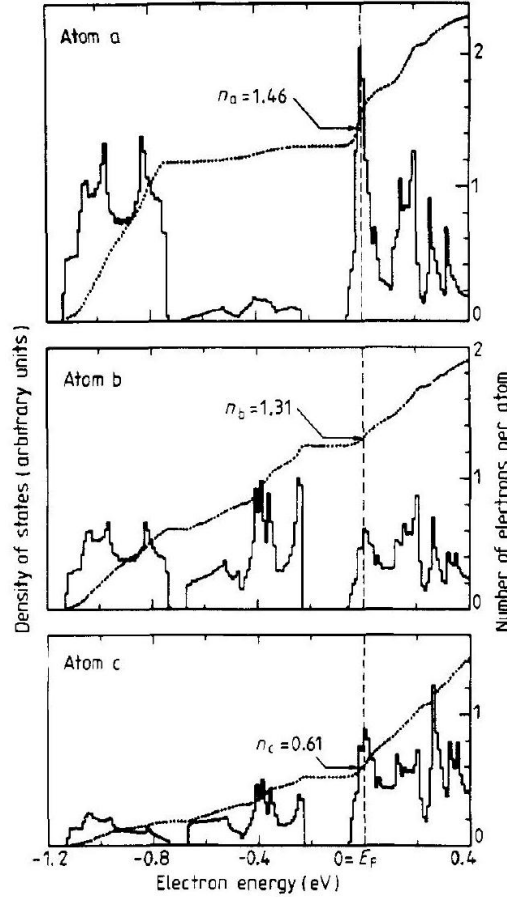


Figure 7. Calculated densities of states for 1 T - TaS₂ for each of the inequivalent atoms in the $\sqrt{13} \times \sqrt{13}$ unit cell.

CDW since that would require a considerably greater charge surfeit on atom a (Wilson 1978). It is also inconsistent with the detailed model of Fazekas and Tosatti (1980) which proposes a charge depletion on atom a. Our empirical LCAO calculations indicate that the charge of the 'thirteenth' electron of the conduction band is distributed 14%, 5% and 9% on atoms a, b and c respectively.

13.4.5 4.5. Joint density of states

A joint density of states was generated using the CDW distorted band structure, and the results are compared in figure 8 with the infrared absorption data of Barker et al (1975). The step in the $\hbar\omega = 0.2 - 0.4$ eV range is attributed to the onset of transitions between states in the intermediate manifold of figure 6(b) and states above E_F .

The experimental data show a weak peak at $\sim 0.1\text{eV}$. A peak is seen at this energy in the joint density of states, and corresponds exclusively to transitions from initial states in the 50 meV -wide conduction band. The available infrared absorption data therefore lend some support to the proposed existence of a 'metallic' band in 1T-TaS₂ (one of the alternatives discussed in § 4.3 above), but it should be emphasised that the experimental feature is uncertain.

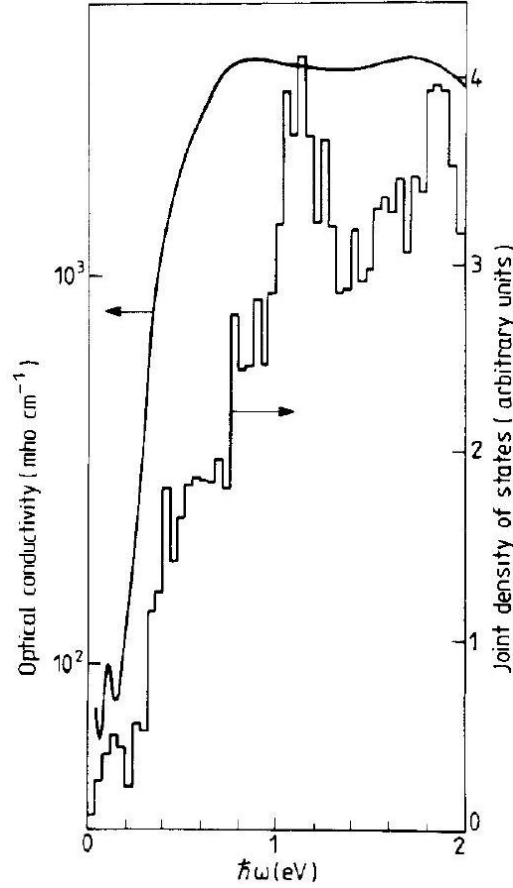


Figure 8. Joint density of states for $\sqrt{13} \times \sqrt{13}$ T – TaS₂ is compared with the infrared absorption data of Barker et al (1975).

13.5 5. 2H – TaSe₂ : results and discussion

13.5.1 5.1. ARPES data

Photoemission spectra taken on 2H – TaSe₂ in the ΓM and ΓK azimuths as a function of θ are shown in figure 9. On increasing θ we observe in both azimuths a prominent Ta d derived peak (designated P) which appears just below E_{F} , disperses down to a minimum energy, disperses upwards and then crosses E_{F} . The behaviour, however, is quantitatively different for the two azimuths in terms of k_{in} range and extent of dispersion. This anisotropy (which is real and cannot be attributed to the different photon energies used in figures 9(a) and 9(b)) is in contrast with the behaviour observed in 1T- TaS₂.

In addition to the prominent peak, a weaker feature (designated W) is discerned in most of the spectra. It shows little if any dispersion.

13.5.2 5.2. cDW structure

The 3×3 unit cell of 2H – TaSe₂ in the presence of the commensurate CDW is shown in figure 10. There are three types of inequivalent atoms designated a, b and c in the numerical proportions 1 : 6 : 2. According to x-ray diffraction and neutron diffraction measurements, the atomic displacements can once again be characterised as an internal contraction of the seven-atom cluster comprising an atom of type a and its six surrounding batoms. We have used a simplified structure extracted from the essentials of the available structural information using the 'ideal' case (phase $\varphi = 120^\circ$ in the terminology of

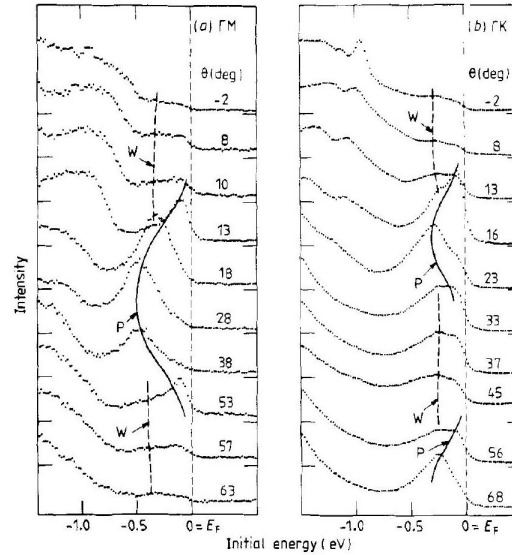


Figure 9. Angle-resolved photoemission spectra on 2H – TaSe₂ in the presence of a commensurate CDW taken as a function of polar angle θ : (a) ΓM azimuth, $\hbar\omega = 21.22\text{eV}$; (b) ΓK azimuth, $\hbar\omega = 16.85\text{eV}$.

Wilson 1978). Following Brouwer and Jellinek (1980), we have adopted the cluster as opposed to the sign-reversed and experimentally indistinguishable structure proposed by Moncton et al (1977) based on neutron scattering. Moncton et al place a lower limit of 2.1% on the contraction of the $a - b$ distance. Using the D^{-5} scaling of the hopping parameters d_1, d_2 and d_3 leads to a rather small effect on the model band structure. For illustrative purposes, we have therefore used a doubled contraction of 4.2% rather than the 2.1% lower limit. Our results are similar in their essentials to those of Doran and Woolley (1981).

Figure 10 shows the Brillouin zones for both the 1×1 unreconstructed and 3×3 superlattice structures. As throughout, we shall refer results to the 1×1 Brillouin zone.

13.5.3 5.3. Comparison between experiment and theory

The experimental $E(k_{\parallel})$ data associated with peak P and weaker feature W are compared with the model band structures in figure 11. The comparison of figure 11(a) shows the 1×1 band structure (full curves) and the Umklapp shifted bands (broken curves) associated with the 3×3 superlattice. The comparison of figure 11(b) superimposes the same experimental data on the model bands in the presence of CDW distortion associated with a 4.2% contraction of the $a - b$ distance.

We find qualitative $E(k_{\parallel})$ agreement in that the strong experimental feature (peak P) follows the behaviour of the 1×1 band structure (a downward excursion along ΓM

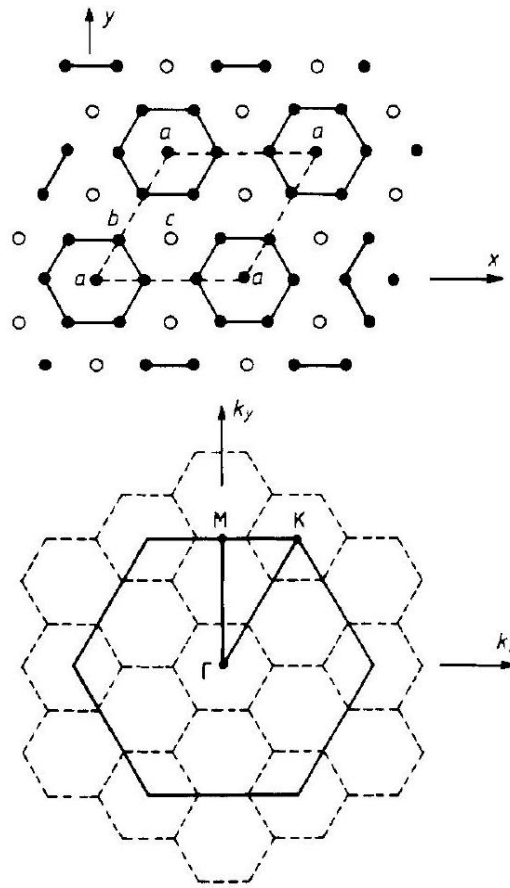


Figure 10. Real-space unit cell and Brillouin zone for the 3×3 superlattice in 2H – TaSe₂.

with a minimum near M, and also an excursion below E_F somewhere midway along ΓK). Inclusion of superlattice effects accounts for the existence of the weaker experimental feature W.

Quantitative aspects of the agreement are not impressive. We have previously mentioned the need to stretch the width of the Ta d band generated by first-principles calculations by about a factor of two. Details of the $E(k_{\parallel})$ dispersion of the weak feature W are not well reproduced. Nor is the agreement significantly improved by explicit inclusion of the CDW distortion (compare figures 11(a) and 11(b)). We advance as the main reason for this lack of detailed agreement our neglect of the interlayer interactions. It should be emphasised that the occupied width of the Ta d band is only 0.5 eV experimentally, and considerably less theoretically. Differences in energies between the TMK-based plane and the ALH plane of the three-dimensional Brillouin zone can be relatively large. We conclude that the modest measure of agreement in figure 11 is about as good as can be expected given the present resolution of the experiment and the approximations in the theory. A CDW superlattice is required to explain the existence of weak feature W, but the ARPES data are not sufficiently incisive to give an estimate of the CDW amplitude.

13.5.4 5.4. Densities of states

The calculated density of states of 2H – TaSe₂ is shown in figure 12 for the unperturbed (1×1) case and, decomposed according to inequivalent a, b, c atoms, for the case in the presence of the (3×3) CDW distortion (4.2% contraction of the a – b distance). In contrast with 1T – TaS₂ the results are not dramatic; no gaps appear. The main differences occur at the bottom of

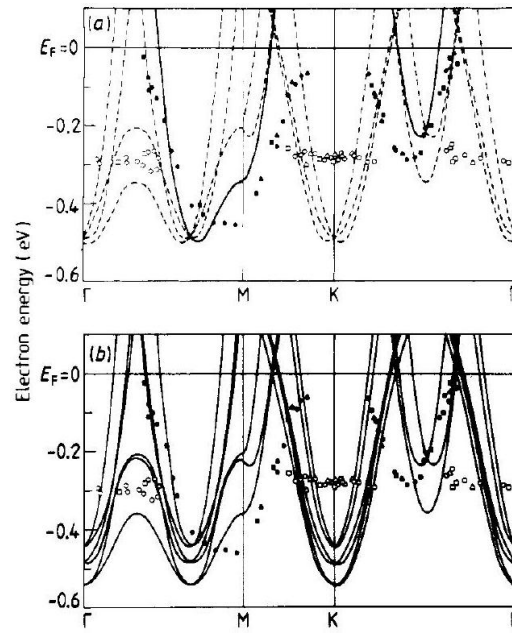


Figure 11. Experimental $E(k)$ results 2H – TaSe₂ are compared with theory. Full and open symbols correspond to features P and W of figure 9 respectively. (a) Unreconstructed bands (full curves) and superlattice Umklapp bands (broken curves). (b) Bands in the presence of a 3×3 CDW.

the occupied d bands, in particular the singularity at -0.48 eV in the a atom density of states. The numbers of Ta d electrons on each of the inequivalent sites are $n_a = 1.014$, $n_b = 1.005$ and $n_c = 0.977$. The departures from unity are relatively small, although once again we have $(n_a - n_b) < (n_b - n_c)$. We conclude that CDW effects on the band structure of 2H – TaSe₂ (even after the deliberate exaggerations of our LCAO model) are weak compared with the dramatic effects in 1T-TaS₂.

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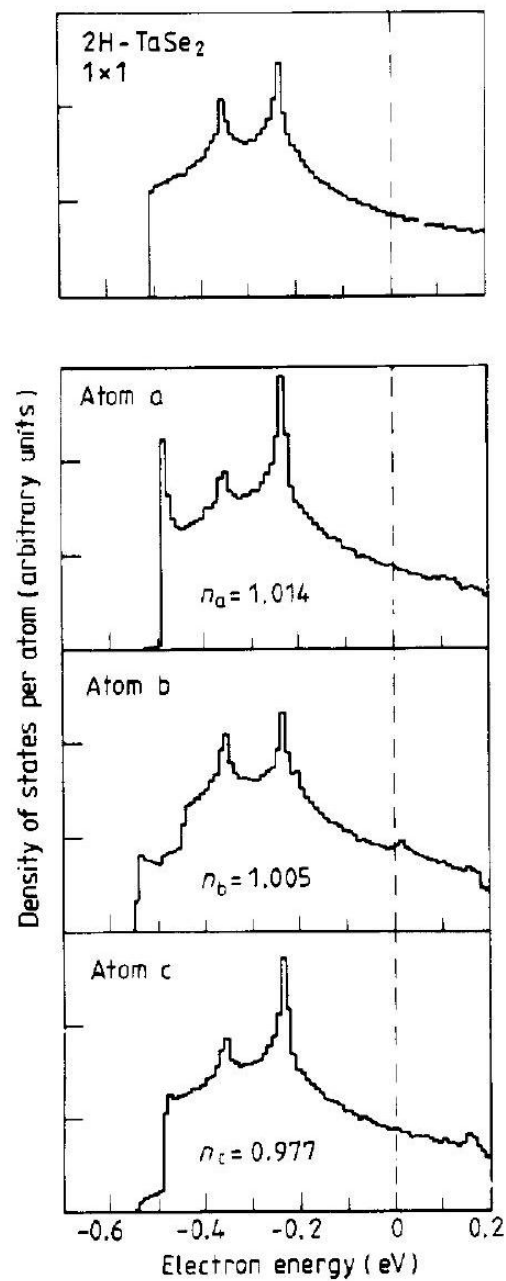


Figure 12. Calculated density of states for 2HTaSe₂ in both unreconstructed states and for each of the inequivalent atoms in the 3×3 reconstructed state.

14 Theory of Two-Dimensional Melting by Halperin, Nelson (1978)

(Dragon said that this is the theory that explains phases of TaSi₂, so it is conceptually important. I'll think later about it)

The consequences of a theory of dislocation-mediated two-dimensional melting are worked out for triangular lattices. Dissociation of dislocation pairs first drives a transition into a "liquid crystal" phase with exponential decay of translational order, but power-law decay of sixfold orientational order. A subsequent dissociation of disclination pairs at a higher temperature then produces an isotropic fluid. The critical behavior, as well as the effect of a periodic substrate, is discussed.

Kosterlitz and Thouless¹ have proposed a model of two-dimensional melting, in which the "topological order" of a solid phase is destroyed by the dissociation of dislocation pairs. Similar ideas,¹ with vortices taking the place of dislocations, have led to a rather detailed theory² of the superfluid transition in two dimensions. In this Letter, we summarize the consequences of dislocation-mediated melting of triangular lattices, on both smooth and periodic substrates. A more detailed derivation will be given elsewhere.³

Consider the properties of a two-dimensional triangular solid on a smooth substrate. By definition, the solid has nonzero long-wavelength elastic constants. The structure factor exhibits⁴ power-law singularities, $S(\vec{q}) \sim |\vec{q} - \vec{G}|^{2+\eta} \vec{G}'$, near a set of reciprocal lattice vectors $\{\vec{G}\}$, with exponents η_G related to the Lamé elastic constants $\mu_R(T)$ and $\lambda_R(T)$ by $\eta_{\vec{G}} = k_{\text{BI}} T |\vec{G}|^2 (3\mu_R + \lambda_R) / 4\pi\mu_R (2\mu_R + \lambda_R)$. These singularities, which replace the δ -function Bragg peaks found in three-dimensional solids, reflect power-law decay at large distances of the correlation function $\langle \exp\{i\vec{G} \cdot [\vec{u}(\vec{r}) - \vec{u}(\vec{0})]\} \rangle$, where $\vec{u}(\vec{r})$ is the lattice displacement at point $\vec{r}$. One can also define an order parameter (analogous to $e^{i\vec{G} \cdot \vec{u}}$) for bond orientations, namely $\psi \equiv e^{6i\theta}$, where $\theta(\vec{r})$ is the orientation, relative to the x axis, of a bond between two nearest-neighbor atoms at $\vec{r}$. In a solid, θ is given in terms of the displacement field, $\theta = \frac{1}{2}(\partial_y u_x - \partial_x u_y)$. The solid phase exhibits longrange orientational order, since $\langle \psi * (\vec{r}) \psi(\vec{0}) \rangle$ approaches a nonzero constant at large $\vec{r}$.⁵

If melting is indeed characterized by an unbinding of dislocation pairs at a temperature T_m , one expects that a density $n_f(T)$ of free dislocations above T_m will lead to exponential decay of the translational order parameter $e^{i\vec{G} \cdot \vec{u}}$, with a correlation length $\xi_+(T) \approx n_f^{-2}$. This length diverges as $T \rightarrow T_m^+$ [see (6) below]. The structure factor $S(\vec{q})$ is now finite at all Bragg points, and the Lamé coefficients vanish at long wavelengths. We shall see, however, that orientational order persists, in the sense that bond-angle correlations now decay algebraically, $\langle \psi * (\vec{r}) \psi(\vec{0}) \rangle \sim 1/r^{\eta_6(T)}$. This phase can be described as a liquid crystal, similar to a two-dimensional nematic, but with a sixfold rather than twofold anisotropy. The exponent $\eta_6(T)$ is related to the Franck constant $K_A(T)$, which is the coefficient of $\frac{1}{2}|\nabla\theta|^2$ in the free-energy density: $\eta_6(T) = 18k_B T / \pi K_A(T)$. We find that K_A is infinite just above T_m , but decreases with increasing temperatures, until a temperature T_i , where dissociation of disclination pairs drives a transition into an isotropic phase in which both the translational and orientational order decay exponentially.

The liquid-crystal phase is isomorphic to a two-dimensional superfluid, except that $\pm 60^\circ$ disclinations play the role of vortices. The transition at T_i should belong to the same universality class as the superfluid transition, and we expect, in particular, that $2\eta_6(T_i) = \frac{1}{4}$. Although disclination pairs are very tightly bound in the solid phase, screening by a gas of free dislocations

produces a weaker logarithmic binding for $T_m < T < T_i$. It is interesting to note that an isolated dislocation can itself be regarded as a tightly bound disclination pair,⁶ separated by one lattice constant.

To see the origin of these results, let us decompose the displacement field of a solid into a smoothly varying phonon field $\vec{\varphi}(\vec{r})$, and a part due to dislocations.¹ The Hamiltonian $\mathcal{H}_E$ for the solid, within continuum elasticity theory,⁶ then breaks into two parts, $\mathcal{H}_E = \mathcal{H}_0 + \mathcal{H}_D$, with

$$\frac{\mathcal{H}_0}{k_B T} = \frac{1}{2} \int \frac{d^2 r}{a_0^2} (2\bar{\mu} \varphi_{ij} + \bar{\lambda} \psi_{ii}^2), \quad (1)$$

$$\begin{aligned} \frac{\mathcal{H}_p}{k_B T} = & -\frac{1}{8\pi} \sum_{\substack{\vec{R}, \vec{R}' \\ \vec{R} \neq \vec{R}'}} \left[K_1 \vec{b}(\vec{R}) \cdot \vec{b}(\vec{R}') \ln \left(\frac{|\Delta \vec{R}|}{a} \right) + K_2 \frac{[\vec{b}(\vec{R}) \cdot \Delta \vec{R}][\vec{b}(\vec{R}') \cdot \Delta \vec{R}]}{|\Delta \vec{R}|^2} \right] \\ & + \frac{E_c}{k_B T} \sum_{\vec{R}} |\vec{b}(\vec{R})|^2, \quad \Delta \vec{R} := \vec{R} - \vec{R}'. \quad (2) \end{aligned}$$

In (1), φ_{ij} is related to the smooth part of the displacement field, $\varphi_{ij} = \frac{1}{2} (\partial_i \psi_j + \partial_j \psi_i)$, and $\bar{\mu}$ and $\bar{\lambda}$ are "reduced" elastic constants, given by the usual Lamé coefficients μ and λ multiplied by the square of the lattice spacing, a_0^2 , and divided by $k_B T$. In (2), $\vec{b}(\vec{R})$ is a dimensionless dislocation Burgers vector of the form $\vec{b}(\vec{R}) = m(\vec{R}) \vec{e}_1 + n(\vec{R}) \vec{e}_2$, where $m(\vec{R})$ and $n(\vec{R})$ are integers, and $\vec{e}_1$ and $\vec{e}_2$ are unit vectors spanning the underlying Bravais lattice. The sums in (2) are over, say, a square mesh with spacing a of sites in physical space, and the $\vec{b}(\vec{R})$ must satisfy a vector charge neutrality condition, $\sum_{\vec{R}} \vec{b}(\vec{R}) = 0$. The quantities K_1 and K_2 are equal, $K_1 = K_2 \equiv K = 4\bar{\mu}(\bar{\mu} + \bar{\lambda})/(2\bar{\mu} + \bar{\lambda})$, and E_c is the core energy of a dislocation.

If dislocations only exist in bound pairs at low temperatures, one expects that they can be ignored, and that the long-wavelength properties of the solid will simply be given by (1), with suitably renormalized elastic constants. The properties of the solid phase quoted above follow directly from this observation.

One of us⁷ has studied the properties of (2) in the absence of the dot product or angular terms ($K_2 = 0$). It was found that dislocations are indeed unimportant at low temperatures (large K_1), and that a dislocation-unbinding transition was controlled by the terminus of a fixed surface, parametrized by K_1 and $\vec{e}_1 \cdot \vec{e}_2$. Here, we restrict ourselves to the triangular lattice ($\vec{e}_1 \cdot \vec{e}_2 = \frac{1}{2}$), and extend this treatment to the full dislocation Hamiltonian $\mathcal{H}_D$, taking into account the neglected angular terms. Recursion relations for K and $y \equiv \exp(-E_c/k_B T)$ can in fact be obtained rather straightforwardly, by considering the renormalization of elastic constants due to dislocation pairs, in analogy to calculations of the effect of vortices on the superfluid density in a ^4He film.⁸ Integrating over mesh sizes between a and ae^l , we obtain partially dressed parameters $\bar{\mu}(l)$, $\bar{\lambda}(l)$, $y(l)$, and $K(l)$, which satisfy, to $O(y^2(l))$,

$$\frac{d\bar{\mu}^{-1}}{dl} = 3\pi y^2 e^{-K/8\pi} I_0 \left(\frac{K}{8\pi} \right), \quad (3)$$

$$\frac{d[\bar{\mu} + \bar{\lambda}]^{-1}}{dl} = 3\pi y^2 e^{-K/8\pi} \left[I_0 \left(\frac{K}{8\pi} \right) + I_1 \left(\frac{K}{8\pi} \right) \right], \quad (4)$$

$$\frac{dy}{dl} = \left(2 - \frac{K}{8\pi} \right) y + 2\pi y^2 e^{-K/16\pi} I_0 \left(\frac{K}{16\pi} \right), \quad (5)$$

where $I_0(x)$ and $I_1(x)$ are modified Bessel functions of the first and second kind. We find that

$$K^{-1}(l) = \frac{1}{4} \{ \bar{\mu}^{-1}(l) + [\bar{\mu}(l) + \bar{\lambda}(l)]^{-1} \}$$

for all l , so that its recursion relation can be obtained trivially from (3) and (4).

As in Ref. 7, $y(l)$ is driven to zero at large l , for all temperatures below a critical value T_m . Above T_m , $y(l)$ is ultimately driven toward large values and $K(l)$ is driven towards zero, an instability we associate with dislocation-pair unbinding.

Following Kosterlitz² and Ref. 7, we determine the behavior near T_m by studying Eqs. (3)-(5) near the critical value $K_c = 16\pi$. We identify the correlation length $\xi_+(T)$ with ae^{l^*} , with l^* chosen such that $K(l^*) \approx \frac{1}{2}K_c$. In this way, we find that

$$\xi_+(T) \approx a \exp [b / (T/T_m - 1)^{0.44817} \dots], \quad (6)$$

as $T \rightarrow T_m^+$, where b is a constant, and $0.44817 \dots$ can be expressed in terms of the roots of a quadratic equation with Bessel-function coefficients. The specific heat exhibits only an essential singularity, $C_p \sim \xi_+^{-2}$, while the structure factor at the Bragg points is given by $S(\vec{G}) \sim \xi_+^{2-\eta_G}$. Taking over the discussion for the superfluid density in Ref. 8, we find that the reduced shear modulus in the solid phase is

$$\bar{\mu}_R(T) = \lim_{l \rightarrow \infty} \bar{\mu}(l)$$

It follows from Eqs. (3)-(5) that $\mu_R(T)$ approaches a finite limiting value as $T \rightarrow T_m^-$. Just below T_m we find $\mu_R(T) = \mu_R(T_m) [1 + \text{const} (T_m - T)^{0.44817 \dots}]$, with a similar result for $\lambda_R(T)$. There is a universal relationship involving the elastic constants at T_m ,

$$\lim_{T \rightarrow T_m^-} \left\{ \frac{1}{\mu_R(T)} + \frac{1}{\mu_R(T) + \lambda_R(T)} \right\} = \frac{a_0^2}{4\pi k_B T_m} \quad (7)$$

This corresponds to the critical value $K_c = 16\pi$, and is also suggested by the "entropy argument" of Kosterlitz and Thouless.¹

The results for orientational correlations above T_m follow from a calculation of the Franck constant K_A :

$$\begin{aligned} \frac{k_B T}{K_A} &= \lim_{q \rightarrow 0} q^2 \langle \hat{\theta}(q) \hat{\theta}(-q) \rangle \\ &= \lim_{q \rightarrow 0} \frac{q_i q_j}{q^2} \langle \hat{b}_i(q) \hat{b}_j(-q) \rangle, \end{aligned} \quad (8)$$

where $\hat{\theta}(q)$ and $\hat{b}_i(q)$ are the Fourier-transformed orientational and Burgers-vector fields, respectively. The second line of (8) follows because the contribution of $\vec{\varphi}(\vec{r})$ to K_A^{-1} is zero and because the dislocation part of $\hat{\theta}(q)$ is just $^{3,6} \hat{\theta}(q) = -iq_j \hat{b}_j(q)/q^2$. To estimate K_A just above T_m , we use its transformation properties under the renormalization group, $K_A(K(0), y(0)) = e^{2l} K_A(K(l), y(l))$. Choosing $l = l^* = \ln(\xi_+/a)$, we can evaluate K_A using Debye-Hückel theory, which amounts to treating $\vec{b}(\vec{R})$ as a continuous vector field, rather than restricting it to discrete points on a Bravais lattice. Upon Fourier transformation, $\mathcal{H}_D$ becomes

$$\frac{\mathcal{K}_D}{k_B T} = \frac{1}{2V} \sum_{\vec{q}} \left[\frac{K}{2q^2} \left(\delta_{ij} - \frac{q_i q_j}{q^2} \right) + \frac{2E_c a^2}{k_B T} \delta_{ij} \right] \hat{b}_i(\vec{q}) \hat{b}_j(-\vec{q}), \quad (9)$$

where V is the volume. Since the term proportional to the transverse projection operator in (9) does not contribute to (8), one obtains $K_A(K(l^*), y(l^*)) \approx 2E_c(l^*)a^2 = O(k_B T_m)$. It follows that the physical Franck constant is $K_A \sim \xi_+^2(T)$. The algebraic decay of orientational order above T_m and the relationship between $\eta_6(T)$ and $K_A(T)$ are straightforward consequences of this result.

Many experimental investigations of two-dimensional melting are carried out on films adsorbed onto a regular substrate,⁹ and so it is important to determine the effect of a periodic potential on our results. One must now distinguish between a "floating solid," characterized by power-law Bragg singularities at reciprocal lattice vectors $\{\vec{G}\}$ which vary continuously with coverage and temperature, and an "epitaxial solid," having δ function Bragg peaks at a lattice of vectors including the substrate reciprocal lattice $\{\vec{K}\}$ as a proper subset. The floating solid should be rather similar to the solid on a smooth substrate discussed in this paper. Figure 1 shows a schematic phase diagram with fluid, floating solid, and epitaxial phases. A region of two-phase coexistence is also shown, separating epitaxial phase I from a dilute fluid or "vapor."^{8,10} We expect an increasing multiplicity and complexity of epitaxial phases with decreasing temperatures.

To understand Fig. 1, consider first the effect of a weak substrate potential commensurate with the lattice of the adsorbed film. Let $\{\vec{M}\}$ be the set of vectors common to $\{\vec{G}\}$ and $\{\vec{K}\}$, and let M_0 be the minimum length of nonzero vectors in $\{\vec{M}\}$. Let us expand the potential on the reciprocal lattice $\{\vec{K}\}$, and focus our attention on

$$\mathcal{H} = \mathcal{H}C_E + \sum_{|\vec{M}|=M_0} h_{\vec{M}} \sum_{\vec{r}} e^{i\vec{M} \cdot \vec{r}(\vec{r})}, \quad (10)$$

where $h_{\vec{M}}$ is the potential strength at $\vec{M}$; the terms displayed in (10) are the most important ones for weak potentials. The renormalization-group eigenvalue for $h_{\vec{M}}$ is easily shown to be $\lambda_{\vec{M}} = 2 - \frac{1}{2}\eta_{\vec{G}}|_{\vec{G}=\vec{M}}$, so that any commensurate perturbation becomes relevant at sufficiently low temperatures. If M_0 is sufficiently small ($M_0 \lesssim 8\pi/a_0$), λ_{M_0} remains relevant out to quite high temperatures and a floating solid can never exist; there is then a transition directly from a low-tempera-

ture epitaxial phase into a fluid, as shown for epitaxial phases I and III. For large enough M_0 ($M_0 \gtrsim 8\pi/a_0$), however, there is a temperature window where $\lambda_{M_0} < 0$ and $K_R > 16\pi$, indicating that a floating solid is stable to both substrate perturbations and dislocation unbinding. The dotted line in Fig. 1 shows a locus of such points, where the floating solid has the same periodicity as epitaxial phase II, which exists at lower temperatures.

It can be shown³ that the transitions from floating solid to fluid and from floating solid to epitaxial phase II (marked A and B in Fig. 1) are both describable at long wavelengths by a Hamiltonian of the form (2) with $K_1 \neq K_2$. Indeed, these transitions are essentially dual to each other.³ The situation is very similar to the " $\cos p\theta$ " perturbations discussed by José et al.¹¹ The transition from epitaxial phase II to a floating solid at points other than B may connect two phases with different periodicities; its nature is not yet known. We expect that the transition from floating solid to fluid will be everywhere qualitatively similar to our discussion of dislocation unbinding on a smooth substrate. The orientational bias imposed by the substrate, however, should alter or eliminate the liquid-crystal isotropic transition discussed above.

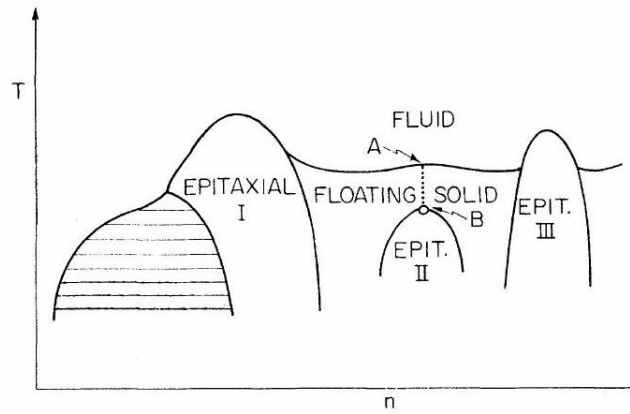


FIG. 1. Hypothetical phase diagram for a submonolayer adsorbed film on a periodic substrate as a function of density n and T .

We wish to emphasize in closing that we have only explored consequences of the dislocation model of melting perturbatively in $y = \exp(-E_c/k_B T)$. Although the theory is stable and self-consistent, we cannot rule out other mechanisms for melting, perhaps leading to a first-order transition. A "premature" unbinding of disclinations (before dislocations dissociate) might constitute such a mechanism.

We have benefitted from discussions with S. Aubry, A. N. Berker, M. Kléman, and R. Peierls. This work was supported by the National Science Foundation, under Grant No. DMR 77-10210, and by the Harvard Materials Research Laboratory program. One of us (D.R.No) received a Junior Fellowship from the Harvard Society of Fellows.

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¹¹ José et al., Ref. 2.

15 Spin-orbit coupling in the band structure of reconstructed 1T-TaS₂ by Rossnagel, Smith (2006)

(Jaka said that this paper tells a lot about TB model of TMDS)

Abstract

Empirical tight-binding simulations of the band structure of 1T-TaS₂ reveal that the combination of spinorbit coupling and the low-temperature $\sqrt{13} \times \sqrt{13}$ reconstruction generates a distinct and very narrow band at the Fermi level. Spin-orbit interaction is therefore important in any understanding of the correlation effects in this material. The states within the split-off band are primarily of $d_{x^2-y^2}$, d_{xy} character and reside preferentially on the central atom of the "Star-of-David" cluster.

Tantalum is a heavy element and so spin-orbit interaction is expected to be important in the valence band structure of compounds such as the intriguing material $1T-\text{TaS}_2$. The transition-metal dichalcogenides are layered materials that provide a fertile field for the study of correlation effects in the two-dimensional electron gas. At low temperatures $1T-\text{TaS}_2$ displays structural changes associated with charge-density-wave formation and undergoes a metal-insulator transition. The possible importance of spin-orbit coupling in driving these phenomena was suggested many years ago¹ but there appears to have been very little follow-up. In this brief report, we report the results of some empirical tight-binding simulations of the band structure of $1T-\text{TaS}_2$ which show that spin-orbit coupling, in combination with the reconstruction that this material undergoes at low temperature, is indeed important. We find a distinct and very narrow split-off band at the Fermi level that is ripe for a Mott-Hubbard transition. We further find that the states within this band have specific orbital character and atomic location. Thus spin-orbit coupling emerges as an ingredient in any understanding of many-body correlations in $1T-\text{TaS}_2$ and related materials.

Our approach is to extend a simple tight-binding scheme presented earlier.² The starting point is a fit of the Slater-Koster parameters, using only Ta $5d$ orbitals and the nearest-neighbor two-center approximation, to an early first-principles band structure calculation by Mattheiss.³ Spin-orbit coupling is added by inclusion of the intra-atomic matrices M and N of Abate and Asdente⁴ and by use of the Herman-Skillman value⁵ of the spin-orbit parameter ($\xi = 0.313\text{eV}$). Band structures with and without spin-orbit coupling are illustrated in Fig. 1(a) for the unreconstructed case. Although there are some large splittings in the bands (e.g., $\approx 0.6\text{eV}$ in the lowest state at Γ), the effect on the Fermi surface and its topology is very small. At first sight, the effects of spin-orbit interaction could easily be dismissed. But, as we shall show below, it is not just spin-orbit coupling but rather the combination of spin-orbit coupling and the reconstruction that leads to dramatic effects. The occupied valence band is sometimes loosely referred to as the Ta d_{z^2} band. This is misleading. The mean energies in the crystal-field diagram of Fig. 1(b) indicate comparable importance for the $d_{x^2-y^2}$ and d_{xy} orbitals giving a foretaste of the results to come.

At low temperatures, $1T-\text{TaSS}_2$ undergoes a commensurate reconstruction into a $\sqrt{13} \times \sqrt{13}$ rotated unit cell containing 13 Ta atoms as illustrated in Fig. 2. There are three inequivalent types of Ta atoms in the unit cell designated as "a," "b," and "c." Clusters centered on atoms of type "a" have a "Star-of-David" structure characterized by a shrinkage of the ab and bc interatomic distances by 6.4 and 3.2%, respectively.⁶

Our tight-binding simulation of the effects of the reconstruction starts as previously described.² The Hamiltonian of the unreconstructed case was opened out into the larger unit cell. To simulate the reconstruction, the Slater-Koster hopping integrals $dd\sigma$, $dd\pi$, and $dd\delta$ were scaled as R^{-5} where R is the Ta-Ta distance.⁷ Bonds within the Star-of-David

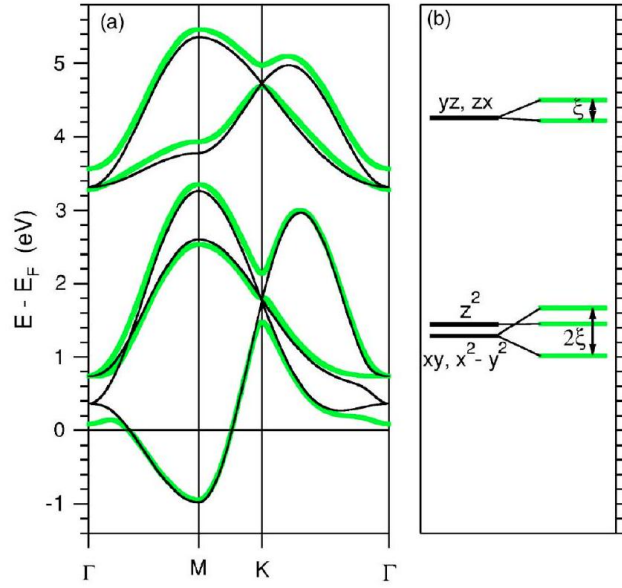


FIG. 1. (Color online) (a) Band structure of $1T - \text{TaS}_2$ both with [bold green (light gray) curves] and without (thinner black curves) the Ta $5d$ spin-orbit coupling. (b) Crystal-field diagram showing the mean energies of the z^2 , $x^2 - y^2/xy$, and yz/zx orbitals. The energy scales have been adjusted to bring the Fermi levels into alignment.

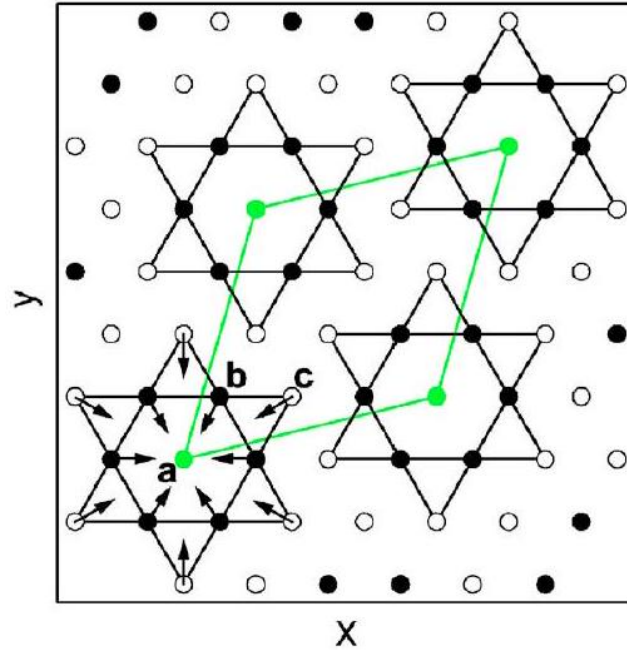


FIG. 2. (Color online) Unit cell of the $\sqrt{13} \times \sqrt{13}$ reconstruction of $1T - \text{TaS}_2$ showing the "Star-of-David" clusters having inequivalent "a," "b," and "c" Ta atoms. The arrows indicate the displacements of the Ta atoms from their original positions.

clusters are thereby strengthened and other bonds are weakened. The bond-length changes are known, so from hereon there are no further disposable parameters. (At this level of approximation, we ignore the slight nonradial movements⁶ in the formation of the clusters.)

Figure 3 summarizes our results by showing the progressive effects of inclusion of reconstruction and spin-orbit interaction. Figure 3(a) shows the effect of opening out into the 13

-atom unit cell; the bold green curves are the original bands and the thinner black curves are the Umklapp or "shadow" bands obtained by translation through the reciprocal lattice vectors of the smaller Brillouin zone.

The effect of introducing the bond strengthenings and weakenings is illustrated in Fig. 3(b). The band structure collapses into submanifolds.² There are two low-lying three-band submanifolds each containing six electrons. The "13th" electron (each Ta atom has one $5d$ valence electron) resides at the bottom of a messy-looking set of bands sometimes referred to as "spaghetti." The existence of the submanifolds has been confirmed by angle-resolved photoemission spectroscopy (ARPES) measurements^{2,8} and some of the substructure within the submanifolds has been resolved.⁹ Our model is two dimensional. First-principles calculations of the reconstructed band structure¹⁰ indicate that three-dimensional interlayer interactions are significant. Band dispersion in the z direction would be very easy to incorporate in our model but is deferred for future study since we wish to highlight here spin-orbit effects. The main effect of z dispersion is a slight broadening of the density-of-states features³ which arises through a $dd\sigma$ -type coupling between Tad_{z^2} orbitals in adjacent layers.

The combined effects of reconstruction and spin-orbit coupling are shown in Fig. 3(c). The changes within the lowlying three-band submanifolds are relatively minor, consisting of some liftings of degeneracies and some second-order energy shifts. The really striking effect is the conspicuous emergence of a distinct and very narrow band at the Fermi level shown in bold green in Fig. 3(c). We offer this effect as the principal result of this brief report. Reconstruction generates a gap just below the spaghetti; spin-orbit coupling splits off a band into this gap. The band has a very small width ($\approx 80\text{meV}$) and is therefore susceptible to a Mott-Hubbard transition, as proposed by Fazekas and

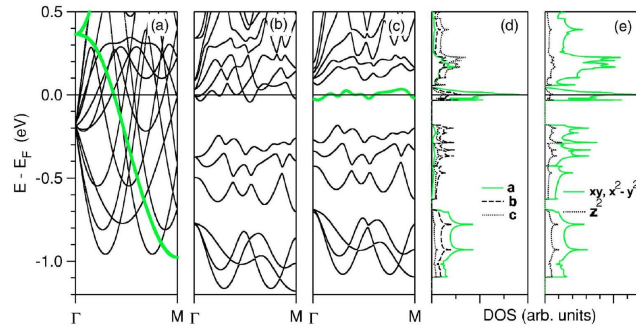


FIG. 3. (Color online) (a) Band structure of $1T - \text{TaS}_2$ in the unreconstructed case [bold green (light gray) curves] and the Umklapp bands (thinner black curves) generated by translation through the reciprocal lattice vectors of the reconstructed Brillouin zone. (b) Reconstructed band structure with inclusion of the bond strengthenings within the Star-of-David as described in the text. (c) Reconstructed band structure with inclusion of Ta spin-orbit coupling revealing [bold green (light gray) curve] a single distinct split-off band. (d) Atom-projected densities of states showing that the states in the split-off band reside primarily on the "a" atoms at the center of the cluster. (e) Orbital-projected densities of states showing that the states in the split-off band are primarily of $x^2 - y^2/xy$ character. The energy scales have been adjusted to bring the respective Fermi levels into alignment.

Tosatti.¹ Reconstruction and spin-orbit interaction are both essential for this effect to occur.

Our tight-binding model generates information on atomic location and orbital content of the electron states. Atomprojected and orbital-projected densities of states are shown, respectively, in Figs. 3(d) and 3(e). It is seen that the states in the narrow split-off band are located

preferentially on the central "a" atom of the Star-of David cluster and are primarily of $d_{x^2-y^2}$ and d_{xy} character with only very weak admixture of d_{z^2} character. The z dispersion of this band should therefore be very small. This information should be of use to many-body theorists seeking a minimal orbital set for MottHubbard type models.¹¹ Specifically, the orbitals of concern are the degenerate $(d_{x^2-y^2} + id_{xy})\alpha$ and $(d_{x^2-y^2} - id_{xy})\beta$ wave functions where α and β are the usual up and down spin functions.

In closing, we have argued that spin-orbit coupling is essential to any understanding of the intriguing properties of $1T - \text{TaS}_2$. We have focused here only on spin-orbit splitting within the Ta-derived valence band. Clerc et al.¹² have recently reported ARPES measurements which resolve the spin-orbit splitting within the chalcogen p -derived bands in both $1T - \text{TaS}_2$ and $1T - \text{TaSe}_2$. They point out that the larger spin-orbit splitting in Se and its greater hybridization with the Ta d bands could be implicated in the different physical properties of these isostructural materials. The need for further theoretical and experimental scrutiny of the role of spinorbit interaction in these and related materials is clearly desirable.

16 Emergent quantum phenomena in two-dimensional $1T - \text{TaS}_2$ by Chen, Sun, Chen (2026)

16.1 Article

Abstract

Strong electron correlation drives (formula for strong electron correlation driving?) $1T - \text{TaS}_2$ from a half-filled metallic state (half-filled metallic state?) into a Mott insulating phase, coexisting with a charge density wave at low temperatures.

(about that phase diagram from Sipos) Under external stimuli such as pressure or ionic gating, superconductivity emerges in $1T - \text{TaS}_2$, exhibiting an intricate relationship of competition and coexistence with the charge density wave order.

In the two-dimensional (2D) limit, enhanced quantum fluctuations can stabilize a quantum spin liquid (QSL) (still todo: QSL) state in the Mott insulator.

(intro to review) This review summarizes recent advances in understanding these quantum states in 2D $1T - \text{TaS}_2$ from the perspective of angle-resolved photoemission spectroscopy (ARPES) and scanning tunneling microscopy (STM), with a focus on the dimensionality effect on its electronic structure.

(we'll discuss QSL) We outline the signatures of QSL state in electronic spectra and discuss how this state can be revealed in the family of this material through experimental approaches beyond conventional probes such as neutron scattering. (and discuss Kondo effect) The role of Kondo effect in detecting spinon excitations is further discussed. (and discuss future experiments) Finally, we suggest future experimental directions and highlight how external perturbations such as gating and light excitation offer versatile pathways to control and exploit these intertwined quantum states.

16.1.1 1 Introduction

(intro that there are many effects) In transition metal dichalcogenides (TMDs), the diverse elemental compositions and variety of accessible chemical phases give rise to rich physics including charge density wave (CDW), superconductivity, quantum spin Hall effect, and exciton condensation [1-15].

(TaS2 has many effects) Within this family, TaS_2 is a prototypical system and decades of in-depth investigations into its CDW orders and Mott insulating behavior have significantly advanced the understanding of strongly correlated electronic states.

(something is not researched) Nevertheless, the underlying driving mechanisms and emergent quantum phenomena remain elusive.

(something is being researched) With the evolution of theoretical models and improvements in experimental techniques, the microscopic picture of these collective excitations is gradually becoming clearer.

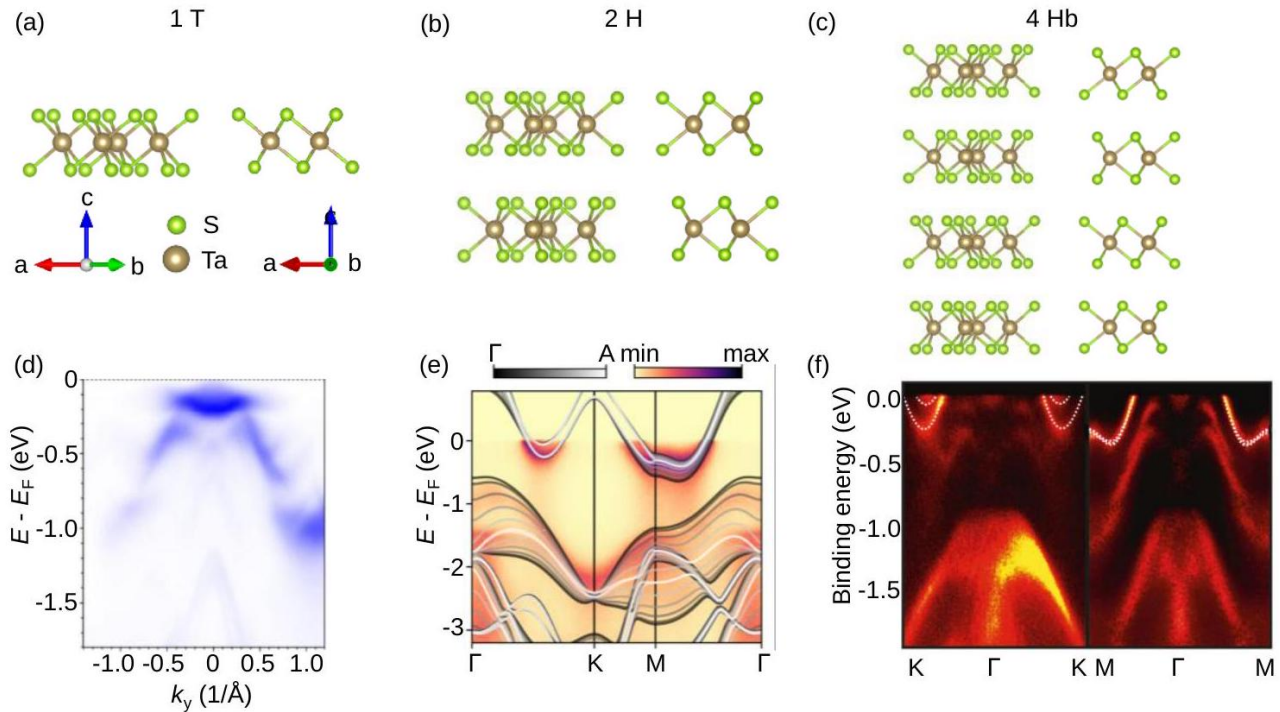


Figure 1 (a-c) Atomic structures of 1T-, 2H- and 4Hb-TaS₂. (d-f) A comparison of ARPES spectra of bulk T-phase, H-phase and 4Hb-TaS₂. (Figures adapted from refs. [18-20])

The crystal structure of TaS₂ is composed of S-Ta-S trilayers that are weakly bonded together by van der Waals forces(reminder, todo: study vdW for this material) , enabling the material to be thinned down to monolayer by exfoliation (=removing something from the outer layer) (Fig. 1).

(there are two phases) The intralayer hybridization between the Ta *d* orbitals and the S *p_z* orbital (still, why there are two phases?) determines the formation of two primary polymorphs: the octahedral coordination structure (T-phase) and the triangular-prismatic coordination structure (H-phase), distinguished by 180° rotation of the top sulfur atomic layer relative to the bottom layer (Fig. 1a, b).

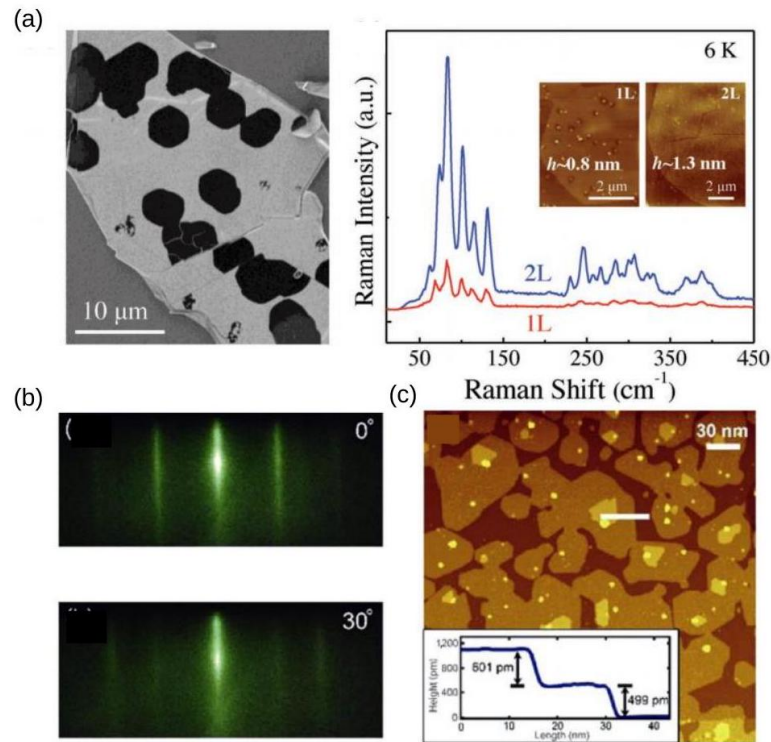
(there are other phases) Alternate stacking of H- and T-type layers can yield other polymorphs such as 4Hb and 6R, which exhibit unconventional superconductivity (Fig. 1c) [16, 17]. (read about them, sounds very unusual!) (see fig. 1d-f) ARPES band structures of these phases are compared in Fig. 1d-f.

1T- TaS₂ is insulating (there is a tiny gap in the spectra, but still it is insulating) with a full gap at low temperatures, whereas the 2 H - and 4Hb – TaS₂ are metallic with bands crossing the Fermi level [18-20]. (why are they metallic based on fig. 1?)

The anomalous insulating behavior of the T phase is attributed to the electron localization, commonly explained by the Mott insulator model. (todo: learn exactly this Mott insulator model)

Notably, the H-phase is energetically more favorable than the T-phase [21]. (why it is more favorable? read citation)

(system tends to go to H-phase) As a result, factors such as thermal fluctuations, light irradiation, or ion implantation can drive an irreversible transition from the metastable T-phase to the H-phase [22, 23].



(the enumeration a,b,c,d is wrong on the image) Figure 2 (a) SEM image of 1T-TaS₂ grown on *h*-BN (hexagonal boron nitride, wide-gap insulator) .

(b) Raman spectra(Raman spectra??) taken from monolayer and bilayer 1T- TaS₂ samples. Insets are corresponding AFM images (Atomic Force Microscopy. Unlike SEM, AFM uses an extremely sharp physical tip that scans across the sample surface) .

(c) RHEED (Reflection High-Energy Electron Diffraction. It is a technique used to study the crystal structure and quality of a surface) patterns of the monolayer TaS₂ thin film along two incident azimuth angles of 0° and 30°.

(d) An STM topographic image shows a coexistence of monolayer and bilayer TaS₂. (Figures adapted from refs. [22, 24])

Single crystals of 1 T – TaS₂ can be synthesized using the chemical vapor transport (CVT)(chemical vapor transport?) method [24].

(CVT makes material often changed to H-phase) However, reducing the dimensionality to thin layers makes it particularly susceptible to degradation or transformation to more stable H phase, posing a significant challenge for obtaining high-quality low dimensional 1T-TaS₂ [25-27].

(CDV (or) MBE + TaS2 = 1T phase) Direct growth of low-dimensional 1T- TaS₂ has been achieved using chemical vapor deposition (CVD) and Molecular beam epitaxy (MBE) methods (Fig. 2) [22, 28-30].

(MBE is good) Compared to CVD, MBE operates under ultra-high vacuum and typically yields atomically flat surfaces, which are advantageous for surface-sensitive techniques such as ARPES and STM.

(still, H phase can occur) Nevertheless, synthesizing monolayer TaS₂ often results in a coexistence of H and T phases [28,29].

Phase selection of TaS₂ can be controlled by the growth temperature and the 1T phase is

favorable at higher growth temperatures (growth temperatures???) .

(still, H phase can occur) Notably, increasing layer coverage will induce a partial conversion to the H-phase [22].

Bulk 1T-TaS₂ undergoes a first-order transition (first-order transition because abrupt resistivity change and hysteresis) into a CDW state [31-33].

According to conventional band theory, this system is expected to be metallic (there was somewhere this statement (in Jung Kim or Rosnagel), still I don't understand this reason) .

(Mott-Hubbard model is the most typical model for TaS₂) The insulating behavior observed in experiments is therefore most naturally explained by the Mott-Hubbard model [34, 35]. (reminder todo: learn MH model)

(typical property of MH model) In this model, the kinetic energy term, governed by the hopping integral t , favors electron delocalization and band formation.

(typical property of MH model) However, when two electrons occupy the same site, they incur a large Coulomb energy cost U .

(typical property of MH model) The competition between these terms defines the system's behavior.

(typical localization crit. of MH model) When the interaction strength U/W (where $W \sim nt$ is the bandwidth, and n is the coordination number) exceeds a critical value, it leads to the electron localization.

(intro to gap and bands of MH model) This strong electron correlation effect splits the metallic band into upper and lower Hubbard bands, consequently opening a Mott gap.

(bilayer structure might also give insulation) However, an ongoing debate suggests that the formation of a bilayer with a specific stacking order could also induce an insulating state [36-38], with some experiments show a clue of such a configuration [39, 40]. (learn about this bilayer argument)

(there is also a AFM because of spins) In Mott insulators, the dominant inter-spin interaction typically arises from superexchange (relearn superexchange) , with an energy scale $J \sim -t^2/U$ (this is maybe a constant in the spin Hamiltonian) , favoring antiferromagnetic coupling.

(AFM superexchange combined with the triangular SOD lattice produces geometric frustration) For 1T-TaS₂, the triangular lattice of localized spins inherently provides the necessary geometric frustration (geometric frustration) .

(there is some degeneracy of spins) In such a lattice, antiferromagnetic interactions between nearest neighbors cannot be simultaneously satisfied (simultaneously satisfied?) , leading to a macroscopic degeneracy of classical spin configurations (macroscopic degeneracy of classical spin configurations???) .

(also, there is no long range order) In a quantum system, this massive degeneracy is lifted by quantum fluctuations (which formula is assumed by "lifted by quantum fluctuations"?) , potentially preventing conventional long-range magnetic order.

(there is a strange RVB state) Instead, spins may form a coherent superposition of entangled singlet pairs, a state famously envisioned by Anderson as a resonating valence bond (RVB) state [41]. (RVB state?? which formulas are assumed?)

(RVB state has some strange spinons) The elementary excitations of such a QSL are spinons - charge-neutral, spin-1/2 quasiparticles that result from the spin-charge separation of electrons.

(spinons can be different) These spinons can be gapped or form a gapless continuum, leading to distinct thermodynamic and spectroscopic signatures, as will be detailed below.

(interlayer effects are miserable) 2D system can effectively eliminate the interlayer coupling effect from various stacking orders that complicates the situation.

(q. fluctuations are big) Moreover, the quantum fluctuations become more pronounced in lower dimensions.

(Mott+fluctuations = QSL) When it is(it is a typo, it should be "they are") sufficiently strong to suppress the spin ordering, a QSL state can emerge in a Mott insulator.

(we pretend that here is a motivation for some research about CDW phase) Therefore, investigation on the CDW-Mott phase in the 2D system is crucial for understanding the rich quantum states in 1T-TaS₂.

(repetition of abstract) This review focuses on emergent quantum phenomena and related recent research in low-dimensional 1T-TaS₂.

(below is just structure of the paper)

The article is organized as follows: Section 2 introduces the basic electronic properties of 1T-TaS₂, the CDW order and its chiral character;

Section 3 discusses the mechanisms of the low temperature insulating phase: strong correlation driven(correlation driven?) Mott insulator or interlayer coupling induced band insulator (interlayer coupling induced band insulator?) ;

Section 4 provides an overview of recent advances in QSL behavior reported in monolayer 1T-TaS₂; finally, Section 5 concludes the review with a discussion of future experiments.

16.1.2 2 Electronic properties and CDW in 1T-TaS₂

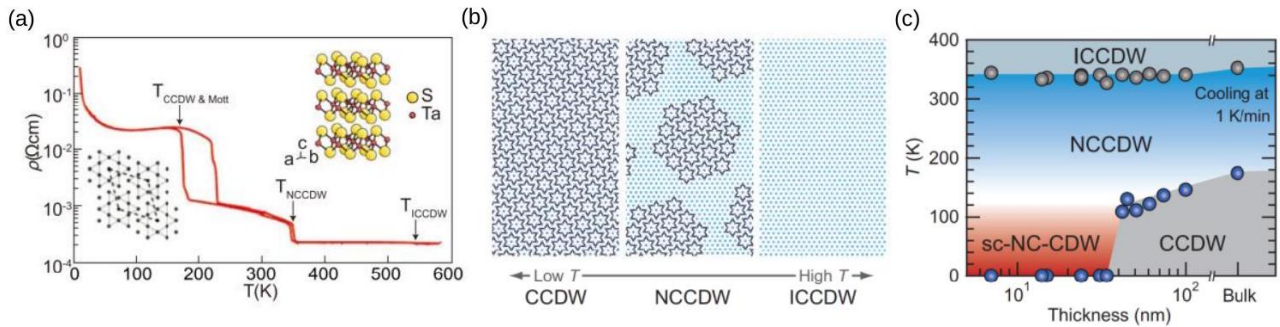


Figure 3 (a) Phase transitions of 1 T – TaS₂ with temperature measured by transport.

(b) Schematic pictures of a Ta atom network in the CCDW (left), hexagonal NCCDW (middle), and ICCDW (right) phases.

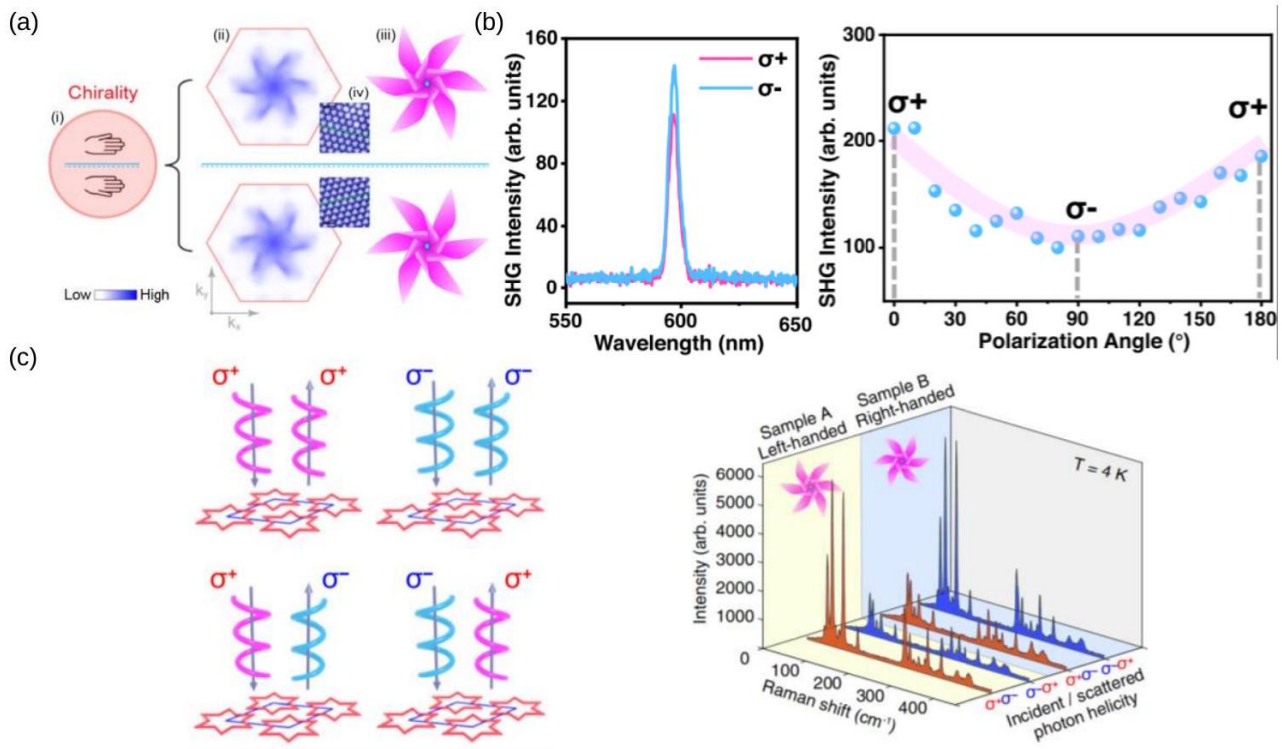
(c) Temperature-thickness phase diagram of 1T-TaS₂ nanoscale crystals. (Figures adapted from refs. [10, 42]) (cool phase diagram, how was it obtained??? I guess there are a lot of layers for each thickness)

(well-known phase transitions of TaS₂) Electrical transport measurements show that 1T-TaS₂ exhibits metallic behavior in the high temperatures and undergoes successive CDW transitions when decreasing temperature: from an incommensurate CDW (ICCDW) to a nearly commensurate CDW (NCCDW) phase at ~350 K, and further to a commensurate CDW (CCDW) phase at ~180 K, as shown in Fig. 3a [10, 31]. In the low temperature CCDW phase, the system becomes insulating.

(there is also a PLD) Within this phase, thirteen in-plane Ta atoms distorted into a Star of David (SOD) to form a ($\sqrt{13} \times \sqrt{13}$) superstructure with one unpaired electron localized on the center Ta atom [33, 42], where the Mott state(I guess, Mott state is about the gap in spectrum) is simultaneously developed.

The superlattice is rotated by 13.9° (is this angle always fixed?) relative to the underlying atomic lattice [32].

(there ia also a NCCDW phase) In the NCCDW phase, commensurate domains form into hexagonal clusters separated by discommensurate areas.



(I'll think later about it) Figure 4 (a) The hidden chiral order in 1 T – TaS₂, which is featured by the chiral CDW and windmill-shape band structure with broken mirror symmetry.

(b) SHG signals of 1T-TaS₂ samples and variation of SHG intensity as a function of the polarization angle.

(c) Schematic of polarization-resolved Raman response measurements and Raman spectra of samples with left- or right-handed domains showing different $\sigma^+\sigma^-/\sigma^-\sigma^+$ response. (Figures adapted from refs. [18, 25, 43])

(CDW PLD had chirality) The CDW superstructure is arranged in a triangular lattice, which breaks the in-plane mirror symmetry, giving rise to two energetically degenerate chiral configurations with opposite handedness (Fig. 4a) [18].

(we can see chirality with experiment) These two chiral structures can be distinguished using chirality dependent Raman response to left-handed (σ^+) and right-handed (σ^-) circularly polarized light (Fig. 4c). (why Raman response shows chirality?)

(we can see chirality with experiment by intensity) The key signature is the inequality of Raman intensities in crosscircular polarization configurations ($I_{\sigma^+\sigma^-} \neq I_{\sigma^-\sigma^+}$) [18, 43]. (so I think they mean fig. 4b)

(CDW structures are in plane, which can be seen by some photons) Specifically, the in-plane Eg (E signifies a two-dimensional irreducible representation (doubly degenerate mode), and subscript g denotes gerade (even) inversion symmetry) phonon modes exhibit distinct intensities under opposite polarizations, confirming the inplane chiral nature of the CDW structure [18]. (and how inplane chiral nature is confirmed?)

Additional evidence (I think it is not a "Additional evidence ", but just the Raman intensities themselves, which were introduced before) for chirality comes from second-harmonic generation

(SHG)(second-harmonic generation???) , a sensitive probe of inversion symmetry breaking.

(again about 4b) 1T-TaS₂ exhibits a clear difference in SHG intensity when excited with the $\sigma+$ versus $\sigma-$ circularly polarized light (Fig. 4b).

Furthermore, chiral electronic band structure, characterized by windmill-shaped Fermi surfaces is revealed by ARPES [18]. (connection of ARPES and chirality?)

(there might be also SC in CDW, which is what we know. The chirality is used in one of that theory of SC) The broken time-reversal symmetry and orbital order in chiral CDW may stabilize a chiral superconducting state, a scenario theoretically predicted in systems such as Kagome superconductors [44].

(there is a strange rotational order of a lattice) The observed planar CDW chirality in TaS₂ is shown to be linked to a ferro-rotational order defined by a structural axial-vector order parameter, where the two chiral domains correspond to globally clockwise and counterclockwise rotations of the SOD lattice [45].

(I guess it is possible to switch from one chirality to another somehow) Recent experiments have achieved non-volatile electrical switching between these ferro-rotational domains in nanometer-thick samples [46].

(this strange switching is because of not prespondence of extrental EM field. It is not clear what is meant here, but it is not an important part of a paper) This switching is remarkable because the ferro-rotational order parameter is invariant under both time reversal and spatial inversion, preventing direct coupling with an external electric field.

(name of this strange switching) It is achieved indirectly by the field-driven motion of domain walls [46].

(maybe this can be used somewhere in industry) This hysteretic and electrically controllable bistability of the chiral/rotational state demonstrates its potential for device applications such as non-volatile memory.

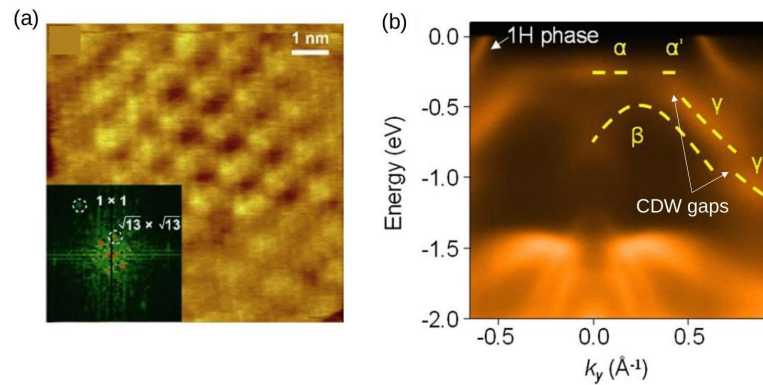
(even thought it wasn't dependent on fields, somehow it is dependent on some perturbations...) (so is it robust to EM field or no?) The CDW state in 1T- TaS₂ is highly sensitive to external perturbations.

(photons can induce excitations which destroy gap) It is shown the phase transition can be driven reversibly by electric fields or laser excitation, attributed to a carrier-induced collapse of the gap [47, 48].

(intro to hidden state) Optical pumping can also induce a hidden or metastable CDW state (H-CDW), and rapid thermal quenching of the sample enables reversible switching between the H-CDW and C-CDW phases [49-52].

(intro to domain walls) STM studies of quenched samples reveal the formation of nanoscale domain structures [53].

(DWs are metallic, CDWs are localized) Despite the metallic nature of the domain walls, the overall electrical behavior of the sample remains insulating - a phenomenon explained by carrier localization effects due to CDW stacking disorder(CDW stacking disorder?) [54].



(I'll think later about it) Figure 5 (a) Atomically resolved STM image of the 1 T – TaS₂. The inset is the fast Fourier transform result. (b) ARPES maps taken along $\bar{\Gamma}\bar{M}$ with 45 eV p polarized light at 10 K. CDW gaps are marked with arrows. (Figures adapted from refs. [22, 30])

(it is an unclear sentence, but it is written that CDW can be exactly in TaS₂) The CDW transition persists down to the 2D limit, as demonstrated by the observation of $\sqrt{13} \times \sqrt{13}$ superstructure in STM topographic images of monolayer 1T-TaS₂ (Fig. 5a) [22].

(spectrum is in fig. 5b) ARPES spectra of monolayer TaS₂ film show a flat band (labeled as α) centered around the $\bar{\Gamma}$ point (Fig. 5b) and the 1T system is insulating with a gap of 0.26 eV. (compare this plot with other ARPESes!!! X axes is different)

(typical band theory gives wrong prediction, so we need MH model) However, such a gap cannot be attributed to the formation of CDW because conventional band theory fails to account for it [30, 55] (read these papers! I want to learn how we can at least try to use the "conventional band theory"), pointing to the essential role of electron correlation effects (I guess it means that we need a MH model).

(CDW gaps are also there in a spectrum) The CDW-related gaps are observed in the deeper binding energies of 0.3 and 0.9 eV and separate the γ band from Ta 5d state into several pieces [30].

(!!! learn finally, what are the origins of gaps! review paper is not enough, I need to read derivation of this!)

(high T = no gap) These gaps are closing with increasing temperature (is there a formula for this by the way?).

(Tc depends also on the number of layers) CCDW phase in monolayer and few-layer 1T-TaS₂ grown via CVD or MBE are more robust, with a transition temperature (~ 230 -353 K) significantly higher than that of bulk [30, 56, 57]. (why does Tc depend also on the number of layers???)

(there is some correlation length also) The dimensionality-dependent CDW correlation length (dimensionality-dependent CDW correlation length??) has been determined to be approximately 7.8 nm [56, 58].

(intro to SC here) The intricate relationship between CDW and emergent superconductivity constitutes a central theme in 1T-TaS₂.

(obvious statement that if we have SC, then insulation is suppressed) While the pristine bulk material is insulating at low temperatures, superconductivity can be induced by perturbations that suppress the Mott-CCDW state and enhance metallic character. (double check that SC is between the CCDW islands and not inside them)

(SC is by pressure and doping and here are citations) Key pathways include applying hydrostatic pressure to broaden the bandwidth, chemical intercalation or ionic gating to inject

carriers, and exploiting chemical substitutions [10,57,59,60].

(SC excludes CDW sometimes) These methods typically lead to a superconducting dome (dome-shaped region in a phase diagram) appearing adjacent to the suppressed CCDW phase, suggesting a competitive relationship.

(SC sometimes does not exclude CDW sometimes) However, evidence of NCCDW phase coexists with superconductivity indicates a more complex, potentially intertwined interplay. (check again coexistence region of SC and CDW, does it exist?)

(SC is maybe between CDW regions) It has been proposed that superconductivity may nucleate specifically within the metallic interdomain spaces of the NCCDW phase [10], suggesting a real-space microscopic phase separation between insulating CCDW domains and superconducting regions.

(such phase separation is known) This scenario is further supported by the observed analogy to cuprate superconductors where electronic phase separation (e.g., stripes) is crucial [61]. (interesting, look at this paper 1 time)

(but another explanation is that there is a special Mott phase or special fluctuations that give SC) However, this model contrasts with scenarios where superconductivity arises from a self-doped Mott phase or is mediated by CDW fluctuations [62,63], as the superconductivity in 1 T – TaS₂ shows remarkable insensitivity to the collapse of the CDW state. (how is it, insensitivity to the collapse of the CDW state???)

(motivation: stabilize SC) Thus, 1T-TaS₂ serves as a pivotal platform for exploring the potential of nanoscale electronic phase separation as a pathway to stabilize superconductivity proximate to insulating orders.

16.1.3 3 A Mott insulator or a band insulator?

(SOD gives a free electron, so one can expect metallicity) The low-temperature insulating behavior of 1 T – TaS₂ is unexpected because of the formation of SOD in the CDW state and presence of one unpaired electron localized on the center Ta atom in $\sqrt{13} \times \sqrt{13}$ superstructure, which gives rise to a metallic band crosses the Fermi level.

(some neutron scattering also proposes metallicity) This picture is supported by neutron scattering that a magnetic moment of $\sim 0.4\mu_B$ per SD cluster is estimated [64] (learn this later, idk what is meant here) .

(but somehow correlations break metallicity) Mott insulator is the widely accepted explanation that strong electron correlations localize electrons and open a Coulomb gap.

(reminder: read how correlations give MH model!)

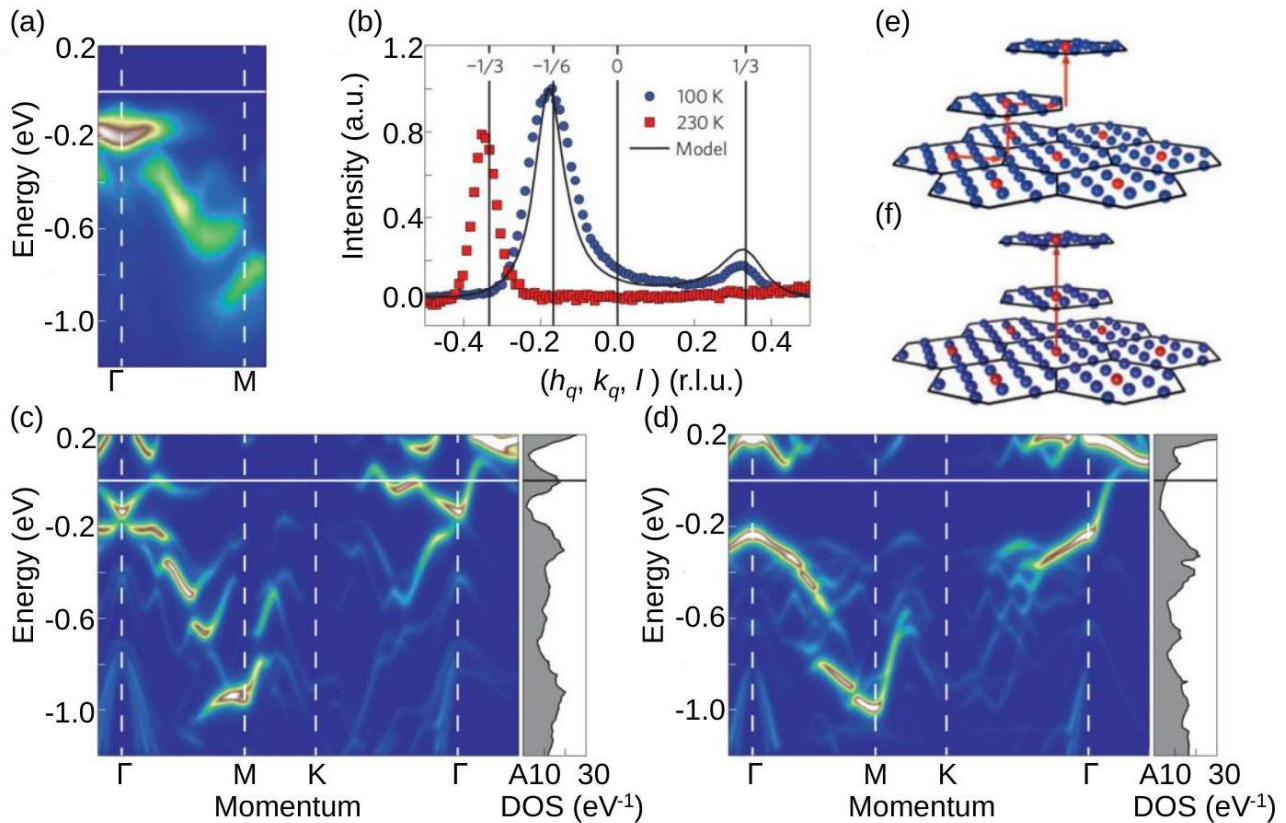
(correlations give bands) This effect splits the metallic band into upper and lower Hubbard bands, as illustrated in Fig. 6a.

(citation for confirmation of bands) Experimental evidences include two separated peaks around the Fermi level and an insulating gap of ~ 420 meV observed in STS spectra(STS spectra?) [65]. (maybe in this paper I can finally see the established band structure of TaS₂?)

(citation for another measurement of bands) ARPES measurements on bulk 1 T- TaS₂ show a "flat band" near the Fermi level, attributed to the lower Hubbard band [66-68]. (really??? I thought from Jung Kim that it is just a band and upper and lower bands are above and below it... think about this flat band)

(band is not precise, maybe because of multilayer structure) This band is dispersive in energy along the out-of-plane momentum, demonstrating the interlayer interaction (why inter-layer interaction?) tends to enhance the inter-site hopping and broaden the bandwidth of the Hubbard band [69].

(another citation for experiments on bands) The upper Hubbard band has been revealed using pump-probe techniques and inverse-photoemission spectroscopy [70, 71].



(I'll think later about it) Figure 7 (a) ARPES data of 1 T – TaS₂ measured at 1 K. (b) XRD intensity of 1T- TaS₂ measured along the l -direction. (c-d) Calculated band structure for $T_S = 2\mathbf{a} + \mathbf{c}$ and $T_S = 1\mathbf{c}$, respectively. a, c are the lattice vectors of the undistorted structure. (e-f) Visualization of the stacking with $T_S = 2\mathbf{a} + \mathbf{c}$ and $T_S = 1\mathbf{c}$, respectively. Red arrows indicate the stacking vectors that connect the central Ta-sites (shown in red) in successive layers. (Figures adapted from ref. [36])

(this story of HM insulator may be fully wrong, maybe just several layers are responsible for insulation) An alternative explanation for the insulating state involves interlayer coupling effects under different stacking configurations [36-40].

(there are some orbitals that can affect bands) As shown in Fig. 7, the relative orientation of the orbitals in adjacent ab -planes(=planes) has a significant effect on band dispersions [36]. (how can orbitals affect bands?)

(DFT confirms insulation in plane + metallicity out of plane) Density functional theory calculations predict a gap around the Γ point but the band structure remains metallic along out-of-plane momentum direction when the SOD central atoms in adjacent layers are aligned along the c -axis (A-stacking) (there is no c -axis in the plot, so the def. is that it is the out of plane direction) . (how do we know that metallicity is direction-dependent???)

(some calculations of gap are done for the other stacking) Further calculations reveal a full gap when a paired stacking shifts by half a unit cell every two layers (AL-stacking)(I am not sure that it is a well-established notation) [37, 69].

(people know all about the orbitals which give this gap) The formation of a gap is due to the interlayer hybridization mostly mediated by the $d_{3z^2-r^2}$ orbitals.

(again: many layers model excludes MH model) These calculations were performed without an on-site repulsion U on Ta, arguing against Mott physics as the origin of the gap.

(some experiments support direction-dependent gap, which is in scope of model layer interactions) Synchrotron-based X-ray diffraction (XRD) shows the half-integer-indexed(half-integer-indexed) diffraction peaks along the c axis in bulk 1T- TaS₂, providing evidence of dimerization(dimerization???) along this direction [68].

(some experiments for gap detection were done) STM studies on the bulk material surfaces have observed the dominant "large-gap" spectra (~ 0.4 - 0.45 eV), "small-gap" spectra (gap ~ 0.1 - 0.2 eV) and occasionally metallic spectra in certain regions [39, 72, 73]. (which images are assumed?)

(some not important features of STM:) Stacking order(=how the layers are aligned corresponding one another) was determined from the single-step areas between neighboring layers.

(but gap does not depend on layers configuration, so MH mechanism can be still working) It turns out different stacking orders exhibit similar large-gap spectra when the measurements are performed away from the step edge(step edge?) , suggesting the large insulating gap in the bulk is independent of stacking order and supports a correlation-induced Mott-Hubbard mechanism.

(several orders + defects (or disorder) = less gap) Note that the misaligned stacking near step edges may disturb the Mott state (it is written that CDW can be explained without MH model, so maybe it should be meant CDW state) to a small-gap or metallic state, likely due to the defects or disorder effects [72].

(Electron doping is also used to learn something useful) Electron doping has been used to study the different behaviors expected for band and Mott insulators [40] (I downloaded this paper, I'll look later) , based on their distinct responses due to the fundamental difference of the half- and full-filled orbitals involved (I don't understand the fundamental difference of the half- and full-filled orbitals, but maybe it is not an important phrase) .

(also systems with doped metals were analyzed) Alkali metal deposition on 1T-TaS₂ surfaces reveals that STS measurements on the paired bilayer surface shows a rigid shift (rigid shift to what???) expected for the doping of an ordinary band insulator.

In contrast, STS on the surfaces with half-filled Ta $5d_{3z^2-r^2}$ states shows suppression of the upper Hubbard band.

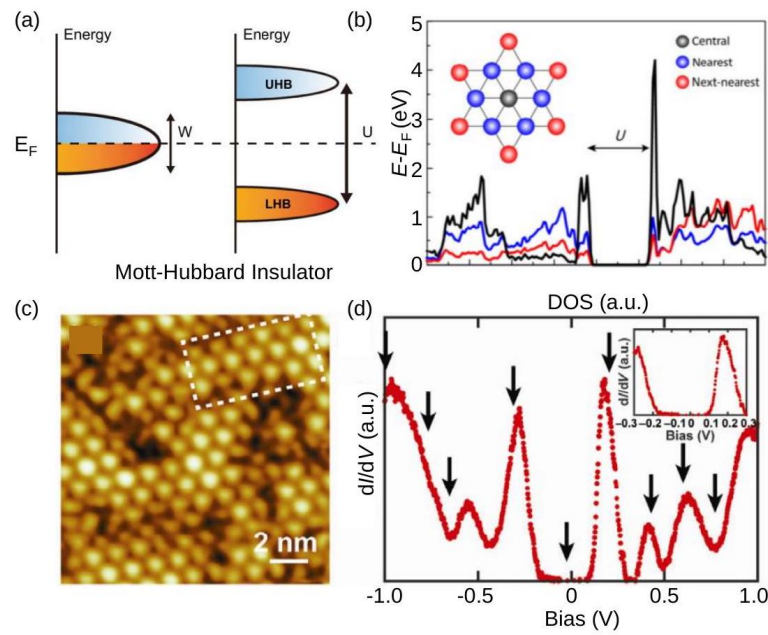
(now we'll discuss TaSe2) Similar stacking order effects have been revealed in isostructural compound 1T-TaSe₂ [74].

(in TaSe2, layers interact stronger) A key difference between 1T- TaSe₂ and 1T- TaS₂ is that stacking order in 1T- TaSe₂ induces more substantial perturbation.

(some experiments show gap, some show metallic properties) While 1T- TaSe₂ exhibit a large spectral gap on the surface, it shows metallic behavior in transport experiments at low temperatures [74-76].

(maybe regions between gap give enough impact to metallicity) This discrepancy may arise from connected metallic areas of electrodes in the transport measurements.

(there is a configuration of layers, which creates domain configuration, and here is the citation for measurement metallicity and insulation) Recent ARPES measurements with micro-size light spot directly show the metallic and insulating band structures coexist in different domains on the surface caused by the different stacking arrangement [77].



(I'll think later about it) Figure 6 (a) Schematic diagram of the Mott-Hubbard Insulator. (b) PDOS of the three types of nonequivalent Ta atoms in an SOD for monolayer 1T-TaS₂. (c) The topographic image of monolayer TaS₂ with randomly distributed defects. (d) The large range dI/dV spectrum obtained on the center of an SOD. (Figures adapted from refs. [10, 23])

(here is the idea that dimerization in bulk gives gap, but in the monolayer there is also a gap and there is no this dimerization) Although dimerization of 1 T – TaS₂ with specific stacking indicates a similar electron structure to a band insulator, it cannot explain why monolayer system - interlayer coupling and stacking order effects are absent - show a large-gap insulating state.

(again, MH might be the real explanation) The Mott physics thus provides the most natural explanation.

(citation for experiment on a monolayer.) STS spectra taken from MBE-grown monolayer 1T-TaS₂ reveal features similar to the large-gap spectra of bulk materials [23].

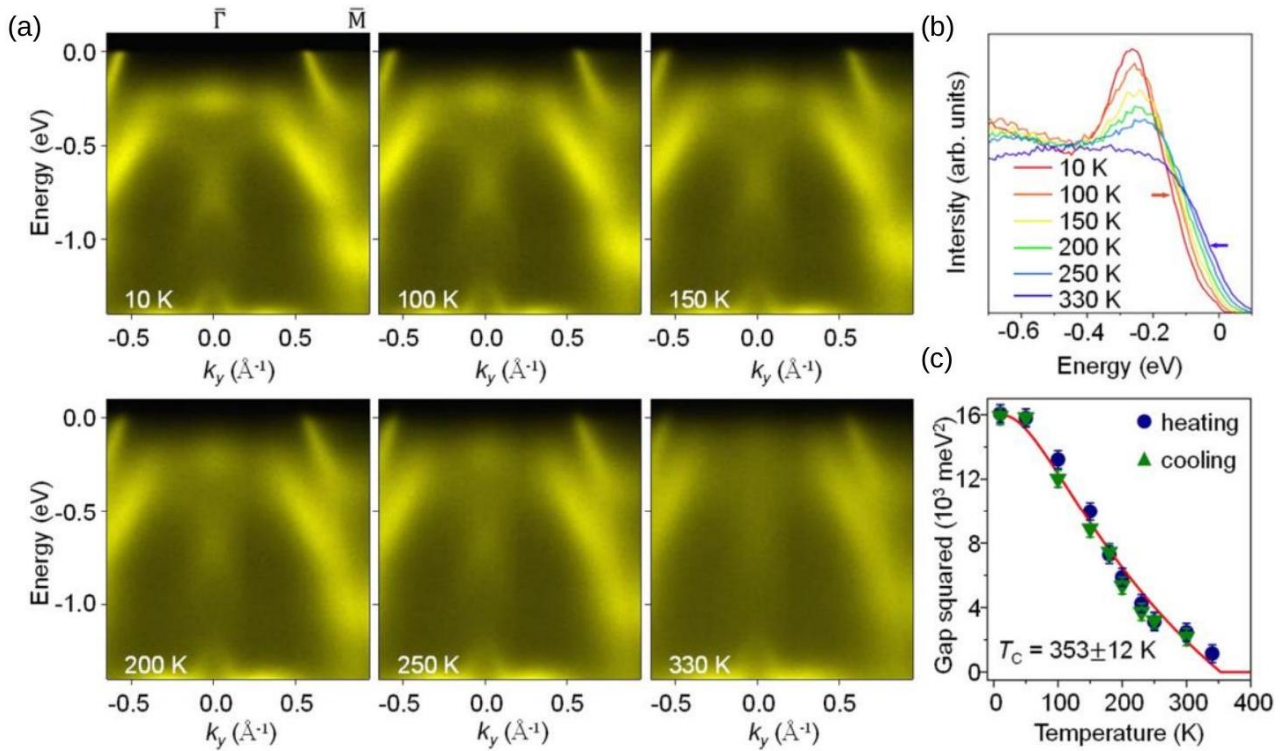
(so this is all, bulk has the same properties as monolayer, and the end of story with that model?)

(there gap was measured) Differential conductance spectra show a clear gap of 0.45 eV near the Fermi level, surrounded by sharp Hubbard peaks (Fig. 6d).

(there are calculations of energy and there are also peaks, and the central Ta atom gives the biggest contribution) These results agree well (it agrees only qualitatively) with the first-principles calculations (in which paper this was made?) that the Hubbard peaks are dominated by the density of states of the central Ta atoms (Fig. 6b).

(first principles calc uses Hubbard model) In these calculations, a Hubbard U is included to account for the Coulomb interaction of Ta 5d orbitals.

(there are also localized spins which can be seen from some exotic experiment) The existence of localized spins in SODs, consistent with the Mott picture, has been confirmed by the observation of Kondo resonance peaks (Kondo resonance peaks ??) around the Fermi level in monolayer 1T-TaS₂ on top of metallic 1H-TaS₂ [78].



(I'll think later about it) Figure 8 (a) Temperature dependence of ARPES spectra of the band structure and the energy gaps. (b) EDCs at the zone center at selected temperatures. (c) The extracted temperature dependence of the square of the energy gap. (Figures adapted from ref. [30])

(see ARPES results) As shown in Fig. 8a, ARPES spectra of monolayer 1T-TaS₂ display a flat band (lower Hubbard band) near the Fermi level and a spectroscopic gap of 0.26 eV (distance btw 0 and the middle of yellow horizontal line), determined from the energy difference between the lower Hubbard band and the Fermi level [30, 79]. (I don't see a band there, I see a lot of yellow region. yes, at low T there is something slightly looking like a band, but I don't understand this spectra)

(if we increase T, the yellow region will go up and close at T_c) Temperature-dependent ARPES measurements track the gradual closing of the Mott gap with increasing temperature, allowing extraction of a CDW-Mott transition temperature $T_C = 353 \pm 12$ K (Figs. 8b and 8c) [30].

(T_c in a layer is x2 of a bulk) It is approximately twice the value observed in bulk material (~ 180 K), demonstrating the robustness of the Mott phase in 2D 1T-TaS₂. (does it tell us that layers have a big influence??? can we derive the T_c??) (what about the substrate for 1 layer, does it influence? maybe it is from special neutral material...)

(hysteresis of gap is only in bulk) The temperature-dependent gap shows no obvious difference between the cooling and heating processes in monolayer samples indicates the hysteresis observed in the bulk [31, 32] likely originates from competing stacking orders in the 3D system. (how layers can lead to hysteresis?)

(MH is better) As a summary, while interlayer stacking effects can induce a gap in specific configurations, the correlation-driven Mott scenario provides a more comprehensive and natural explanation for the insulating behavior in 1 T – TaS₂, particularly in its monolayer limit.

(both MH and interlayer interaction give the gap in spectrum) The key experimental signatures expected for the two pictures exhibit systematic differences: the Mott gap arises

from on-site Coulomb repulsion, manifesting in spectroscopic data as separated Hubbard bands (a lower and an upper band) around the Fermi level.

(if we add layers and don't use Hubbard model, then we'll have a better description of a changes in the gap) However, the insulating gap in the stacking picture originates from inter-layer hybridization in specific stacking geometries, which modifies the band dispersion without necessarily generating distinct Hubbard band features (next sentence specify the Hubbard band features?) .

(MH model predicts redistribution of spectral weight with changes of layers and doping) A Mott insulator involves a half-filled orbital (a site in a lattice has several orbitals for electrons) (reminder, learn MH: why half-filled?) , leading to a non-rigid shift (not a shift, but a change) and significant spectral weight redistribution of its Hubbard bands upon doping (suddenly we also return to doping) (e.g., suppression of the upper Hubbard band) [40]. (learn, how exactly the plot changes look like?)

(stacking-induced assumes different filling of bands and gives another doping predictions) In contrast, a stacking-induced band insulator involves filled/empty bands, and its doping response resembles a more rigid shift of the entire band structure.

(it is not written here, which compares better with experiment?)

(and what we have physically, filled/empty bands or half field band structures?)

16.1.4 4 Quantum spin liquid behavior in monolayer 1T-TaS₂

(intro to QSL) QSLs represent a novel class of quantum matter characterized by highly entangled spins that fail to develop a long-range magnetic order (=they are strong correlated, not random, but with decaying correlations) even at 0 K [80]. (this is the world cited paper about QSL, all the questions here should be addressed there, so I'll not write them)

(there are strange fractionalized excitations) One of the most exotic phenomena predicted in QSLs is the emergence of fractionalized excitations leading to the separation of the spin and charge components of an electron.

(QSL are not understood yet) Despite intense study since the concept was introduced by P.W. Anderson in 1973 [41], the experimental identification of QSLs remains elusive, as no "smoking gun" evidence can provide definitive conclusion.

(if a system is described by MH model, we can add frustration/fluctuations can give in it QSL) Mott insulators offer a promising platform for realizing a QSL state when long-range spin order is suppressed, which can be realized through frustration and/or quantum fluctuations. (which model is assumed here? that quantum fluctuations gives the QSL)

(Frustration gives the system many nearly/equally favorable magnetic configurations, and quantum fluctuations prevent it from settling into one of them and establishing long-range magnetic order =) Frustration (Frustration means that, even in the global energy minimum, not all local interactions can simultaneously be in their individual minimum-energy configurations) creates a massively degenerate manifold of competing ground states, while quantum fluctuations act to destabilize any incipient order.

(intro: QSL in TaS₂?) 1 T – TaS₂ has been proposed as a gapless QSL candidate [81].

The SOD clusters formed at low temperatures are arranged in a triangular lattice, which exhibits strong geometric frustration. (here, antiferromagnetic interactions between the effective local moments associated with these clusters are geometrically frustrated because they cannot be simultaneously satisfied on a triangular lattice)

(why AFM? because $H_{\text{Hubbard}} \longrightarrow H_{\text{Heisenberg}} = J \sum_{\langle ij \rangle} \mathbf{S}_i \cdot \mathbf{S}_j$, where $J \simeq \frac{4t^2}{U} > 0$. it is also called superexchange)

(intro to the experiments that confirm that Mott's model is good for QSL) While the Mott mechanism behind its insulating ground state is still debated (since e.g. there is the interlayer interaction mechanism), subsequent experiments on 1T-TaS₂ suggested to be consistent with QSL scenario.

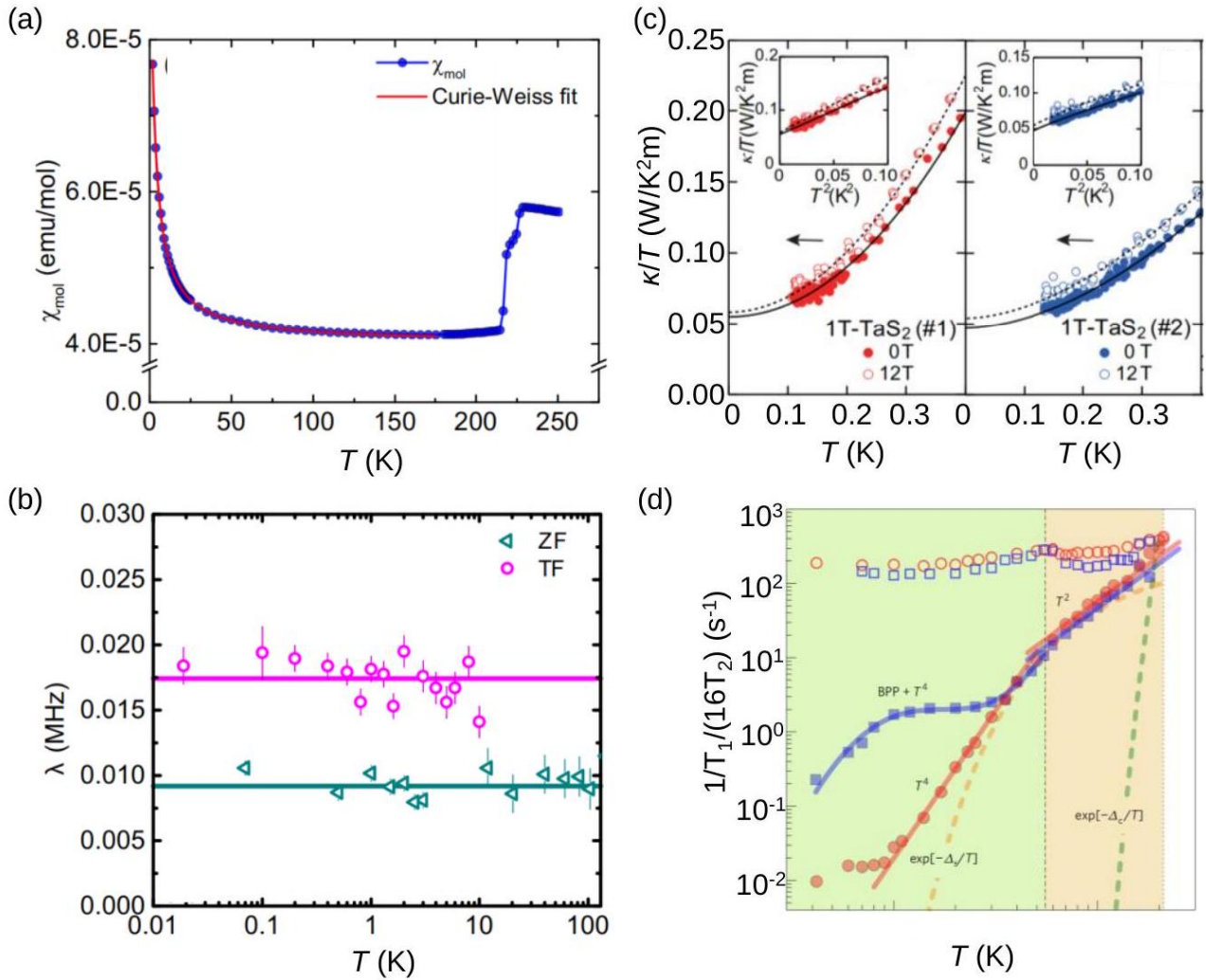
(magnetic susceptibility, muon spin relaxation shows that maybe there is a QSL) For instance, magnetic susceptibility of bulk 1T-TaS₂ shows a nearly temperature-independent Pauli paramagnetic susceptibility, and muon spin relaxation measurements reveal the absence of any signs of static magnetic order or spin freezing down to 20 mK, as shown in Figs. 9a and 9b [64, 82]. (learn these experiments, idk how they are done at all??)

(thermal conductivity and specific heat suggest QSL) Low-temperature specific heat measurements reveal a linear term γT and thermal conductivity exhibits the finite residual linear term in the zero-temperature limit (Fig. 9c), consistent with the presence of gapless spinons with a Fermi surface [83, 84] (but there are a lot of other factors for thermal conductivity and specific heat, why we can select spins for them?? maybe now there is a field?..) .

(experiments with nuclear physics suggest also QSL) Nuclear quadrupole resonance provides a local probe of electronic spin fluctuations via nuclear spin-lattice relaxation measurements (nuclear spin-lattice relaxation measurements??) in zero field, showing gapless QSL dynamics in 1T-TaS₂ (Fig. 9d) [85].

(but another experiment on heat thermal conductivity disproves QSL) However, some controversial results exist, including report of no discernible residual linear term of thermal conductivity at zero field [86].

(there are many other factors which gave non QSL behavior, if they were not there, the QSL should be, we promise) These discrepancies are attributed to differences in sample quality, such as varying degrees of disorder, defects, or stacking faults. (how exactly they can hinder - I guess nearly no one knows)



(I'll think later about it) Figure 9 (a) Magnetic molar susceptibility vs temperature, obtained from SQUID magnetization measurements at constant magnetic fields of 1 and 3 T. (b) Temperature dependence of the muon spin damping rate λ . (c) Temperature dependences of κ/T for 1T-TaS₂ in zero magnetic field and at $\mu_0 H = 12$ T applied along c axis. (d) The temperature dependences of the Ta spin-lattice relaxation rate $1/T_1$ and of the Ta spin-spin relaxation rate $1/T_2$ for the Ta α and β sites. (Figures adapted from refs. [83-85])

(another intro, but now for monolayer TaS₂) High quality monolayer TaS₂, free from the interlayer stacking issue, is ideal for studying the potential QSL behavior.

(monolayers remove one of the biggest complications of the bulk material: interlayer coupling and stacking, this is why we are interested in their studies)

(again about q. fluctuations) Furthermore, enhanced quantum fluctuation as reduced dimensionality can help stabilize such a state. (since fluctuations give the QSL)

(there are problems with experimental detection) However, experimental verification remains a major challenge because traditional bulk-sensitive techniques such as neutron scattering, specific heat measurements, and nuclear magnetic resonance have difficulties when applied to ultra-thin samples due to insufficient signal strength, and dominant substrate interference.

(we need better experimental methods) The development of surface sensitive and local-probe approaches is therefore essential for uncovering signatures of QSLs in 2D materials.

(again about spinons) In a QSL, electrons fractionalize into spinons and chargons with independent of the spin and charge components, respectively.

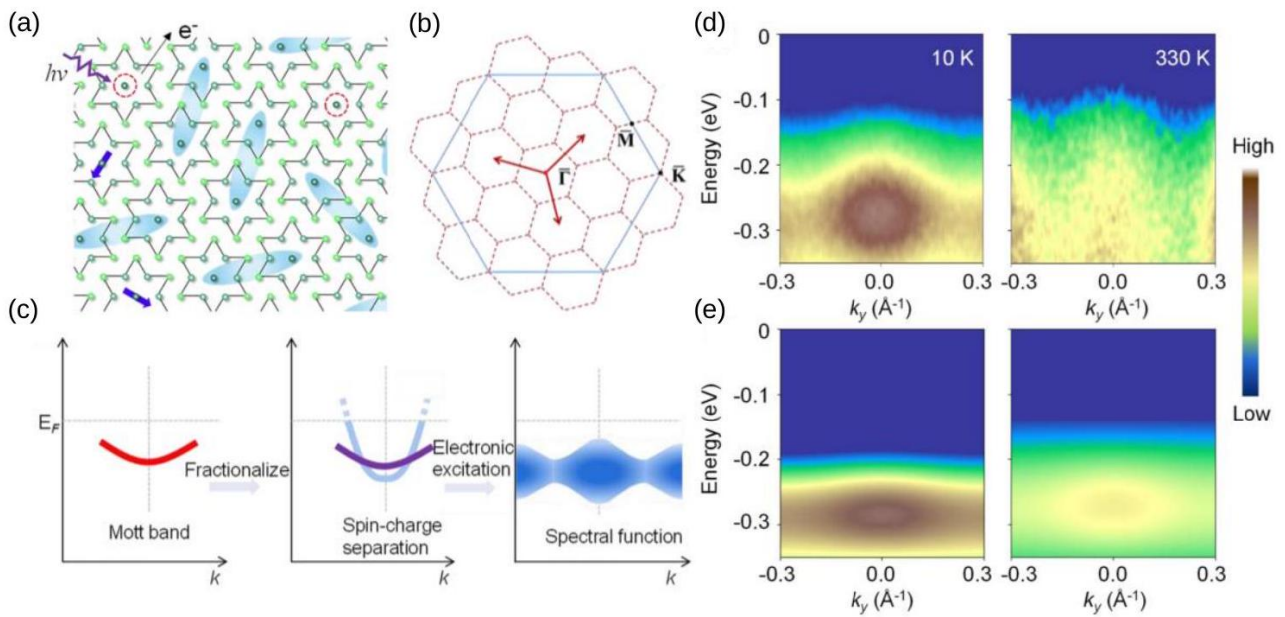
(now there are spinon hole, anyway, some advanced theory is assumed, read original papers to understand it.) When an electron is removed from a QSL, the resulting hole state separates into a spinon hole and a holon (this is the announced spin-charge separation) .

(somehow it is possible to predict spectrum for measurements) Within a mean-field approximation, the convolution of their dispersions ($A_e(\mathbf{k}, \omega) \sim \sum_{\mathbf{q}} A_s(\mathbf{q}, \omega') A_h(\mathbf{k} - \mathbf{q}, \omega - \omega')$) (no, I did not understand this convolution, think later about it) can be expressed as the electronic spectral function, resulting in a characteristic composite spectrum that should be readily probed by ARPES (Figs. 10a and 10c) [87]. (see cited paper for derivation of spectra, interesting)

(same as for ARPES, but for STM) A similar process occurs in STM measurement, where the tunneling rate of an electron at a particular energy can be expressed as a convolution of spinons and chargons.

(one clever experiment measured monolayer modulation of spins and confirmed QSL in TaSe2. Note that not for TaS2!) An STM study on monolayer 1T-TaSe₂ revealed long-wavelength super-modulations at the energies of lower and upper Hubbard bands [88], consistent with the predictions of spinon density modulation arising from a spinon Fermi surface instability [81, 89].

(also it was confirmed that there is a QSL in NbSe2) Similar STM results have been reported for monolayer 1T-NbSe₂ [90].



(I'll think later about it) Figure 10 (a) A schematic diagram of excitations in the QSL state. (b) Brillouin zones of the (1 x 1) and ($\sqrt{13} \times \sqrt{13}$) structures are outlined in blue and red, respectively. (c) Schematic of the electron fractionalization process and spectral dispersion after convolution in monolayer 1T-TaS₂. (d) ARPES spectra taken along the $\Gamma\bar{M}$ direction at 10 and 330 K. (e) Spectral function simulation results based on a low energy effective model at 10 and 330 K. (Figures adapted from ref. [30]) (what are these (e) and (d) plots?????)

(intro to confirmation of QSL in TaS2) Recently, an ARPES study provided spectroscopic evidence supporting a QSL state in monolayer 1T-TaS₂ grown by MBE method [30].

(so where is the QSL on a phase diagram???)

(we see an insulator behavior (gap)) At low temperatures, the observations of a flat band below the Fermi level and a gap (gap between E_F and this flat band) opening of about 200 meV demonstrate 2D Mott insulating nature in the system.

This flat band exhibits several "unusual" features: it is nearly dispersionless with an extremely narrow width (~ 10 meV) (the line itself is nearly horizontal), yet shows anomalous broadening in momentum space (that black vertical dispersion), and the spectral weight decays rapidly with increasing momentum (the black area in ARPES stops soon).

(some easier theory is not working (which theory - was not clarified)) In contrast, conventional band theory predicts a single and continuous band around the Fermi level. (learn later how to predict it with some easier theory even though it is a wrong prediction!)

(we need to modify typical theory with fractionalization) This observation is interpreted as a spectral continuum arising from electron fractionalization. (I don't understand what exactly is meant here, GPT does not give a good formula, I'll think later)

(somehow we can calculate spectral function and get as what is measured) Spectral function simulation results based on a low-energy effective model agree well with the ARPES spectra (Figs. 10d and 10e) ($I(k, E - E_F) \propto |M(k)|^2 f(E - E_F) A(k, E - E_F)$ is meant there. I think, that the difference with Rossnagel's paper is that here we have a monolayer, there we had a bulk. Also, there are different axes on X. I need to read more about plot on fig. 10 to understand it).

(some experiments on spinons are hard) Directly probing the spinon Fermi surface (idk what is in formulas the spinon Fermi surface, but it is a general big question about what this model is) is challenging due to its charge-neutral character.

(some Kondo effect measurements tell us something) As illustrated in Fig. 11, the Kondo effect involving spinons can give rise to new peaks near the edges of Hubbard bands [90, 91] (I don't understand these peaks and the idea of experiment).

(details of experiment) Such resonance peaks have been observed via STS in monolayer 1T-TaSe₂ and 1T-NbSe₂ by depositing magnetic atoms on the surfaces [91].

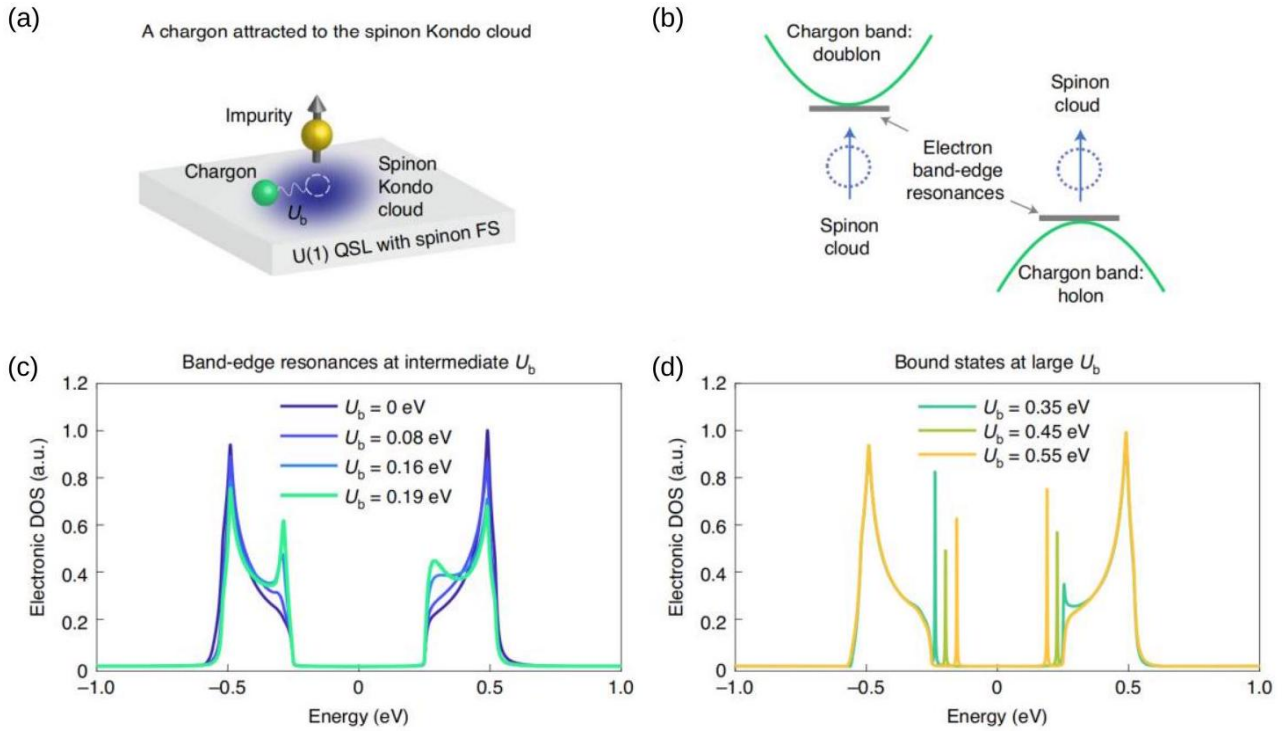
(here is a short version of a very complicated theory which explains peaks. some coupling to impurities gives peaks...) When itinerant spinons couple to the magnetic impurities, the formation of a spinon Kondo cloud can induce detectable resonance peaks through emergent gauge-field fluctuations.

(other coupling gives change of a gap) Furthermore, the coupling between spin impurities-spinons and the chargons will lead to a charge redistribution and influence the Mott gap.

(TaS₂+ magn impurities = less intensity in the band, more above) With doping magnetic impurities (Fe or Co) on the monolayer 1T-TaS₂ surface, ARPES measurements show the reduced intensity of the flat band and some spectral intensity filling up the Mott gap around the lower Hubbard band edge.

(TaS₂+ non magn impurities = shift of E_F (I guess this is meant here)) In contrast, non-magnetic impurity (Na or K) doping primarily induces a rigid chemical potential shift [30] (learn about chemical potential shift!!!) (I am not sure that this is a good explanation, I looked at that article, it does not have much formulas, okay, I'll try to understand it later).

(just another citation, now for monolayer) Similar doping effects have been observed by ARPES in other monolayer 1T-MX₂ (M = Ta, Nb; X = Se, S) [55].



(I'll think later about it) Figure 11 (a) Sketch of chargin binds to the spinon Kondo cloud. (b) Schematic diagram of formation of spinon-chargon band-edge resonance states. (c) With increasing binding interaction U_b , resonance peaks emerge at the Hubbard band edges. (d) With larger U_b , the spinon-chargon resonance states move inside the Mott gap and exhibit narrow peaks. (Figures adapted from ref. [91]) (what is the model here??? sounds like a complicated model)

(confirmation that there is no static magnetic order is the most important) Among these experimental observations discussed, the absence of static magnetic order down to 20 mK (as established by μ SR) serves as a robust prerequisite, which confirms that the system remains in a dynamic, highly entangled state far below its interaction energy scale, ruling out conventional magnetic ground states.

(there are other signatures of QSL) Highly suggestive, yet more model-dependent, signatures come from bulk thermodynamic and transport measurements.

(again about monolayers, it is important for SQL. That ARPES, STM...) The most intriguing and direct spectroscopic evidence for fractionalization emerges from monolayer studies, particularly the ARPES observation of an anomalous spectral continuum and STM signatures of spinon density modulations, representing a newer frontier whose interpretation within specific QSL frameworks would benefit from further theoretical consolidation.

16.1.5 5 Conclusion and outlook

(there are a lot of effects) Recent studies on bulk and monolayer 1T-TaS₂ have revealed a rich landscape of quantum phenomena, arising from the complex interplay of CDW order and Mottness in the ground state.

(QSL is maybe experimentally confirmed) The proposed QSL state in the Mott phase (Mott ph = when the resistance is high, it is not the CDW by default) of monolayer 1T-TaS₂ is supported by converging experimental evidences, including spectroscopic signatures of electron fractionalization observed via ARPES, local electronic structure studies through STM/STS,

and distinctive responses to magnetic impurity doping. (It is a big work to understand how exactly each method explains QSL in Mott state)

(maybe we can work out other models) These studies open up new avenues for investigating QSL physics from the perspective of electronic degrees of freedom.

(monolayer TaS₂ has some complicated physics) While the study of monolayer 1T-TaS₂ eliminates the variable of interlayer stacking order, it introduces other extrinsic factors whose potential influence warrants careful consideration. (factors are discussed in my discussion section and also below, one by one)

(different disorders are important) Disorder - arising from point defects, sulfur vacancies, or domain boundaries inherent to the growth and transfer processes - can locally perturb the electronic structure.

(disorder somehow creates states inside the gap) In a Mott insulator, disorder can create in-gap states, leading to a spurious "filling" of the spectroscopic gap in STS measurements.

(citation for influence of strain) Strain can collapse the Mott gap and drive an insulator-metal transition in 1T-TaS₂ [92].

(substrate coupling is also important, somehow it influences charges) Another significant factor is the substrate coupling. Even van der Waals substrates can induce charge transfer, modify dielectric screening, and impose symmetry-breaking potentials. (it is not clear what is meant here and it is not important)

(citation for slight influence of substrate) As an example, increased screening strength in HOPG substrate (Highly Oriented Pyrolytic Graphite substrate. It is basically a very high-quality piece of graphite whose graphene layers are strongly aligned with one another) slightly reduces the gap in monolayer 1T-TaSe₂ [88].

(some extra strange charge modulation can be because of substrate) However, an additional 2×2 super-modulation (with respect to the CDW lattice) has been revealed with HOPG substrate, which is attributed to the higher harmonics of the Spinon Fermi surface instability wavevectors [93].

(there are a lot of phases) The rich phase diagram and tunability of 1T-TaS₂ present a vast landscape for future exploration.

(list of possible topics to think about) Building on the recent demonstration of ferro-rotational domain switching by electric field (some strange experiment was done, I don't know anything about it) [46], future work can explore the role of disorder in switching fidelity, and gating experiments in monolayer devices to continuously tune the Mott gap and probe the quantum critical point.

(maybe you can make memory devices) The electrically-driven switching between insulating and metallic states can be exploited for ultra-low-power non-volatile memory.

(Time-resolved studies can give good insights) Time-resolved studies can disentangle the intertwined degrees of freedom based on distinct characteristic timescales for electron-phonon interactions and electron-electron correlations [94]. (I'll read it later, looks like a cool paper)

(ultrafast pump-probe method should give us something good) Therefore, ultrafast pump-probe method is intriguing to reveal the relationship between Mott phase and CDW orders in 1T-TaS₂ and track the non-equilibrium dynamics.

(what is meant by "relationship between Mott phase and CDW orders"?????)

(we can create heterostructures) Another promising direction has emerged with the development of van der Waals heterostructures based on 1T-TaS₂.

(some heavy-fermion system is shown in the heterostructures) The artificial stacking of 1H/1T-TaS₂ bilayer heterostructure has successfully demonstrated the realization of a heavy-

fermion system in two dimensions [78].

This is achieved by engineering the Kondo coupling between the lattice of localized magnetic moments in the Mott-insulating 1T layer and the itinerant(=traveling from place to place) electron sea in the metallic 1H layer.

(maybe we can create unconventional SCs) Given that strongly correlated systems such as Mott insulators and heavy-fermion compounds are fertile ground for unconventional superconductivity (why Mott insulators and heavy-fermion compounds can give U_c SC?) , the tunable nature of 1T – TaS₂ – based heterostructures provides a promising platform for engineering such superconducting states through controlled dimensional tuning and proximity effects.

(ARPES can give some valuable results) Nano- or micro-focused ARPES is ideally suited for detecting the local CDW domains and link the local structure to the electronic structure.

(comment about ARPES) By focusing the photon beam to a sub-micron spot, this technique can selectively probe electronic bands from individual domains or at domain walls.

(ARPES can check spectra between domains) This would provide a direct, momentum-resolved answer to whether the proposed metallic interdomain regions in the NCCDW phase host a distinct electronic signature that differs from the insulating domains. (but why wasn't it yet done?)

(ARPES can show us something about interlayer coupling) Furthermore, it could map the electronic structure across intentionally engineered heterointerfaces (e.g., 1T/1H stacking regions), revealing the momentum-space footprint of proximity effects and interlayer coupling.

16.2 Discussion

16.2.1 My Conclusion and Summary of the Articles

Conclusion

This article lacks also a polaronic description, so a lot of things are missing there (??? which???? I don't know polarons that well yet to answer it).

All the theories are not well-explained, and the main comparison of band interaction and HM model is very unclear.

What are the open problems which authors propose to research?

What is the true origin of the insulating state?

A long-standing question in 1T-TaS₂ is whether its low-temperature insulating state originates primarily from strong electronic correlations, as in a Mott insulator, or from interlayer stacking and dimerization that can produce a band-insulating state. Recent monolayer experiments have significantly clarified this issue. Since interlayer coupling and stacking are absent in a monolayer, the observation of a large insulating gap together with Hubbard-like spectral features strongly supports a correlation-driven Mott picture. The authors therefore conclude that Mott physics provides the most comprehensive and natural explanation of the insulating state, particularly in the two-dimensional limit, while stacking remains an important additional degree of freedom that strongly modifies the electronic structure of bulk 1T-TaS₂.

Is the ground state really a quantum spin liquid?

One of the central unresolved questions is whether the low-temperature state of 1T-TaS₂ is genuinely a quantum spin liquid. Several observations are consistent with this interpretation:

static magnetic order is absent down to approximately 20 mK, bulk thermodynamic and transport measurements show signatures compatible with gapless spin excitations, and monolayer ARPES and STM experiments reveal unusual spectral continua and modulations that have been interpreted in terms of electron fractionalization and spinons. However, the authors emphasize that there is still no definitive “smoking-gun” demonstration of a QSL. In particular, the interpretation of the ARPES and STM spectra remains model dependent. An important theoretical task is therefore to develop more quantitative QSL models that reproduce the observed spectral functions and distinguish fractionalization from alternative explanations.

How can spinons be detected more directly?

A major experimental difficulty is that spinons are electrically neutral and therefore cannot be observed directly in the same way as ordinary electronic quasiparticles. The authors highlight the Kondo effect as a possible indirect probe of spinons. If magnetic impurities such as Fe or Co are deposited on a monolayer 1T-TaS₂ surface, itinerant spinons may couple to the impurity moments and form a spinon Kondo cloud. The coupling of this state to the charge sector can produce detectable resonance features near the Hubbard-band edges in STM/STS or modify the ARPES spectral weight. Related resonance effects have already been reported in monolayer 1T-TaSe₂ and 1T-NbSe₂. A natural next step is therefore to perform controlled magnetic-impurity experiments in 1T-TaS₂ and test quantitatively whether the observed impurity response agrees with predictions for a spinon Fermi surface.

How can intrinsic two-dimensional physics be separated from disorder, strain, and substrate effects?

Although the monolayer geometry removes the complications associated with interlayer stacking, it introduces a different set of extrinsic effects. Point defects, sulfur vacancies, domain boundaries, strain, charge transfer from the substrate, dielectric screening, and substrate-induced symmetry breaking can all modify the electronic structure. Disorder can generate in-gap states and artificially fill the Mott gap in STS spectra, while sufficiently strong strain may collapse the gap altogether and induce an insulator-to-metal transition. Substrate screening can also modify the magnitude of the correlation gap. A major experimental challenge is therefore to produce cleaner and more controlled monolayer samples and systematically determine which observed Mott and QSL signatures are intrinsic to 1T-TaS₂ and which depend on the environment.

What is the microscopic relationship between the CDW and the Mott state?

The charge-density-wave order and Mott localization are strongly intertwined in 1T-TaS₂, but their causal relationship is still not completely understood. In equilibrium experiments they are difficult to separate because the structural distortion, electron-phonon coupling, and electron-electron correlations evolve together. The authors therefore identify ultrafast time-resolved experiments as a particularly promising direction. Electron-phonon and electron-electron processes occur on different characteristic timescales, so pump-probe measurements may allow the electronic and lattice degrees of freedom to be disentangled dynamically. Such experiments could determine whether the correlation gap collapses before the CDW lattice distortion disappears, or vice versa, thereby providing a more microscopic understanding of how Mottness and CDW order stabilize one another.

What happens electronically at CDW domain walls, and how is superconductivity generated?

Another major unresolved problem concerns the metallic regions separating commensurate CDW domains in the nearly commensurate phase. One proposed scenario is that superconductivity nucleates in these interdomain regions while the commensurate domains remain insulating. This would imply a microscopic real-space coexistence or phase separation between insulating CDW regions and superconducting metallic regions. However, competing explanations exist, including superconductivity emerging from a self-doped Mott state or from CDW fluctuations. The authors suggest nano- or micro-focused ARPES as a direct way to address this problem. By measuring the momentum-resolved electronic structure separately inside a CDW domain and at a domain wall, one could determine whether the proposed metallic interdomain regions really possess a distinct electronic structure and whether they provide the electronic states from which superconductivity develops.

Can the Mott transition and quantum criticality be controlled electrically?

The strong tunability of 1T-TaS₂ offers the possibility of continuously controlling its correlated electronic states. In particular, the authors propose gating experiments on monolayer devices to tune the Mott gap and potentially drive the system through an insulator-to-metal transition. Such experiments could provide access to a quantum critical point separating different electronic phases and reveal how the spectral weight, Hubbard bands, and CDW order evolve as the transition is approached. Electrically driven switching between insulating and metallic states is also technologically interesting because it could be exploited in low-power non-volatile memory devices.

What new states can be engineered in 1T-TaS₂ heterostructures?

A rapidly developing direction is the construction of van der Waals heterostructures containing different TaS₂ phases. Artificial 1H/1T-TaS₂ bilayers have already demonstrated two-dimensional heavy-fermion behavior, where localized magnetic moments in the Mott-insulating 1T layer interact through Kondo coupling with itinerant electrons in the metallic 1H layer. This establishes 1T-TaS₂ as a platform in which correlated states can be deliberately engineered through stacking and proximity effects. Since both Mott insulators and heavy-fermion systems are closely associated with unconventional superconductivity, an important future direction is to search for and control superconducting phases in such heterostructures by tuning dimensionality, interlayer coupling, carrier density, and proximity effects.

Overall direction of the field

The broader message of the recent work is that 1T-TaS₂ is no longer viewed simply as a peculiar bulk CDW insulator whose insulating mechanism has to be identified. The focus is shifting toward using it as a controllable two-dimensional platform for strongly correlated quantum matter. The major goals are now to establish whether genuine electron fractionalization and a quantum spin liquid exist in the monolayer, to understand quantitatively how Motttness, CDW order, domain structure, and superconductivity are connected, and to control transitions between insulating, metallic, superconducting, and heavy-fermion states using gating, optical excitation, impurity engineering, and heterostructure design. In this sense, the field is moving from identifying the individual phenomena toward understanding and ultimately controlling the microscopic relationships between them.

Can I say that there are four different theoretical descriptions in the article: DFT, the interlayer interaction model, the Mott–Hubbard model, and the QSL model, and that they predict different electronic spectra?

(GPT:) Yes, approximately, but it is important to distinguish between a theoretical model, a computational method, and a physical state. DFT, the interlayer interaction model, the Mott–Hubbard model, and the QSL description can all make predictions about the electronic spectrum, but they are not four models at exactly the same conceptual level.

DFT.

Density functional theory (DFT) is not a method for solving the Mott–Hubbard model. Standard DFT starts from the interacting electronic system in the potential of the nuclei and maps it onto an effective Kohn–Sham single-particle problem,

$$\left[-\frac{\hbar^2 \nabla^2}{2m} + V_{\text{ext}}(\mathbf{r}) + V_{\text{H}}(\mathbf{r}) + V_{\text{xc}}(\mathbf{r}) \right] \psi_{n\mathbf{k}} = \epsilon_{n\mathbf{k}} \psi_{n\mathbf{k}}. \quad (16.1)$$

The resulting eigenvalues $\epsilon_{n\mathbf{k}}$ give the Kohn–Sham band structure. Thus, DFT provides an effective single-particle description of the electronic bands. In the conventional band-theory description of the CDW state of 1T-TaS₂, a narrow SOD-derived band can remain partially filled and cross the Fermi level, giving a metallic prediction. Standard DFT therefore does not automatically produce the Mott splitting of this band into lower and upper Hubbard bands.

Mott–Hubbard model.

The Mott–Hubbard description starts from a different Hamiltonian in which electron hopping competes explicitly with the energy cost of double occupation,

$$H_{\text{Hub}} = - \sum_{i,j,\sigma} t_{ij} c_{i\sigma}^\dagger c_{j\sigma} + U \sum_i n_{i\uparrow} n_{i\downarrow}. \quad (16.2)$$

The hopping amplitudes t_{ij} favor electron delocalization, whereas the interaction U suppresses double occupation. For a sufficiently narrow, approximately half-filled SOD-derived band, strong correlations can produce lower and upper Hubbard spectral features separated by a Mott gap,

$$\text{half-filled band} \rightarrow \text{LHB} + \text{Mott gap} + \text{UHB}. \quad (16.3)$$

Therefore, the Mott–Hubbard description can predict a qualitatively different spectral function from a conventional single-particle DFT calculation.

Relation between DFT and the Mott–Hubbard model.

Although DFT and the Hubbard model are different theoretical descriptions, they can be combined. For example, DFT can first be used to determine the relevant low-energy orbitals and their hopping parameters,

$$\text{DFT} \rightarrow \text{low-energy orbitals} \rightarrow t_{ij}. \quad (16.4)$$

These parameters can then be used to construct an effective Hubbard model by adding the interaction U ,

$$H_{\text{effective}} = H_{\text{TB}} + U \sum_i n_{i\uparrow} n_{i\downarrow}. \quad (16.5)$$

The resulting interacting problem can then be treated using methods such as DMFT. Therefore, DFT is not a solution of the Hubbard model, although DFT calculations can be used as an input for constructing a Hubbard-type description.

Interlayer interaction and stacking model.

The interlayer picture provides another possible mechanism for the insulating state, particularly in bulk and multilayer $1T$ -TaS₂. In this description, SOD-derived states belonging to neighboring layers hybridize through an interlayer hopping amplitude $t_{\perp}$. A minimal two-layer Hamiltonian can be written as

$$H_{\text{inter}} = \begin{pmatrix} \epsilon_{\mathbf{k}} & t_{\perp} \\ t_{\perp}^* & \epsilon_{\mathbf{k}} \end{pmatrix}. \quad (16.6)$$

The corresponding eigenenergies are

$$E_{\pm}(\mathbf{k}) = \epsilon_{\mathbf{k}} \pm |t_{\perp}|. \quad (16.7)$$

Thus, interlayer hybridization produces bonding and antibonding states with a splitting

$$\Delta E = 2|t_{\perp}|. \quad (16.8)$$

For appropriate stacking and filling, this mechanism can produce an insulating band structure without requiring a Mott gap. Different stacking configurations modify $t_{\perp}$ and can therefore produce different electronic spectra.

QSL description.

A quantum spin liquid is somewhat different conceptually. A QSL is a possible many-body quantum state rather than a unique Hamiltonian. Therefore, saying only that the system is a QSL is not sufficient to calculate a unique electronic spectrum. A particular microscopic or mean-field QSL model must first be specified. In a fractionalized description, for example, the electron operator can be decomposed schematically into a spinon and a chargon,

$$c_{i\sigma} = f_{i\sigma} b_i. \quad (16.9)$$

The spinon and chargon can then have their own dispersions,

$$\epsilon_s(\mathbf{k}) \quad (16.10)$$

and

$$\epsilon_c(\mathbf{k}). \quad (16.11)$$

Because ARPES removes a physical electron rather than an isolated spinon or chargon, the electronic spectral function contains combinations of the two excitations. Schematically,

$$A_e(\mathbf{k}, \omega) \propto \sum_{\mathbf{q}} \delta[\omega - \epsilon_s(\mathbf{q}) - \epsilon_c(\mathbf{k} - \mathbf{q})]. \quad (16.12)$$

For a fixed electron momentum $\mathbf{k}$, many different values of $\mathbf{q}$ are possible. Consequently, instead of obtaining only a sharp electronic band $E(\mathbf{k})$, the model can produce a broad continuum of electronic spectral weight in $A(\mathbf{k}, \omega)$. This is the type of QSL-related spectral prediction that can be compared with ARPES.

Relation between the Mott and QSL descriptions.

The QSL description should not normally be regarded as an alternative to Mott physics in the same sense as the interlayer mechanism. Instead, a QSL can emerge within a correlated Mott-insulating system. In the strong-coupling limit of a half-filled Hubbard model, charge

motion is suppressed and approximately one localized spin remains on each effective site. The low-energy spin physics can then be described approximately by a Heisenberg model,

$$H_{\text{spin}} = J \sum_{\langle i,j \rangle} \mathbf{S}_i \cdot \mathbf{S}_j, \quad (16.13)$$

with antiferromagnetic superexchange

$$J = \frac{4t^2}{U}. \quad (16.14)$$

For the triangular lattice of SOD clusters, these antiferromagnetic interactions are geometrically frustrated. If frustration and quantum fluctuations suppress conventional long-range magnetic order, a QSL state can potentially emerge. The conceptual sequence is therefore

Hubbard model $\rightarrow$ Mott localization $\rightarrow$ localized spins $\rightarrow$ frustrated spin system $\rightarrow$ possible QSL. (16.15)

A particular QSL model can then make additional predictions for the excitation spectrum and the electronic spectral function, including fractionalized spinon–chargon continua.

Summary.

It is therefore reasonable to identify four different theoretical descriptions discussed in the article, each of which is associated with different expectations for the spectrum:

$$\text{DFT} \rightarrow \text{single-particle Kohn-Sham bands}, \quad (16.16)$$

$$\text{interlayer interaction} \rightarrow \text{stacking-dependent hybridized bands}, \quad (16.17)$$

$$\text{Mott-Hubbard} \rightarrow \text{Hubbard spectral features and Mott gap}, \quad (16.18)$$

and

$$\text{QSL fractionalization} \rightarrow \text{spinon-chargon spectral continuum}. \quad (16.19)$$

However, these should more precisely be called different theoretical descriptions or frameworks rather than four equivalent models. In particular, DFT is a computational formalism, the interlayer and Hubbard descriptions specify different microscopic mechanisms for the electronic structure and insulating behavior, and a QSL is a possible many-body state whose spectral predictions depend on the particular QSL model used.

16.2.2 What I Understood Wrongly (Maybe)

GPT version: I am wrong at interpreting the 1T and H phases as different stacking configurations.

The 1T and H phases are not simply different stacking arrangements of otherwise identical layers. In the review, the T phase and H phase correspond to different intralayer coordination geometries: the T phase has octahedral coordination, whereas the H phase has trigonal-prismatic coordination. The distinction can be described by a 180° rotation of the top sulfur layer relative to the bottom sulfur layer. Stacking then becomes a separate issue when several layers are present; for example, alternating H- and T-type layers can produce other polymorphs such as 4Hb.

GPT version: I am wrong at saying that dimensionality is not really related to this article.

Dimensionality is actually one of the central themes of the review. The authors explicitly state that they focus on the dimensionality dependence of the electronic structure. In particular, approaching the two-dimensional limit suppresses complications associated with interlayer stacking and strengthens quantum fluctuations, which is important for the discussion of the Mott state and the possible quantum spin liquid state.

GPT version: I am wrong at saying that one electron per Star of David simply means that there are many conduction electrons and therefore the system should be metallic.

The more precise statement is that the Star-of-David reconstruction leaves one unpaired electron per $\sqrt{13} \times \sqrt{13}$ cluster, producing a half-filled narrow band in the non-correlated band picture. Conventional band theory therefore predicts a metallic state because this band crosses the Fermi level. The key point is the half-filled band, not simply the existence of “many conduction electrons.”

GPT version: I am wrong at saying that neutron scattering confirms metallicity.

The neutron-scattering result discussed in the review does not confirm metallic transport. Instead, it gives an estimate of a magnetic moment of approximately $0.4 \mu_B$ per Star-of-David cluster. This supports the existence of an unpaired magnetic degree of freedom associated with the cluster. It is therefore relevant to the localized-electron and Mott picture rather than being direct evidence for metallicity.

GPT version: I am wrong at treating the Mott and interlayer-coupling pictures as mutually exclusive descriptions.

The Mott picture and interlayer physics should not be understood as two descriptions that cannot coexist. Interlayer hopping is present even when correlations are important. The review notes, for example, that the lower Hubbard band disperses along the out-of-plane momentum direction because interlayer interactions enhance inter-site hopping and broaden the Hubbard band. The real debate concerns what primarily causes the insulating gap.

The review ultimately argues that particular stacking configurations can produce a band-insulating gap, but the correlation-driven Mott picture gives a more comprehensive explanation, especially in the monolayer limit where interlayer stacking is absent but a large insulating gap remains.

GPT version: I am wrong at describing triangular-lattice frustration in terms of spins being approximately orthogonal.

Orthogonality is not the relevant condition. For antiferromagnetic nearest-neighbor interactions on a triangular lattice, each pair would prefer to be antiparallel, but all three bonds of a triangle cannot satisfy this condition simultaneously. This is the origin of geometric frustration. In the classical isotropic Heisenberg model, the compromise configuration is characterized by 120° angles between neighboring spins rather than 90° angles. The review states the essential point as the impossibility of simultaneously satisfying all nearest-neighbor antiferromagnetic interactions on the triangular lattice.

GPT version: I am wrong at describing quantum fluctuations as spins simply jumping between classical configurations.

This picture can be used as a rough intuition, but it is not the correct quantum-mechanical description. Quantum fluctuations mix different spin configurations, and the quantum state can be a coherent superposition of them. In the quantum-spin-liquid discussion, the review connects this to the suppression of conventional long-range magnetic order and to a coherent superposition of entangled singlet configurations, such as the resonating-valence-bond picture.

GPT version: I am wrong at implying that a quantum spin liquid has no correlations but has entanglement.

A quantum spin liquid is not characterized by an absence of correlations. Rather, it lacks conventional long-range magnetic order while retaining strong quantum correlations and entanglement. Depending on the type of quantum spin liquid, spin correlations may decay rapidly or follow a power law, but the state itself is strongly correlated. The review emphasizes highly entangled spins and the absence of long-range magnetic order as defining features.

GPT version: I am wrong at treating the absence of a QSL region on the usual phase diagram as evidence against the QSL interpretation.

The proposed quantum spin liquid does not necessarily appear as a separate labeled thermodynamic phase on the usual temperature-pressure or temperature-thickness phase diagrams. In this review, the QSL is discussed as a possible state of the spin sector inside the low-temperature Mott-insulating regime. The relevant question is whether long-range magnetic order is suppressed in the frustrated Mott state, not whether a separate region labeled “QSL” appears on the conventional structural or transport phase diagram.

GPT version: I am wrong at suggesting that the QSL may simply correspond to a region without a charge-density wave.

In the review, the possible quantum spin liquid is discussed in connection with the CDW-Mott phase, not as an alternative state that appears when the CDW disappears. In monolayer 1T-TaS₂, the $\sqrt{13} \times \sqrt{13}$ CDW superstructure persists while the system remains insulating. The authors explicitly argue that investigation of the CDW-Mott phase in the two-dimensional system is important for understanding the possible QSL state.

GPT version: I am wrong at saying that every individual Star of David has its own chirality.

The chirality discussed in this review is a collective property of the CDW superstructure rather than an independent chirality attached to each isolated Star-of-David cluster. The triangular arrangement of the CDW superstructure breaks in-plane mirror symmetry and gives rise to two energetically degenerate chiral configurations of opposite handedness. The associated ferro-rotational order is described in terms of globally clockwise or counterclockwise rotations of the Star-of-David lattice.

GPT version: I am wrong at saying that an external electric field cannot switch the chiral or ferro-rotational state.

The important distinction is between direct and indirect coupling. The ferro-rotational order parameter does not couple directly to the external electric field because it is invariant under time reversal and spatial inversion. Nevertheless, electrical switching is still possible

indirectly through field-driven motion of domain walls. Therefore, “no direct coupling” does not mean “no electrical switching.”

GPT version: I am wrong at summarizing the Mott-versus-band-insulator discussion as simply “two models and no clear answer.”

That is a reasonable description of the historical debate, but it misses the conclusion emphasized by Chen et al. The authors acknowledge that interlayer stacking can generate an insulating gap in specific bulk configurations. However, they argue that the correlation-driven Mott scenario provides a more comprehensive and natural explanation of the insulating state, particularly in the monolayer limit, where interlayer coupling and stacking are absent but a large insulating gap and Hubbard-like spectral features remain.

16.2.3 My General Questions about the Articles

1H or 2H phase, what is more important?

(GPT:) For this paper, the more relevant distinction is actually between the 1T phase and the H phase. For bulk TaS₂, the common H polytype is 2H-TaS₂, whereas an isolated H-type monolayer is called 1H-TaS₂. If the discussion concerns the correlated physics of 1T-TaS₂, the H phase is mainly important as a competing, energetically more stable structural phase and as a metallic reference. For monolayer heterostructures, 1H-TaS₂ becomes directly important, for example in the 1H/1T heterostructure discussed later in the paper.

Is there a QSL in the layer interaction model? (it is in the MH model)

(GPT:) Not naturally. The QSL scenario relies on localized spin-1/2 degrees of freedom on the triangular lattice of SOD clusters and therefore fits naturally into the Mott-Hubbard picture. In the pure interlayer-interaction picture, the insulating state is essentially a band insulator produced by interlayer hybridization/dimerization, so there is no corresponding lattice of localized moments from which the QSL would arise. One could in principle construct a model containing both correlations and interlayer coupling, but the pure stacking-induced band-insulator model does not by itself imply a QSL.

do we have a Mott insulating state in the layer interaction model? we have a insulation, but is it a Mott one?

(GPT:) No. In the pure interlayer-interaction model discussed in Sect. 3, the insulating state is a stacking-induced band insulator rather than a Mott insulator. The gap arises from interlayer hybridization, particularly involving the $d_{3z^2-r^2}$ orbitals, and the relevant calculations can produce the gap even without an on-site Hubbard U . This distinction is exactly why the paper compares the two mechanisms.

what really is essential to understand from experiments on TaS₂?

(GPT:) For the logic of this review, the essential experimental questions are: whether the low-temperature gap is primarily a Mott gap or a stacking-induced band gap; how the CDW changes with dimensionality; whether the insulating state survives in a monolayer where interlayer coupling is absent; whether localized spins and fractionalized excitations exist; and how CDW, Mott physics, QSL behavior, and superconductivity are connected. The monolayer experiments are particularly important because they remove stacking as a possible explanation of the insulating gap.

was there ever a 1H phase?

(GPT:) Yes. A single layer with trigonal-prismatic H coordination is conventionally called 1H-TaS₂. In fact, this review explicitly mentions monolayer 1T-TaS₂ placed on metallic 1H-TaS₂ and later discusses artificial 1H/1T-TaS₂ heterostructures. The terminology differs from bulk 2H-TaS₂: “1H” refers to one H-type layer per unit cell, whereas 2H is the common two-layer bulk stacking.

what is the phase diagram of 1H or 2H phase?

(GPT:) This review does not provide a detailed temperature–pressure phase diagram for 1H- or 2H-TaS₂. Its phase diagrams concern primarily 1T-TaS₂. To answer this properly, one should go to literature specifically on 2H-TaS₂ and monolayer 1H-TaS₂. Their physics is different from 1T-TaS₂: the H phases are metallic rather than the low-temperature Mott-CDW insulator emphasized here.

What is the difference between STM and SEM?

(GPT:) SEM images a surface using a focused electron beam and detected secondary/backscattered electrons, typically giving morphology over relatively large areas. STM instead measures the tunnelling current between an atomically sharp conducting tip and the surface, allowing atomic-scale topography and, through STS (dI/dV), information about the local electronic density of states. Thus, STM is particularly useful here for resolving the SOD CDW lattice and measuring the insulating gap, while SEM is mainly useful for imaging the morphology and location of grown flakes.

revise AFM, why there is a minus in front of J in the article?

(GPT:) The sign depends on the convention used for the Heisenberg Hamiltonian. If one writes

$$H = -J \sum_{\langle ij \rangle} \mathbf{S}_i \cdot \mathbf{S}_j,$$

then $J < 0$ corresponds to antiferromagnetic coupling, so superexchange can be written as $J \sim -t^2/U$. If instead one uses

$$H = J \sum_{\langle ij \rangle} \mathbf{S}_i \cdot \mathbf{S}_j,$$

antiferromagnetism corresponds to $J > 0$ and one normally writes $J \sim 4t^2/U$. Therefore, the minus sign in the review is a sign-convention issue rather than a different physical mechanism.

fig. 3. di we need david stars in ICCDW?

(GPT:) Not as a long-range, well-defined $\sqrt{13} \times \sqrt{13}$ SOD lattice. The complete Star-of-David superstructure characterizes the commensurate CCDW phase. In the NCCDW phase, locally commensurate SOD domains survive and are separated by discommensurations. In the ICCDW phase, the modulation is incommensurate with the atomic lattice, so one should not think of the whole system as a regular triangular lattice of identical SOD clusters. Figure 3b is schematic and is mainly intended to illustrate this evolution.

inplane chiral nature of CDW - why Rossnagel wrote that materials are not exactly 2D?

(GPT:) These statements concern different things. “In-plane chiral nature” describes symmetry breaking of the CDW pattern inside an individual ab plane. Calling 1T-TaS₂ not strictly

two-dimensional means that real bulk crystals still have finite interlayer coupling, c -axis dispersion, and stacking effects. Thus, the electronic structure can be strongly quasi-2D while still being affected significantly by the third dimension.

why do we need chirality at all? Do I understand correctly that it is not important?

(GPT:) It is not essential for the basic explanation of the Mott gap or for the simplest QSL argument. However, it is physically important because it represents an additional broken symmetry of the CDW state, produces distinct chiral domains, is connected with ferro-rotational order, and can be electrically switched. It may also matter for possible chiral superconductivity. Therefore, for understanding “why is 1T-TaS₂ insulating?” it is secondary, but for the full phase structure and possible applications it is important.

finally, SC coexists with CDW or excludes CDW state at low T? And what about higher T?

(GPT:) According to the picture summarized in this review, superconductivity competes strongly with the insulating CCDW state, but it can coexist with the NCCDW state. Under pressure or doping, the low-temperature Mott-CCDW state is suppressed and superconductivity appears. In the coexistence regime, superconductivity may develop in the metallic regions between commensurate CDW domains rather than inside the insulating domains themselves. At higher temperature, superconductivity disappears at T_c , while NCCDW can remain present to much higher temperatures before eventually transforming into ICCDW and then the normal metallic phase.

how to derive that CDW/polaronic bulb is 1 nm?

(GPT:) The relevant scale follows directly from the $\sqrt{13} \times \sqrt{13}$ SOD superlattice. The in-plane Ta lattice constant is approximately $a \simeq 0.33$ nm, so the CDW period is

$$\lambda_{\text{CDW}} = \sqrt{13}a \simeq \sqrt{13} \times 0.33 \text{ nm} \simeq 1.2 \text{ nm}.$$

Thus, saying that a CDW/SOD or polaronic object has a characteristic size of approximately 1 nm is an order-of-magnitude statement based on the SOD supercell.

what about the gap on fig. 7c, in the middle of a band?

(GPT:) Figure 7c is showing the calculated band structure for a particular stacking configuration. The apparent splitting inside what would otherwise look like one continuous band results from interlayer hybridization: states from neighboring layers hybridize and split into bonding- and antibonding-like branches. The important question is whether this splitting produces a full gap at the Fermi level throughout the three-dimensional Brillouin zone. Therefore, one should not interpret every visible separation between branches as an independent Mott gap.

On fig. 7, there is a dependence of gap to the stacking order, why is it written, that it does not dependent on them in the text?

(GPT:) The paper is comparing two different results. The calculations in Fig. 7 predict that the band structure and even the existence of a full band gap can depend strongly on stacking. However, STM experiments discussed immediately afterwards find similar large-gap spectra, approximately 0.4–0.45 eV, for different stacking orders when the spectra are measured

sufficiently far from step edges. Therefore, “stacking dependent” refers to the theoretical band-structure mechanism, whereas “independent of stacking order” refers to the experimentally observed dominant large gap. This experimental discrepancy is one of the arguments in favor of the Mott interpretation.

fig. 8, what is going on there on the spectrum? why there are such details?

(GPT:) Figure 8a is temperature-dependent ARPES, so the intensity map contains several dispersing electronic states, CDW-related folded/hybridized bands, finite linewidths, and matrix-element effects. The authors are not trying to explain every small feature. The main feature to follow is the flat lower-Hubbard-band-like state near the Fermi level and its evolution with temperature. Figure 8b extracts the energy-distribution curve at the zone center, and Fig. 8c reduces this complicated spectrum to the temperature dependence of the gap.

fig. 8: why we cool and heat and don’t have hysteresis, but we have it in the plot of resistivity?

(GPT:) The crucial difference is dimensionality. Figure 8 concerns monolayer 1T-TaS₂, whereas the conventional strong hysteresis in resistivity is associated with bulk 1T-TaS₂. The review explicitly argues that the absence of obvious heating–cooling hysteresis in the monolayer suggests that the bulk hysteresis may originate from competing interlayer stacking configurations. A monolayer has no such stacking degree of freedom.

note that plot from Sipos et al. is for layer, not for a bulk! is it true? what about Rossnagel???

(GPT:) No. The Sipos et al. Nature Materials paper “From Mott state to superconductivity in 1T-TaS₂” concerns bulk single-crystalline 1T-TaS₂ under pressure, not an isolated monolayer. Therefore, the pressure–temperature phase diagram adapted from Sipos et al. should be interpreted as a bulk phase diagram. Rossnagel’s discussion of the standard temperature-driven ICCDW–NCCDW–CCDW sequence also primarily refers to bulk layered 1T-TaS₂, unless a thin-film or monolayer experiment is explicitly specified.

most likely statement that 180 degr trans temp in bulk is not true

(GPT:) It is better to say that 180 K is an oversimplified value rather than that it is simply false. Bulk 1T-TaS₂ has a strongly hysteretic first-order NCCDW–CCDW transition, so the transition temperature depends on whether the sample is being cooled or heated. Approximately 180 K is commonly quoted for the transition on cooling, while the reverse transition on warming occurs at a substantially higher temperature, around 220 K. Thus, assigning one unique “bulk transition temperature” loses the hysteresis information.

what is the advantage of an interlayer interaction model at all comparing to Mott’s model?

(GPT:) Its main advantage is that it explains several explicitly three-dimensional observations without requiring a large Hubbard U . It naturally incorporates the strong dependence of the calculated band dispersion on stacking, the observed c -axis dispersion, XRD evidence for interlayer dimerization, and the possibility of large-gap, small-gap, and metallic electronic structures associated with different stacking configurations. Its main weakness is that it cannot explain the large insulating gap of an isolated monolayer, where there is no interlayer coupling. This is why the review ultimately regards the Mott picture as the more comprehensive explanation.

why there is no QSL in Sipos et al plot?

(GPT:) Because the Sipos et al. diagram was constructed to describe the experimentally established CDW, Mott-insulating, metallic, and superconducting regions under pressure. A QSL is a more specific characterization of the spin state inside a Mott-insulating region, and it was not established as a separate thermodynamic phase in that experiment. Therefore, the region labelled as the Mott state could in principle contain QSL-like spin physics, but Sipos et al. did not have sufficient evidence to label a separate QSL phase.

what is the role of monolayer for QSL? Which theory is more applicable for a monolayer?

(GPT:) The monolayer is particularly important because it removes the interlayer stacking degree of freedom. Therefore, a purely interlayer-induced band-insulator explanation cannot work there. Nevertheless, experiments still observe a large insulating gap and Hubbard-like spectral features, making the correlation-driven Mott picture much more natural. In addition, reduced dimensionality enhances quantum fluctuations, which can suppress magnetic long-range order and therefore favor a QSL on the frustrated triangular lattice of SOD spins. Thus, for a monolayer, the Mott-Hubbard picture is much more applicable than the pure interlayer band-insulator model.

Why exactly QSL can be not confirmed?

(GPT:) Because there is no single experimentally unique “smoking-gun” signature of a QSL in 1T-TaS₂. Absence of magnetic order is necessary but not sufficient, and signatures such as a linear specific heat, residual thermal conductivity, continua in spectroscopy, or spinon-like spectral features can sometimes have alternative explanations. Moreover, some bulk measurements give contradictory results. For monolayers the problem becomes harder because conventional probes such as neutron scattering, NMR, and specific heat have insufficient signal, while substrates, defects, strain, and charge transfer can modify the electronic structure. Therefore, the current evidence is consistent with a QSL but does not constitute an absolutely unambiguous proof.

Is QSL says that CDW state is destroyed at some region where it is present?

(GPT:) No. A QSL refers to the spin degrees of freedom, specifically the absence of conventional long-range magnetic order despite strong interactions between localized spins. It does not imply destruction of the CDW. In the standard picture for 1T-TaS₂, the CCDW creates the SOD superlattice, each SOD provides an effective localized spin-1/2, and those spins may then form a QSL on the triangular SOD lattice. Thus, CDW order and a QSL can coexist: the CDW organizes the charge/lattice sector, while the QSL describes the spin sector.

What is this charge-spin separation?

(write some formulas about it)

Which extrinsic factors can affect monolayer 1T-TaS₂?

(GPT:)

Although studying monolayer 1T-TaS₂ eliminates interlayer coupling and stacking-order effects, an experimentally realized monolayer is generally not an isolated two-dimensional system. Its electronic properties can be influenced by several extrinsic factors associated with the substrate, sample preparation, and measurement conditions.

Charge transfer and substrate-induced doping.

Charge transfer can occur between the substrate and the TaS₂ monolayer, changing the electronic filling of the SOD-derived states,

$$n_{\text{SOD}} \rightarrow n_{\text{SOD}} + \delta n. \quad (16.20)$$

This is particularly important for the Mott picture because the relevant SOD-derived band is approximately half-filled in the ideal system. Substrate-induced electron or hole doping can therefore modify the Mott insulating state and its spectral properties.

Dielectric screening.

The substrate modifies the dielectric environment of the monolayer and screens electron-electron Coulomb interactions. Consequently, the effective on-site and intersite interactions U and V can differ from those of a free-standing monolayer. Since the importance of correlations is controlled approximately by

$$\frac{U}{W}, \quad (16.21)$$

where W is the bandwidth of the relevant SOD-derived band, substrate screening can influence the stability and magnitude of the Mott gap.

Strain.

Lattice mismatch between the substrate and TaS₂, as well as differences in thermal expansion, can produce strain in the monolayer. This modifies Ta–Ta and Ta–S distances and therefore changes the hopping amplitudes,

$$t_{ij} = t_{ij}(r_{ij}), \quad (16.22)$$

which in turn modify the bandwidth W and potentially the stability and structure of the CDW. Thus, strain can indirectly affect the ratio U/W and the correlated electronic state.

Interface hybridization.

Electronic states of TaS₂ can hybridize with electronic states of the substrate. Schematically, an interface contribution can be written as

$$H_{\text{hyb}} = \sum_{\mathbf{k}, \sigma} \left(t_{\text{int}}, c_{\mathbf{k}\sigma}^\dagger d_{\mathbf{k}\sigma} + \text{h.c.} \right), \quad (16.23)$$

where c and d describe TaS₂ and substrate states, respectively. Such hybridization can shift, broaden, or reconstruct TaS₂-derived bands, meaning that the experimentally observed electronic structure may differ from that of an isolated monolayer.

Defects and disorder.

S vacancies, structural defects, impurities, and CDW domain boundaries can introduce additional localized states and scattering. Disorder can broaden electronic spectral features and modify the measured spectral function,

$$A(\mathbf{k}, \omega), \quad (16.24)$$

potentially complicating the identification of intrinsic Mott or QSL-related features in ARPES.

Thus, removing the interlayer degree of freedom does not produce a perfectly isolated realization of two-dimensional 1T-TaS₂. Substrate-induced charge transfer, dielectric screening, strain, interface hybridization, and disorder must therefore be considered when interpreting monolayer experiments.

How do atomic Ta 5d orbitals evolve into the low-energy correlated bands of 1T-TaS₂?

(GPT:)

The electronic structure of 1T-TaS₂ can be understood as a sequence from atomic orbitals to Bloch bands and, after the CDW reconstruction, to narrow SOD-derived states. An isolated Ta atom has five 5d orbitals,

$$d_{xy}, \quad d_{xz}, \quad d_{yz}, \quad d_{x^2-y^2}, \quad d_{z^2}. \quad (16.25)$$

In a crystal, orbitals belonging to different Ta atoms overlap. This allows electrons to hop between different atomic sites. A tight-binding Hamiltonian can be written as

$$H_{\text{TB}} = \sum_{i,m,\sigma} \epsilon_m n_{im\sigma} + \sum_{i,j,m,n,\sigma} t_{mn}^{ij} c_{im\sigma}^\dagger c_{jn\sigma}, \quad (16.26)$$

where ϵ_m is the energy of orbital m , while t_{mn}^{ij} describes hopping from orbital n on site j to orbital m on site i . Because the crystal is periodic, the eigenstates can be labelled by momentum $\mathbf{k}$. After Fourier transformation, the Hamiltonian becomes a matrix $H(\mathbf{k})$, and its eigenvalues determine the electronic bands,

$$H(\mathbf{k})u_{\nu\mathbf{k}} = E_\nu(\mathbf{k})u_{\nu\mathbf{k}}. \quad (16.27)$$

Thus, the discrete Ta 5d atomic levels become dispersive Ta-5d-derived Bloch bands.

In the commensurate CDW phase, 13 Ta atoms reconstruct into a Star-of-David (SOD) cluster,

$$13 \text{ Ta} \rightarrow 1 \text{ SOD}. \quad (16.28)$$

The real-space unit cell therefore becomes larger and the corresponding Brillouin zone becomes smaller. The original bands are folded into this smaller Brillouin zone, and folded states can hybridize with one another. Instead of describing the low-energy states purely in terms of individual Ta orbitals, it becomes useful to introduce molecular orbitals distributed over an entire SOD cluster,

$$|\Phi_\alpha^{\text{SOD}}\rangle = \sum_{i=1}^{13} \sum_m C_{im}^\alpha |d_{im}\rangle. \quad (16.29)$$

The CDW reconstruction produces several SOD-derived states. Approximately one electron per SOD remains in the relevant low-energy cluster orbital. The corresponding orbitals on different SOD clusters hybridize and form a band. A simple effective tight-binding description of this band is

$$H_{\text{SOD}} = \epsilon_{\text{SOD}} \sum_{i,\sigma} n_{i\sigma} + \sum_{\langle i,j \rangle, \sigma} t_{ij} c_{i\sigma}^\dagger c_{j\sigma}. \quad (16.30)$$

Because hopping between different SOD clusters is relatively weak, the resulting bandwidth W is small. Schematically,

$$W \sim z |t_{\text{SOD}}|, \quad (16.31)$$

where z is the number of relevant neighboring clusters. Since there is approximately one electron per effective SOD orbital and each orbital can accommodate two electrons with opposite spins, the resulting narrow band is approximately half-filled.

If electron-electron interactions are neglected, this narrow half-filled band is expected to be metallic. To describe correlation effects, an on-site Coulomb interaction is added,

$$H_U = U \sum_i n_{i\uparrow} n_{i\downarrow}. \quad (16.32)$$

The effective Hubbard Hamiltonian is therefore

$$H = H_{\text{SOD}} + H_U. \quad (16.33)$$

When the Coulomb interaction U becomes sufficiently large compared with the bandwidth W , double occupation of the effective SOD orbital becomes energetically unfavorable. The electrons can then become localized, and the narrow half-filled band develops lower and upper Hubbard spectral features separated by a Mott gap. The overall physical sequence can therefore be summarized as

$$\text{Ta } 5d \text{ orbitals} \rightarrow \text{Bloch bands} \rightarrow \text{CDW reconstruction} \rightarrow \text{SOD molecular orbitals} \rightarrow \text{narrow half-filled band} \quad (16.34)$$

What is the connection between CDW and Mott insulation?

(GPT:)

A charge-density wave (CDW) and a Mott insulating state are distinct phenomena, and in general a CDW does not imply Mott insulation. In $1T\text{-TaS}_2$, however, the CDW reconstruction creates favorable conditions for Mott localization. In the commensurate CDW phase, 13 Ta atoms reconstruct into a Star-of-David (SOD) cluster,

$$13, \text{Ta} \rightarrow 1, \text{SOD}. \quad (16.35)$$

The corresponding Ta- $5d$ states are reconstructed into molecular orbitals of the SOD cluster. Approximately 12 of the 13 Ta-derived electrons occupy lower-energy cluster states in pairs, leaving one electron in the highest relevant SOD-derived orbital. When the SOD clusters form a periodic lattice, these orbitals hybridize between neighboring clusters and form a band. Since the inter-SOD hopping t_{SOD} is small, this band has a small bandwidth,

$$W_{\text{SOD}} \sim z|t_{\text{SOD}}|, \quad (16.36)$$

and, because there is approximately one electron per SOD orbital, it is half-filled. Thus, the essential consequence of the CDW reconstruction is

$$\text{CDW} \rightarrow \text{SOD reconstruction} \rightarrow \text{narrow half-filled band}. \quad (16.37)$$

Without sufficiently strong electron-electron interactions, a half-filled band would remain metallic. However, the narrow bandwidth makes the Coulomb interaction U large relative to the kinetic-energy scale,

$$\frac{U}{W_{\text{SOD}}} \gtrsim 1. \quad (16.38)$$

Electron hopping between neighboring SOD clusters can produce virtual configurations such as

$$(1, 1) \rightarrow (0, 2), \quad (16.39)$$

where the doubly occupied SOD costs an energy of order U . For sufficiently large U/W_{SOD} , double occupancy is suppressed and approximately one electron becomes localized on each SOD cluster. The narrow half-filled band is then split into lower and upper Hubbard features,

$$\text{half-filled SOD band} \xrightarrow{U} \text{LHB} + \text{Mott gap} + \text{UHB}. \quad (16.40)$$

Therefore, in the conventional Mott picture of $1T\text{-TaS}_2$, the CDW does not itself produce the Mott gap. Instead, the CDW reconstructs the electronic structure and produces a narrow half-filled SOD-derived band, while strong Coulomb interactions acting on this band can subsequently produce Mott localization:

$$\text{CDW} \rightarrow \text{SOD} \rightarrow \text{narrow half-filled band} \rightarrow U/W \text{ large} \rightarrow \text{Mott insulating state}. \quad (16.41)$$

This last step is not universally established for $1T\text{-TaS}_2$: particularly in bulk systems, interlayer hybridization and stacking can also modify or gap the SOD-derived states. Therefore, the CDW reconstruction is well established, whereas the extent to which the resulting insulating state should be interpreted as a purely Mott state remains debated.

What is the difference between the CDW gap, the Mott gap, and the stacking-induced gap in $1T\text{-TaS}_2$?

(GPT:)

Several physically different mechanisms can produce gaps in the electronic spectrum of $1T\text{-TaS}_2$, and they should not be identified with one another. First, the formation of the CDW changes the translational periodicity of the crystal and reconstructs the electronic bands. The enlarged Star-of-David unit cell reduces the Brillouin zone, causing the original bands to fold and hybridize. When two folded states are coupled by the CDW potential, their crossing can be avoided and a CDW-related hybridization gap can appear. In a simple two-state description,

$$H_{\text{CDW}} = \begin{pmatrix} \epsilon_{\mathbf{k}} & \Delta_{\text{CDW}} \\ \Delta_{\text{CDW}}^* & \epsilon_{\mathbf{k}+\mathbf{Q}} \end{pmatrix}, \quad (16.42)$$

where $\mathbf{Q}$ is a CDW wave vector. The corresponding eigenenergies are

$$E_{\pm} = \frac{\epsilon_{\mathbf{k}} + \epsilon_{\mathbf{k}+\mathbf{Q}}}{2} \pm \sqrt{\left(\frac{\epsilon_{\mathbf{k}} - \epsilon_{\mathbf{k}+\mathbf{Q}}}{2}\right)^2 + |\Delta_{\text{CDW}}|^2}. \quad (16.43)$$

Thus, the CDW can open hybridization gaps at particular crossings of the reconstructed bands. These gaps do not by themselves imply Mott insulation.

Second, the CDW reconstruction produces a narrow, approximately half-filled SOD-derived band near the Fermi level. If the Coulomb interaction U is sufficiently strong compared with the bandwidth W , double occupation of the effective SOD orbital becomes energetically unfavorable. This physics is described by a Hubbard-type Hamiltonian,

$$H = \sum_{\langle i,j \rangle, \sigma} t_{ij} c_{i\sigma}^\dagger c_{j\sigma} + U \sum_i n_{i\uparrow} n_{i\downarrow}. \quad (16.44)$$

For sufficiently strong correlations, the low-energy spectral weight is separated into lower and upper Hubbard features, producing a correlation-induced Mott gap. Therefore, the Mott gap

originates from electron-electron interactions acting on the narrow SOD-derived band rather than directly from CDW band folding.

Third, in multilayer and bulk $1T$ -TaS₂, an insulating gap can also arise from interlayer hybridization associated with particular stacking configurations. If relevant SOD-derived orbitals in two neighboring layers are coupled by an interlayer hopping $t_{\perp}$, a minimal bilayer Hamiltonian can be written as

$$H_{\text{inter}} = \begin{pmatrix} \epsilon_{\mathbf{k}} & t_{\perp} \\ t_{\perp}^* & \epsilon_{\mathbf{k}} \end{pmatrix}. \quad (16.45)$$

Its eigenenergies are

$$E_{\pm}(\mathbf{k}) = \epsilon_{\mathbf{k}} \pm |t_{\perp}|, \quad (16.46)$$

so interlayer hybridization produces bonding and antibonding states separated by

$$\Delta E = 2|t_{\perp}|. \quad (16.47)$$

For suitable stacking and electronic filling, this splitting can produce a band-insulating state without requiring a Mott mechanism.

The three mechanisms should therefore be distinguished as

$$\text{CDW reconstruction} \rightarrow \text{band folding and hybridization gaps}, \quad (16.48)$$

$$\text{strong correlations in a narrow half-filled band} \rightarrow \text{Mott gap}, \quad (16.49)$$

and

$$\text{interlayer hybridization in particular stackings} \rightarrow \text{bonding-antibonding splitting}. \quad (16.50)$$

Consequently, the observation of a spectral gap alone does not determine its microscopic origin. In $1T$ -TaS₂, CDW reconstruction, electron correlations, and, in multilayer systems, interlayer stacking can all modify the spectrum through physically distinct mechanisms.

What are the formulas for SQL?

(I don't know, but this question goes beyond this article)

Part V

Old, Fundamental Theories

17 Single-layer MoS₂ transistors by Radisavljevi, Radenovic, Brivio, Giacometti, Kis

Two-dimensional materials are attractive for use in next-generation nanoelectronic devices because, compared to one-dimensional materials, it is relatively easy to fabricate complex structures from them. The most widely studied two-dimensional material is graphene^{1,2}, both because of its rich physics^{3–5} and its high mobility⁶. However, pristine graphene does not have a bandgap, a property that is essential for many applications, including transistors⁷. Engineering a graphene bandgap increases fabrication complexity and either reduces mobilities to the level of strained silicon films^{8–13} or requires high voltages^{14,15}. Although single layers of **MoS₂** have a large intrinsic bandgap of 1.8 eV (ref. 16), previously reported mobilities in the **0.5 – 3 cm²V⁻¹s⁻¹** range¹⁷ are too low for practical devices. Here, we use a hafnium oxide gate dielectric to demonstrate a room-temperature single-layer MoS₂ mobility of at least **200 cm²V⁻¹s⁻¹**, similar to that of graphene nanoribbons, and demonstrate transistors with room-temperature current on/off ratios of 1×10^8 and ultralow standby power dissipation. Because monolayer MoS₂ has a direct bandgap^{16,18}, it can be used to construct interband tunnel FETs¹⁹, which offer lower power consumption than classical transistors. Monolayer MoS₂ could also complement graphene in applications that require thin transparent semiconductors, such as optoelectronics and energy harvesting.

MoS₂ is a typical example from the layered transition-metal dichalcogenide family of materials. Crystals of MoS₂ are composed of vertically stacked, weakly interacting layers held together by van der Waals interactions (Fig. 1a). Single layers, 6.5 Å thick (Fig. 1b,c), can be extracted using scotch tape^{17,20} or lithium-based intercalation^{21,22}. Large-area thin films can also be prepared using MoS₂ suspensions. Bulk MoS₂ is semiconducting with an indirect bandgap of 1.2 eV (ref. 23), whereas single-layer MoS₂ is a direct gap semiconductor^{16,18} with a bandgap of 1.8 eV (ref. 16). MoS₂ nanotubes²⁴ and nanowires²⁵ also show the influence of quantum-mechanical confinement in their electronic and optical properties. Other features that could make MoS₂ interesting for nanoelectronic applications include the absence of dangling bonds and thermal stability up to 1,100°C.

Single-layer MoS₂ could also be interesting as a semiconducting analogue of graphene, which does not have a bandgap in its pristine form. Bandgaps up to 400 meV have been introduced by quantummechanical confinement in patterned⁸ or exfoliated graphene nanoribbons⁹, but always at the price of significant mobility reduction ($200 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for a 150 meV bandgap)^{9,10}, loss of coherence¹¹ or increased off-state currents due to edge roughness¹². Bandgaps have also been induced by applying a perpendicular electric field in bilayer graphene^{14,15}, but the highest reported optical gap is 250 meV, requiring the application of a voltage exceeding 100 V (ref. 14). This makes it very difficult to build logic circuits based on graphene that would operate at room temperature with low standby power dissipation. In fact, for any potential replacement of silicon in CMOS-like digital logic devices, a current on/off ratio⁷

$I_{\text{on}}/I_{\text{off}}$ between 1×10^4 and 1×10^7 and a bandgap exceeding 400 meV (ref. 26) are desirable.

The starting point for the fabrication of our transistors was scotch tape-based micromechanical exfoliation^{1,17} of single-layer MoS₂. MoS₂ monolayers were transferred to degenerately doped silicon substrates covered with 270 -nm-thick SiO₂ (Fig. 2a). We have previously found that this oxide thickness is optimal for optical detection of single-layer MoS₂, and have established

the correlation between contrast and thickness as measured by atomic force microscopy (AFM)²⁷. Electrical contacts were fabricated using elec-tron-beam lithography followed by deposition of 50 -nm-thick gold electrodes. The device was then annealed at 200°C to remove resist residue²⁸ and decrease contact resistance (for more details see Supplementary Information). At this point our single-layer devices show a typical mobility in the range $0.1 - 10 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, similar to previously reported values for single layers¹⁷ and thin crystals containing more than 10 layers of MoS₂ (ref. 29). This is lower than the previously reported phonon-scattering-limited room-temperature mobility in the $200 - 500 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ range for bulk MoS₂ (ref. 30). Encouraged by recent theoretical predictions of mobility improvement by dielectric screening³¹ and its successful application to graphene³², we proceeded with atomic layer deposition (ALD) of 30 nmHfO₂ as a high- κ gate dielectric for the local top gate and mobility booster to realize the full potential of the single-layer MoS₂. We chose HfO₂ because of its high dielectric constant of 25, bandgap of 5.7 eV and the fact that it is commonly used as a gate dielectric both by the research community and major microprocessor manufacturers^{33,34}. The resulting structure, composed of two field-effect transistors connected in series, is shown in Fig. 2b. A schematic depiction of the device is shown in Fig. 2c. The width of the top gate of our device was $4\mu\text{m}$ and the top gate length, source-gate and gate-drain spacing were 500 nm .

We performed electrical characterization of our device at room temperature using a semiconductor parameter analyser and shielded probe station with voltage sources connected in the configuration depicted in Fig. 3a. We first characterized our MoS₂ transistors with 6.5 -Å-thick conductive channels by applying a drain-source bias V_{ds} to a pair of gold electrodes and gate voltage V_{bg} to the degenerately doped silicon substrate while leaving the top gate electrically floating³⁵. The gating characteristics of the left-most transistor shown in Fig 2b are presented in Fig. 3b; these are typical of FET devices with an n-type channel. We concentrate on this device in the remainder of this Letter. Characterization details for other devices and fabrication batches are available in the Supplementary Information. All the MoS₂ transistors we fabricated, regardless of the number of layers or contacting material, show behaviour typical of FET devices with n-type channels. Repeated V_{bg} sweeps on the same device do not show significant variation, while keeping all the voltages constant results in constant I_{ds} , indicating that the top gate is not likely to accumulate charge during measurements. We estimate that a constant surface charge of $n \approx 4.6 \times 10^{12} \text{ cm}^{-2}$ trapped on the top gate would shift the threshold voltage by $\sim 1 \text{ V}$ but not change the

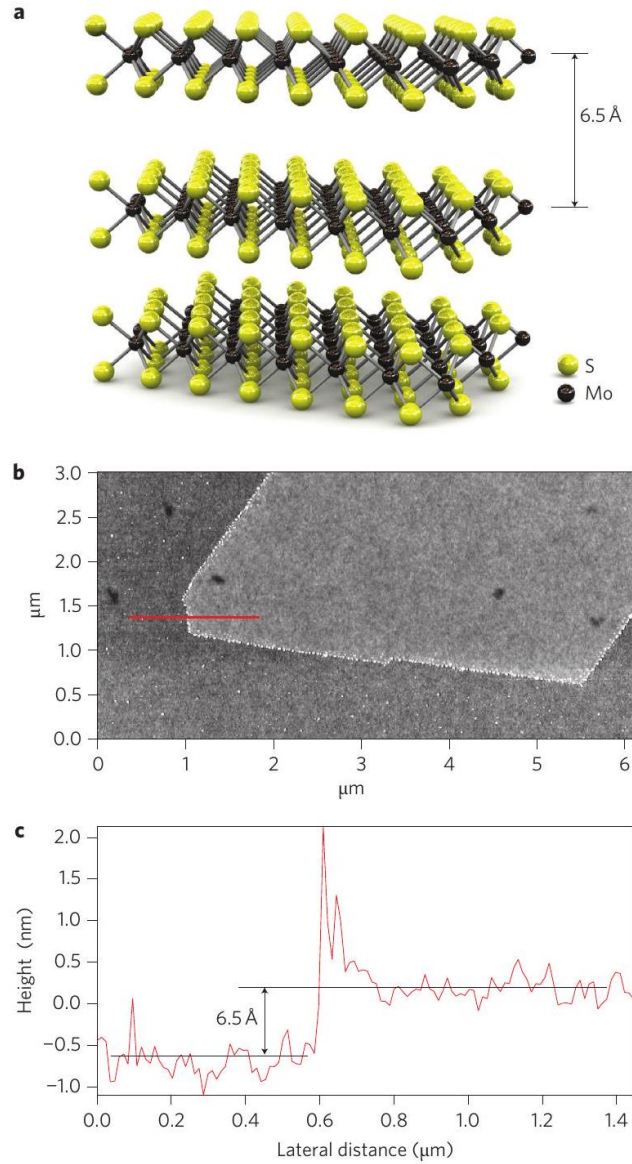


Figure 1 | Structure and AFM imaging of monolayer MoS₂. a, Threedimensional representation of the structure of MoS₂. Single layers, 6.5Å thick, can be extracted using scotch tape-based micromechanical cleavage. b, Atomic force microscope image of a single layer of MoS₂ deposited on a silicon substrate with a 270 -nm-thick oxide layer. c, Cross-sectional plot along the red line in b.

slope of the $I_{ds} - V_{bg}$ curve in Fig. 3b used for estimating channel mobility. The source current versus source bias characteristics (Fig 3b, inset) is linear in the ± 50 mV range of voltages, indicating that our gold contacts are ohmic.

The on-resistance of our transistor was 27 kΩ for $V_{ds} = 10$ mV and $V_{bg} = 10$ V, with a gate width of $4 \mu\text{m}$ and bottom gate length of $1.5 \mu\text{m}$. We have noticed that the device resistance can increase during storage at ambient conditions for a period of two months. This could be attributed to absorption of oxygen and/or water from the environment and could be mitigated by device encapsulation.

From the data presented in Fig. 3b we can extract the low-field field-effect mobility of $\sim 217 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ using the expression $\mu = [dI_{ds}/dV_{bg}] \times [L / (WC_i V_{ds})]$, where $L = 1.5 \mu\text{m}$ is the channel length, $W = 4 \mu\text{m}$ is the channel width and $C_i = 1.3 \times 10^{-4} \text{ F m}^{-2}$ is the capacitance between the channel and the back gate per unit area ($C_i = \epsilon_0 \epsilon_r / d$; $\epsilon_r = 3.9$; $d = 270 \text{ nm}$).

Note that this value represents the lower limit because of contact resistance. As our device displays ohmic $I_{\text{ds}} - V_{\text{ds}}$ behaviour (Fig. 3b, inset), we exclude the possibility that our field-effect behaviour is dominated by Schottky barriers at the contacts.

Although the room-temperature value of phonon-scattering limited³⁰ mobility for bulk MoS₂ is in the $200500 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ range, exfoliation of single layers onto SiO₂ results in a decrease of mobility to $0.1 - 10 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. The improvement in mobility with the deposition of a high- κ dielectric could be due to suppression of Coulomb scattering due to the high- κ dielectric environment³¹ and modification of phonon dispersion³⁶ in MoS₂ monolayers. Extensive future theoretical work including the calculation of phonon dispersion relations in single-layer MoS₂, calculation of scattering rates on phonons and charge impurities would be needed to provide a complete picture.

Before we compare the value of mobility in our case with the mobility of graphene or thin-film silicon we should note that semiconductors such as carbon nanotubes or graphene nanoribbons mostly follow the general trend of decreasing mobility with increasing bandgap²⁶. Even though graphene has a high room-temperature mobility of $120,000 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, this value relates to large-area, gapless graphene⁶. On the other hand, measurements on $10 - \text{nm}$ -wide graphene nanoribbons with $E_{\text{g}} \approx 400 \text{ mV}$ indicate mobilities lower than $200 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ (ref. 9), in good agreement with theoretical models that predict decreased mobility in small-width graphene nanoribbons due to electron-phonon scattering¹³. This is comparable to the mobility of $250 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ found in 2 nm thin strained silicon films³⁷. Our MoS₂ monolayer has similar mobility but a higher bandgap than graphene nanoribbons⁹, and a smaller thickness than the thinnest silicon films fabricated to date³⁷.

One of the crucial requirements for building integrated circuits based on single layers of MoS₂ is the ability to control charge density in a local manner, independently of a global back gate. We can do this by applying a voltage V_{tg} to the top gate, separated from the monolayer MoS₂ by 30 nm of HfO₂ (Fig. 3a), while keeping the substrate grounded. The corresponding transfer characteristic is shown in Fig. 4a. For a bias of 10 mV we observe an

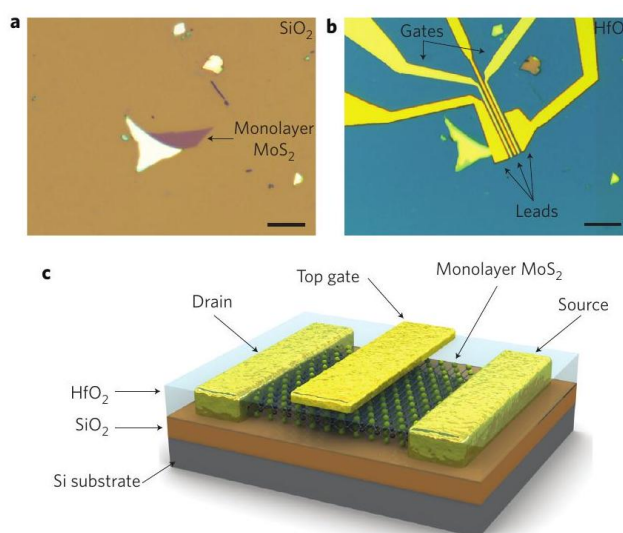


Figure 2 | Fabrication of **MoS₂** monolayer transistors. **a**, Optical image of a single layer of MoS₂ (thickness, 6.5 Å) deposited on top of a silicon substrate with a 270 -nm-thick SiO₂ layer. **b**, Optical image of a device based on the flake shown in **a**. The device consists of two field-effect transistors connected in series and defined by three gold leads that serve as source and drain electrodes for the two transistors. Monolayer MoS₂ is covered by 30 nm of ALD-deposited HfO₂ that acts both as a gate dielectric and a mobility booster. Scale bars (**a**, **b**), 10 μm. **c**, Three-dimensional schematic view of one of the transistors shown in **b**.

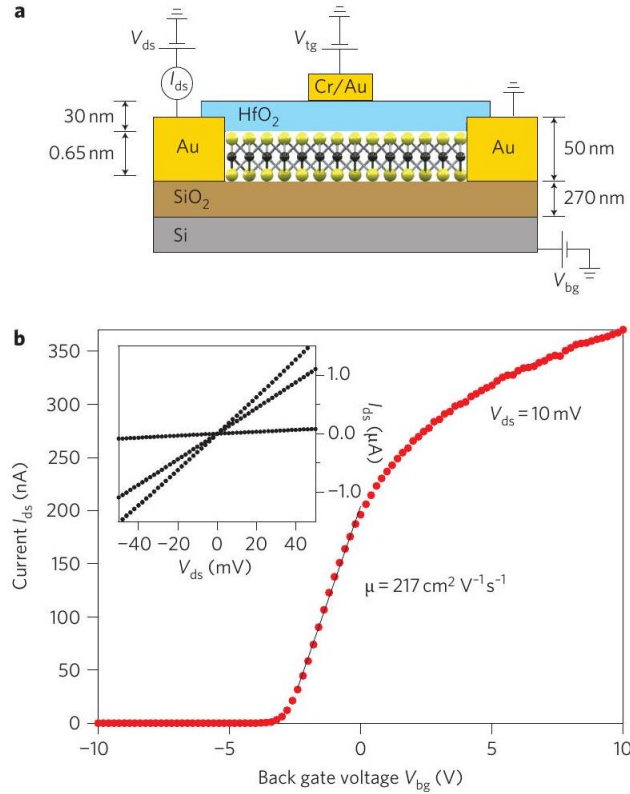


Figure 3 | Characterization of **MoS₂** monolayer transistors. a, Crosssectional view of the structure of a monolayer MoS₂ FET together with electrical connections used to characterize the device. A single layer of MoS₂ (thickness, 6.5 Å) is deposited on a degenerately doped silicon substrate with 270 – nm-thick SiO₂. The substrate acts a back gate. One of the gold electrodes acts as drain and the other source electrode is grounded. The monolayer is separated from the top gate by 30 nm of ALD-grown HfO₂. The top gate width for the device is 4 μm and the top gate length, source-gate and gate-drain spacing are each 500 nm. b, Room-temperature transfer characteristic for the FET with 10 mV applied bias voltage V_{ds} . Backgate voltage V_{bg} is applied to the substrate and the top gate is disconnected. Inset: $I_{ds} - V_{ds}$ curve acquired for V_{bg} values of 0,1 and 5 V.

on-current of 150 nA ($37 \text{ nA } \mu\text{m}^{-1}$), current on/off ratio $I_{on}/I_{off} > 1 \times 10^6$ for the ± 4 V range of V_{tg} , an off-state current that is smaller than 100 fA ($25 \text{ fA } \mu\text{m}^{-1}$) and gate leakage lower than $2 \text{ pA } \mu\text{m}^{-2}$. The observed current variation for different values of V_{tg} indicates that the field-effect behaviour of our transistor is dominated by the MoS₂ channel and not the contacts.

At the bias voltage $V_{ds} = 500 \text{ mV}$, the maximal measured oncurrent is $10 \mu\text{A}$ ($2.5 \mu\text{A } \mu\text{m}^{-1}$), with I_{on}/I_{off} higher than 1×10^8 for the ± 4 V range of V_{tg} . The device transconductance, defined as $g_m = dI_{ds}/dV_{tg}$ at $V_{ds} = 500 \text{ mV}$ is $\sim 4 \mu\text{S}$ ($1 \mu\text{S } \mu\text{m}^{-1}$), similar to values obtained for high-performance CdS nanoribbon array transistors ($2.5 \mu\text{S } \mu\text{m}^{-1}$ at $V_{ds} = 1 \text{ V}$)³⁸. High-performance top-gated graphene transistors can have normalized transconductance values as high as $1.27 \text{ mS } \mu\text{m}^{-1}$ (ref. 39). The large degree of current control in our device is also clearly illustrated in Fig. 4b, where we plot the drain-source current versus drain-source bias for different values of voltage applied to the local gate. From the channel current dependence on top-gate voltage, we deduce a subthreshold slope for the transition between the on and off states of 74 mVdec^{-1} for a bias $V_{ds} = 500 \text{ mV}$. Being a direct gap semiconductor, single layers of MoS₂ offer the intriguing possibility for the realization of an interband tunnel FET, which is characterized by a turn-on sharper than the theoretical limit of 60 mVdec^{-1} for classical transistors and consequently smaller power dissipation. This feat has remained difficult in the

case of silicon, an indirect gap

semiconductor, because interband transitions there require phonons and recombination centres.

To summarize, we have realized a field-effect transistor with a single, two-dimensional layer of the semiconductor MoS₂ as a conductive channel and HfO₂ as a gate insulator. The conductive channel in our device is only 6.5Å thick. Our transistor exhibits a room-temperature current on/off ratio exceeding 1×10^8 and mobility of $\sim 200 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, comparable to the mobility achieved in thin silicon films³⁷ or graphene nanoribbons⁹. Such a transistor could form the backbone of future electronics based on layered materials in which MoS₂ transistors could be fabricated on insulating boron nitride substrates⁴⁰. Our results provide an important step towards the realization of electronics and low-standby-power integrated circuits based on two-dimensional materials. Being a thin, transparent semiconducting material, MoS₂ monolayers also present a wealth of new opportunities in areas that include mesoscopic physics, optoelectronics and energy harvesting. With the possibility of fabricating large-area circuits using solution-based

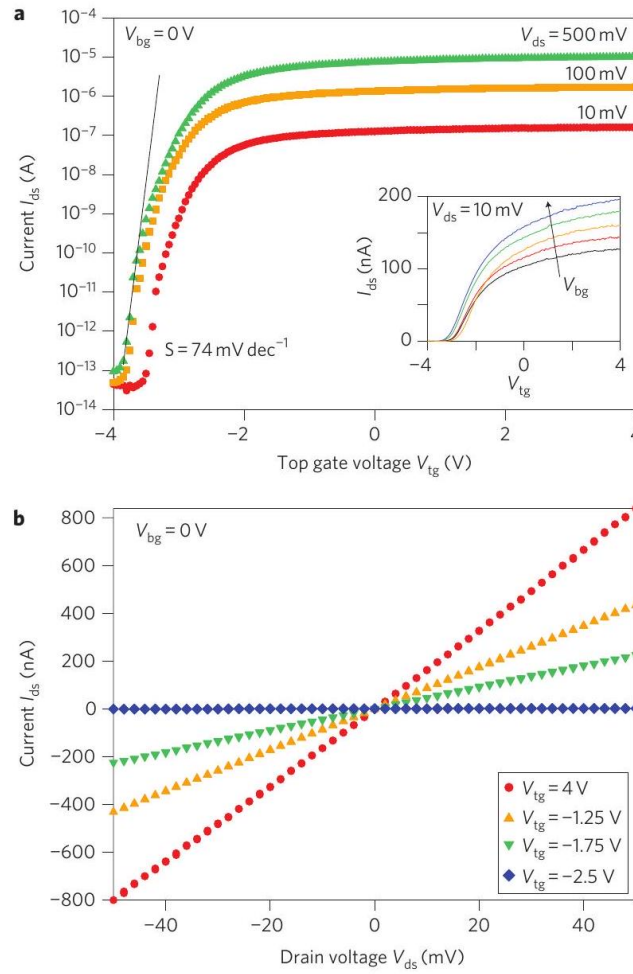


Figure 4 | Local gate control of the MoS₂ monolayer transistor. **a**, $I_{ds} - V_{tg}$ curve recorded for a bias voltage ranging from 10 mV to 500 mV. Measurements are performed at room temperature with the back gate grounded. Top gate width, $4\mu\text{m}$; top gate length, 500 nm. The device can be completely turned off by changing the top gate bias from -2 to -4 V. For $V_{ds} = 10\text{mV}$, the I_{on}/I_{off} ratio is $> 1 \times 10^6$. For $V_{ds} = 500\text{mV}$, the I_{on}/I_{off} ratio is $> 1 \times 10^8$ in the measured range while the subthreshold swing $S = 74\text{mVdec}^{-1}$. Top and bottom gate leakage is negligible (Supplementary Fig. S3). Inset: $I_{ds} - V_{tg}$ for values of $V_{bg} = -10, -5, 0, 5$ and 10 V . **b**, $I_{ds} - V_{ds}$ curves recorded for different values of V_{tg} . The linear dependence of the current on bias voltage for small voltages indicates that the gold contacts are ohmic.

processing, our finding could be important for producing electronic devices that could combine the ease of processing associated with organic conductors with performance figures commonly associated with silicon-based electronics.

Methods

Single layers of MoS₂ were exfoliated from commercially available crystals of molybdenite (SPI Supplies Brand Moly Disulfide) using the scotch-tape micromechanical cleavage technique method pioneered for the production of graphene¹. AFM imaging was performed using the Asylum Research Cypher AFM. After gold contact deposition, devices were annealed in 100 s.c.c.m. of argon and 10 s.c.c.m. H₂ flow at 200°C for 2 h (ref. 28). ALD was performed in a home-built reactor using a reaction of H₂O with tetrakis(dimethylamido)hafnium (Sigma Aldrich). Electrical characterization was carried out using an Agilent E5270B parameter analyser and a home-built shielded probe station with micromanipulated probes.

Received 12 November 2010; accepted 13 December 2010; published online 30 January 2011; corrected online 17 February 2011

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18 Emerging Photoluminescence in Monolayer MoS₂ by Splendiani, Liang Sun, Zhang, Li, Kim, Chim, Galli, Wang (2010)

Abstract

Novel physical phenomena can emerge in low-dimensional nanomaterials. Bulk MoS₂, a prototypical metal dichalcogenide, is an indirect bandgap semiconductor with negligible photoluminescence. When the MoS₂ crystal is thinned to monolayer, however, a strong photoluminescence emerges, indicating an indirect to direct bandgap transition in this d-electron system. This observation shows that quantum confinement in layered d-electron materials like MoS₂ provides new opportunities for engineering the electronic structure of matter at the nanoscale.

Recent advances in fabrication of ultrathin layered materials down to unit cell thickness (monolayers) ¹ have enabled explorations of new low-dimensional physics, as exemplified by massless Dirac fermions and anomalous quantum Hall effects observed in monolayer graphene. ^{2,3} Layered transition metal dichalcogenides represent another class of materials, in which d-electrons' interactions can give rise to new physical phenomena. ^{4,5} MoS₂ is a prototypical transition metal chalcogenide material. It is composed of covalently bonded S – Mo – S sheets that are bound by weak van der Waals forces. In its bulk form, MoS₂ is a semiconductor with an indirect bandgap of about 1eV^{6,7} and it has been exploited for photovoltaic ⁶ and photocatalytic ⁷ applications due to its strong absorption in the solar spectrum region. Quantum confinement effects on the electronic structure and optical properties of MoS₂ have been previously observed in MoS₂ thin films ^{8,9} as well as in MoS₂ nanoplates ¹⁰ and nanotubes. ¹¹ However, little is known about the properties of extended two-dimensional MoS₂ sheets down to unit cell thickness.

Here we report the emergence of photoluminescence in ultrathin layers of MoS₂. We found that MoS₂ photoluminescence, surprisingly, increases with decreasing layer thickness, and that luminescence from a monolayer is the strongest while it is absent in bulk material. This unusual luminescence behavior is in accord with a recent theoretical prediction; MoS₂, an indirect bandgap material in its bulk form, becomes a direct bandgap semiconductor when thinned to a monolayer. Our results demonstrate that quantum confinement in layered d-electron materials have manifestations drastically different from those found in spbonded semiconductor nanostructures.

Ultrathin MoS₂ layers were fabricated using microexfoliation techniques on both quartz and Si/SiO₂ wafers following the prescription of ref 1 . Few-layer MoS₂ flakes were first identified by optical contrast in a microscope. Figure 1 a displays an optical microscope image of a typical ultrathin MoS₂ sample on Si/SiO₂ substrate. The silicon wafer with 280 nm thermal

SiO₂ is represented by the purple-colored background, and regions with different shades of blue correspond to MoS₂ layers of different thicknesses. Comparisons between the observed optical contrast and theoretical estimates indicate that region "1 L" is covered by a monolayer of MoS₂. This identification is confirmed by atomic force microscopy (AFM) images of the same sample (Figure 1b); the average step height from the substrate to flake "1 L" is measured to be 0.7 nm and agrees well with the monolayer thickness of 0.6 nm for S – Mo – S structures.¹² Similarly, we were able to identify region "2L", "4L", and "6L" as bilayer, quadrilayer, and hexalayer MoS₂, respectively (Figure 1c). For few-layer MoS₂ crystals on quartz substrate, we relied on optical contrast for estimation of the layer thickness.

We investigated optical properties in few-layer MoS₂ structures through optical reflection, Raman scattering, and photoluminescence spectroscopy. All the spectroscopy measurements were carried out in a confocal microscopy setup in which we can readily locate and selectively excite MoS₂ flakes of different layer thicknesses. Spatial resolution of the microscopy system is $\sim 1\mu$ m. In reflection spectroscopy, we employed a supercontinuum laser source (Fianium SC-450) to probe MoS₂ samples on the quartz substrate. For Raman scattering and photoluminescence measurements, we used a 532 nm solid state laser to excite few-layers MoS₂ on a Si/

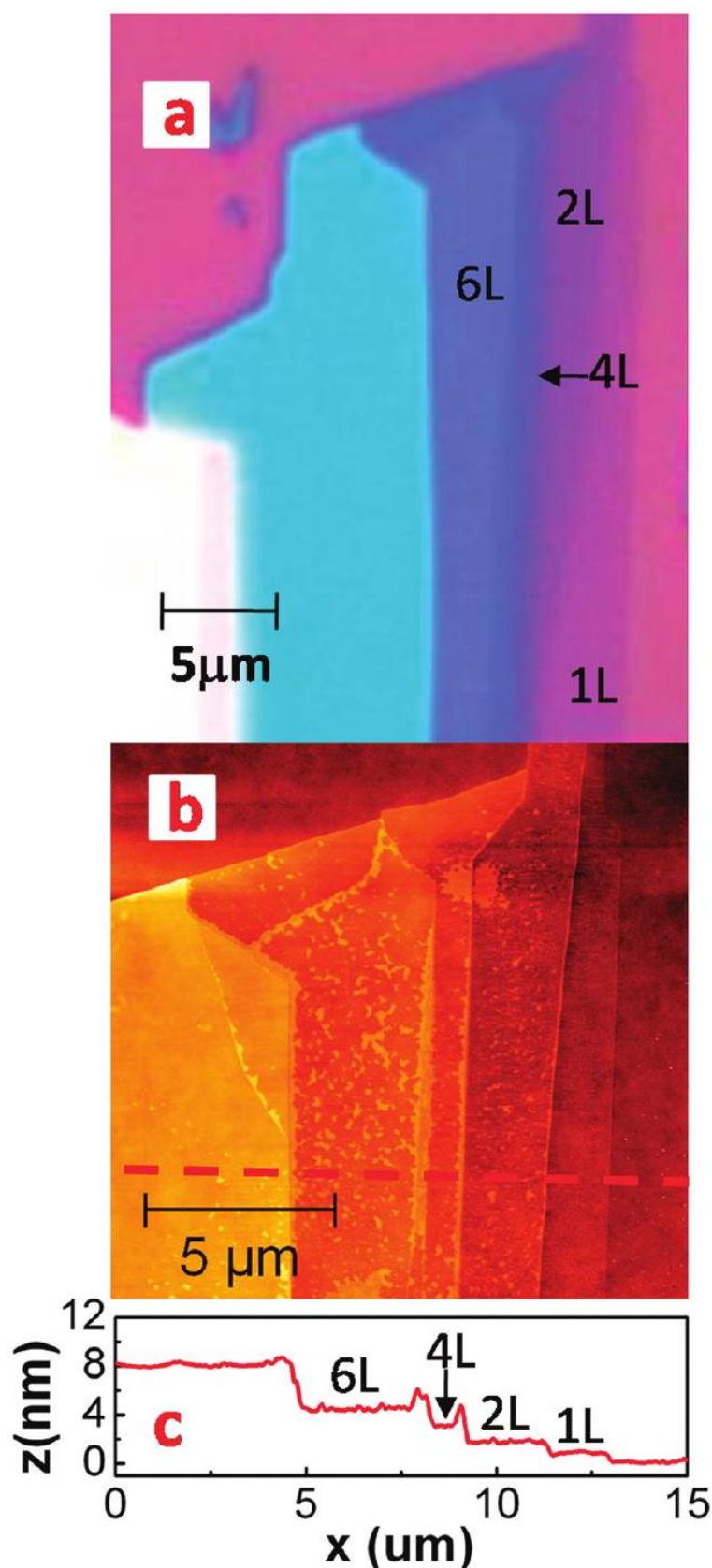


FIGURE 1. Exfoliated MoS₂ flakes on a Si/SiO₂ substrate. (a) Optical microscope image of the exfoliated MoS₂ sample. The purple background is from the Si/SiO₂ substrate and areas with different contrast correspond to MoS₂ flakes of different thicknesses. On the basis of the contrast, we infer areas labeled as "1 L", "2 L", and "4 L" to be monolayer, bilayer, and quadrilayer, respectively. (b) Atomic force microscope (AFM) image of the same sample. (c) Sample height along the red line in *b*, which confirms the optical determined thicknesses of areas 1 L, 2 L, and 4 L. It also shows area 6 L to be a hexalayer.

SiO₂ wafer. In both cases, the spectra were recorded by a spectrometer equipped with a liquid nitrogen cooled camera.

We first determine the optical transitions in few-layer MoS₂ samples using reflection spectroscopy in a microscopy setup. Reflectivity differences between the bare quartz substrate and regions with ultrathin MoS₂ layers were measured across the visible and near IR spectral range (Figure 2a). For ultrathin layers of MoS₂, the difference in reflectivity is directly proportional to the absorption constant.¹³ Two prominent absorption peaks can be identified at 670 and 627 nm in the spectrum. These two resonances have been well established to be the direct excitonic transitions (Figure

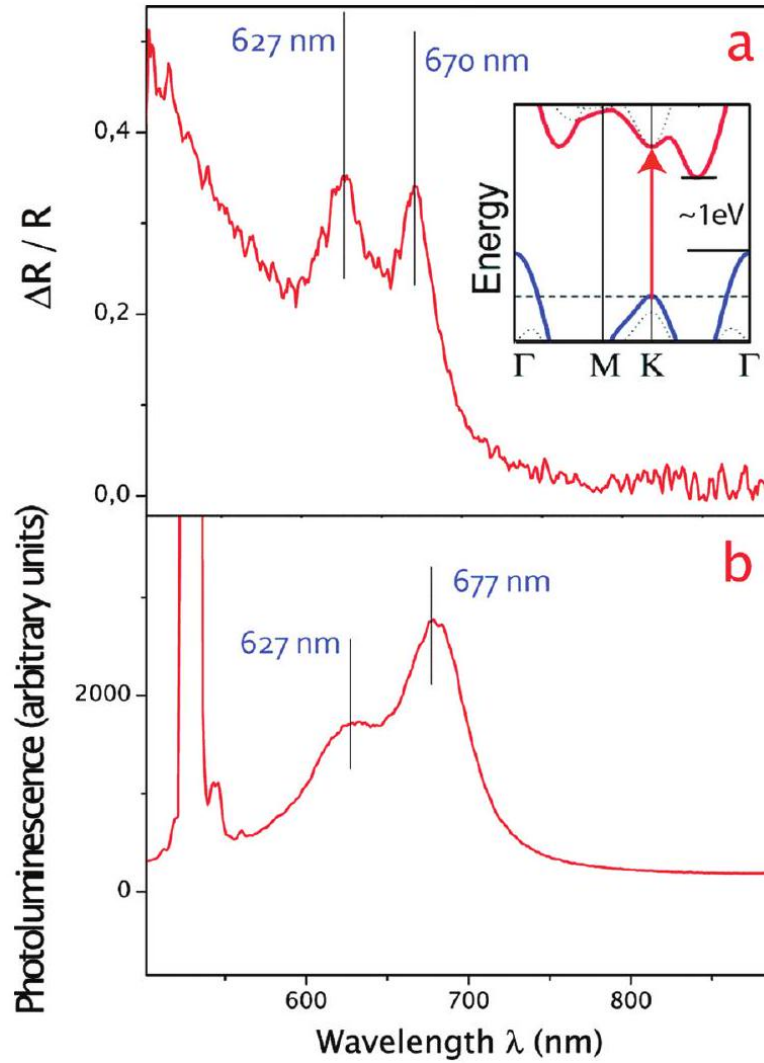


FIGURE 2. Reflection and photoluminescence spectra of ultrathin MoS₂ layers. (a) Reflection difference due to an ultrathin MoS₂ layer on a quartz substrate, which is proportional to the MoS₂ absorption constant. The observed absorption peaks at 1.85 eV (670 nm) and 1.98 eV (627 nm) correspond to the A1 and B1 direct excitonic transitions with the energy split from valence band spin-orbital coupling. The inset shows the bulk MoS₂ band structure neglecting the relatively weak spin-orbital coupling, which has an indirect bandgap around 1 eV and a single higher energy direct excitonic transition at the K point denoted by an arrow. (b) A strong photoluminescence is observed at the direct excitonic transitions energies in a monolayer MoS₂. Such luminescence is absent in the indirect bandgap bulk MoS₂ sample.

2a inset) at the Brillouin zone K point. Their energy difference is due to the spin-orbital

splitting of the valence band (not included in the calculation of Figure 2a inset), and the two resonances are known as A 1 and B 1 excitons, respectively.^{14,15} (The strong peak at 532 nm is the elastic scattered laser radiation.) Optical absorption at energies between the direct excitonic transitions and the indirect bandgap ($\sim 1\text{eV}$) is very weak. For thin layers of MoS_2 , absorption peaks from the direct excitonic states exhibit little change with layer thicknesses.

Photoluminescence, however, exhibits a very different behavior. Figure 2b displays a photoluminescence spectrum of a monolayer MoS_2 . Pronounced luminescence emissions are observed at the A1 and B1 direct excitonic transitions. This photoluminescence emission in monolayer is in striking contrast to its absence in bulk MoS_2 , a consequence of bulk MoS_2 being an indirect bandgap semiconductor like silicon. In Figure 3a, we examine in more detail photoluminescence spectra from monolayer, bilayer, hexalayer, and bulk MoS_2

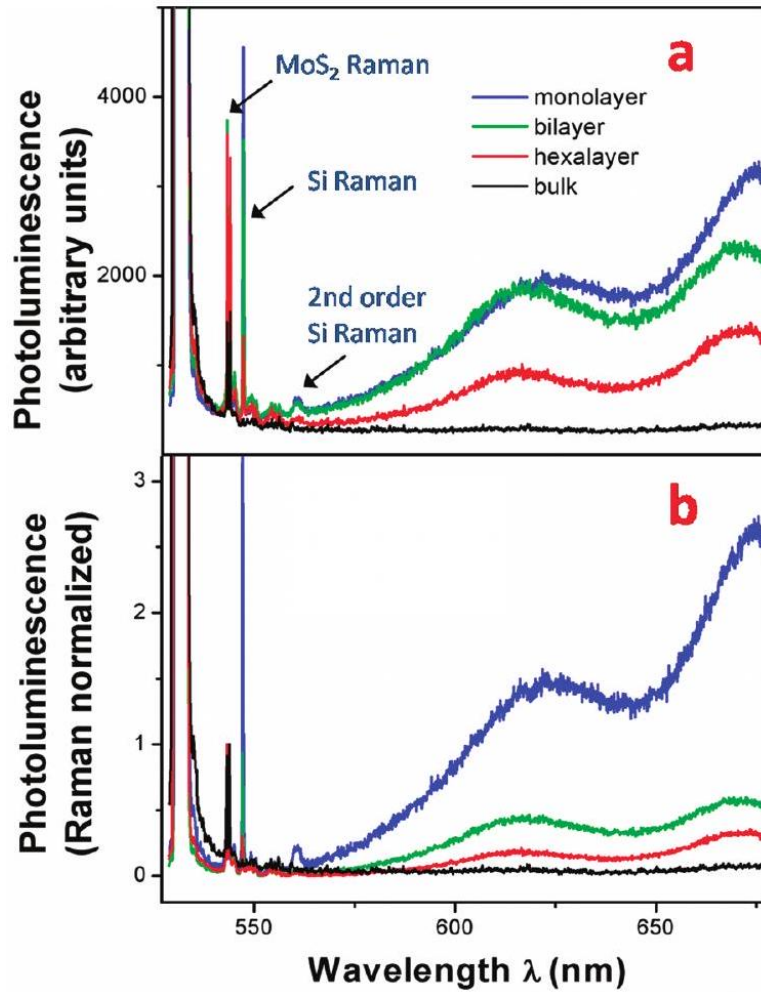


FIGURE 3. Layer dependence of photoluminescence efficiency in MoS_2 . (a) Photoluminescence and Raman spectra of MoS_2 monolayer, bilayer, hexalayer, and bulk sample. Different Raman peaks can be assigned to the MoS_2 and silicon vibration modes. For MoS_2 thin layers, monolayer MoS_2 Raman signal is relatively weak because less material is being excited. However, photoluminescence is the strongest in monolayer MoS_2 in spite of reduced material. (b) Photoluminescence spectra normalized by Raman intensity for MoS_2 layers with different thickness, showing a dramatic increase of luminescence efficiency in MoS_2 monolayer.

(in the form of very thick flakes). In addition to the relatively broad photoluminescence, three prominent Raman modes can be identified in the spectra: the first peak corresponds to a MoS_2 Raman excitation with a 408 cm^{-1} Raman shift¹² and the next two at 520 and

1030 cm^{-1} are the first and second order Raman peaks from the silicon substrate.¹⁶ In bulk MoS_2 , no photoluminescence is observable and the MoS_2 Raman signal is weak because of the local field effect, that is, the local electric field at a high refractive index material like MoS_2 is much weaker than the incident electrical field. For ultrathin MoS_2 layers where local field effects are relatively small, the Raman and photoluminescence intensities show opposite layer dependence: MoS_2 Raman signal is the weakest in the monolayer MoS_2 (due to reduced amount of material), while photoluminescence is the strongest in spite of the reduced amount of material. This surprising behavior of the photoluminescence indicates that luminescence quantum efficiency is much higher in MoS_2 monolayer than in multilayer and in the bulk.

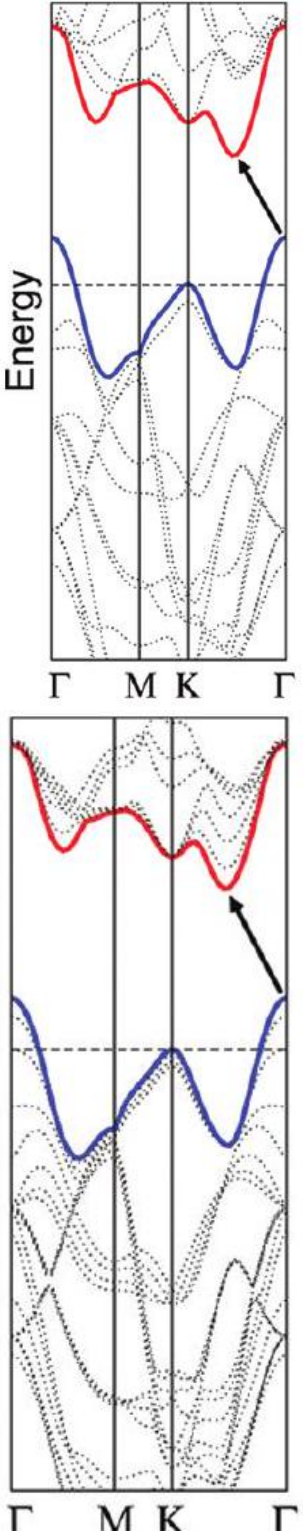
Next we determine layer dependent luminescence quantum efficiency η_{Lum} using an internal calibrator provided by MoS_2 Raman signal. MoS_2 Raman intensity I_{Raman} and luminescence intensity I_{Lum} are affected in the same manner by effects such as laser excitation intensity, quantity of material, and local electric field factors; therefore such external effects are canceled out in the ratio $I_{\text{Lum}}/I_{\text{Raman}}$ and this ratio provides a measure of intrinsic luminescence quantum efficiency through the quantity $\eta_{\text{Lum}} \approx \eta_{\text{Raman}} (I_{\text{Lum}}/I_{\text{Raman}})$. In this equation, we have neglected the small energy difference between luminescence and Raman scattered photons. Because Raman scattering efficiency η_{Raman} usually has little layer thickness dependence, the photoluminescence spectra normalized by Raman intensity (Figure 3b) reflects directly the luminescence efficiency η_{Lum} . A dramatic jump of luminescence quantum efficiency in MoS_2 monolayer is evident.

The observed optical behavior in few-layer MoS_2 has several unique characteristics. Bulk MoS_2 does not exhibit luminescence and has strong direct excitonic absorption at energies much larger than the indirect bandgap. These excitonic states become strongly luminescent in MoS_2 monolayer, but they remain at the same transition energies as in the bulk. These characteristics are profoundly different from the behaviors reported in other low dimensional semiconductor nanostructures. Nanostructures obtained from direct bandgap semiconductors usually emit strongly upon photoexcitation, but the luminescence is present in the bulk as well. Nanostructures obtained from indirect bandgap semiconductors such as silicon show some apparent similarities to MoS_2 in that silicon nanocrystals display enhanced photoluminescence compared with bulk silicon.¹⁷ However, the underlying physics is markedly different. In silicon nanocrystals, the photoluminescence originates from quantum confined electronic states with increased emission energy at decreased nanoparticle size. More importantly, the optical transitions in silicon nanocrystals larger than $\sim 2 - 3\text{ nm}$ are still indirect-gaplike with strong optical vibronic origins,¹⁸ and the radiative transition rate remains quite low (at kHz). In addition, optical transitions in small Si nanoparticles are strongly dependent on the surface structure.¹⁹ In contrast, MoS_2 luminescence arises from direct electronic transitions, which are allowed and thus show a much higher radiative recombination rate. Therefore no previously known mechanism in other nanostructures can account for the photoluminescence behavior in MoS_2 .

The observed MoS_2 monolayer photoluminescence must be an intrinsic material property rather than due to external perturbations such as defect states, since the luminescence resonances match perfectly the direct excitonic transitions. Luminescence quantum efficiency from such direct excitonic state in MoS_2 can be approximated by $\eta_{\text{Lum}} \approx k_{\text{rad}} / (k_{\text{rad}} + k_{\text{defect}} + k_{\text{relax}})$, where k_{rad} , k_{defect} , and k_{relax} are, respectively, rates of radiative recombination, defect trapping, and electron relaxation within the conduction and valence bands. Because the rate of intraband relaxation to band minimum (k_{relax}) is extremely high, photoluminescence from direct excitonic transitions is usually not observable in indirect bandgap semiconductors. In monolayer MoS_2 , k_{rad} is not

a
b

C
d



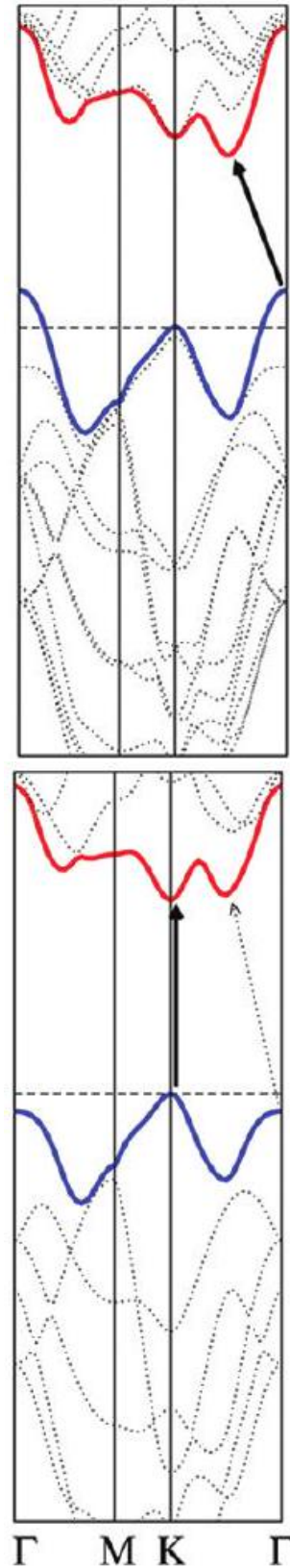


FIGURE 4. Calculated band structures of (a) bulk MoS₂, (b) quadrilayer MoS₂, (c) bilayer MoS₂, and (d) monolayer MoS₂. The solid arrows indicate the lowest energy transitions. Bulk MoS₂ is characterized by an indirect bandgap. The direct excitonic transitions occur at high energies at K point. With reduced layer thickness, the indirect bandgap becomes larger, while the direct excitonic transition barely changes. For monolayer MoS₂ in d, it becomes a direct bandgap semiconductor. This dramatic change of electronic structure in monolayer MoS₂ can explain the observed jump in monolayer photoluminescence efficiency.

likely to change appreciably with respect to bulk value, because the direct excitonic transitions remain at the same energy. Therefore, the enhanced photoluminescence in monolayer has to be attributed to a dramatically slower electronic relaxation k_{relax} . The decrease of interband relaxation rate strongly suggests a substantial change in MoS₂ electronic structure when going from the bulk to monolayer.

Electronic structure of bulk and monolayer MoS₂ has been previously investigated through ab initio calculations.^{20,21} Recent theoretical results using improved algorithm and computation power predict that the indirect bandgap bulk MoS₂ becomes a direct bandgap semiconductor when thinned to a monolayer,²¹ which can readily account for our experimental observations. For a detailed comparison between experiment and theory, we calculated the band structures of bulk MoS₂ and ultrathin MoS₂ layers with different thicknesses. We employed density functional theory with generalized gradient approximation using the PWscf package.²² The calculation results are displayed in Figure 4. It is shown that the direct excitonic transition energy at the Brillouin zone K point barely changes with layer thickness, but the indirect bandgap increases monotonically as the number of layers decreases. Remarkably, the indirect transition energy becomes so high in monolayer MoS₂ that the material changes into a two-dimensional direct bandgap semiconductor. The variation of the electronic structure in few-layer MoS₂ is in accord with our experimental data. With the increase of the indirect bandgap in thinner MoS₂, the intraband relaxation rate from the excitonic states decreases and the photoluminescence becomes stronger. In the case of monolayer MoS₂, a qualitative change into a direct bandgap semi-

conductor renders $k_{\text{relax}} = 0$, leading to a dramatic jump of luminescence that is only limited by the defect trapping rate k_{defect} . In MoS₂ of all thicknesses, the direct excitonic transition at the K point remains at roughly the same energy.

The unusual electronic structure of few-layer MoS₂ and the resulting unique optical behavior stem from the characters of d-electron orbitals that comprise MoS₂ conduction and valence bands. Our theoretical calculations show that electronic states of different wave vectors have electron orbitals with different spatial distributions. Specifically, conduction band states at the K point are primarily composed of strongly localized d orbitals at Mo atom sites. They have minimal interlayer coupling since Mo atoms are located in the middle of the S – Mo – S unit cell. On the other hand, states near the Γ point and the point of indirect bandgap originate from a linear combination of d orbitals on Mo atoms and antibonding p_z orbitals on S atoms. They have strong interlayer coupling and their energies depend sensitively on layer thickness.

In conclusion, our study reveals a surprising emergence of photoluminescence in MoS₂ layers. This observation is consistent with the theoretical prediction of indirect to direct bandgap transition in going from multilayer to monolayer MoS₂. Such behavior, arising from d-orbital related interactions in MoS₂, may also arise in other layered transition metal dichalcogenides. It points out a new direction for controlling electronic structure in nanoscale materials by exploiting rich d-electron physics. Such capability can lead to engineering novel optical behaviors not found in spbonded materials and holds promise for new nanophotonic applications.

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19 On the properties of monolayers of adsorbed atoms by Pokrovsky, Uimin (1977)

(Viktor said that here, the analytical calculation was done for 2d lattice, but if one adds atoms, not electrons. I'll learn it later)

Abstract

The structure of monolayers adsorbed on solids is investigated and the consequences of particular force laws explored. The dipole-dipole interaction is assumed to predominate and a model is developed which explains the experimentally observed commensurate and incommensurate monolayer structures and the behaviour of the Debye-Waller factor.

19.0.1 1. Introduction

During recent years both experimental as well as theoretical activity in the physics of adsorbed monolayers has increased rapidly. Proper experimental methods, especially electron diffraction (Bolshov et al 1977) and neutron scattering (Nielsen et al 1977) made it possible to determine the monolayer structures as well as static and dynamic response functions. The preceding theoretical works have been concerned mainly with the character of the interaction between adsorbed atoms (hereafter abbreviated as 'adatoms'). One can find the full list of references on this topic in the reviews (Schrieffer 1972, Grimley 1975, Bolshov et al 1977). The structural consequences of particular force laws have hitherto drawn much less attention. Only the works of Bolshov (1973) and Kaburagi and Kanamori (1974) can be mentioned in this

connection. The existence of crystal structures at $T = 0$ and rational concentration of adatoms was first indicated by Lifshitz and Tanatarov (1955-60).

Experimentally there are two different classes of monolayers. The first class consists of monolayers of sodium or potassium metals adsorbed on a surface of monocrystalline tungsten or molybdenum. The adatoms give their external electrons to a substrate metal and become ions. Their electrical images have negative charge and together with initial ions form dipoles. The main force in these systems is the dipole-dipole interaction (repulsion), which decreases as the cube of the distance between dipoles. However if adatoms are small and positioned too close to a surface of substrate metal the interaction with conduction electrons appears. In this case the forces between adatoms are Friedel oscillation ones (Gabovich and Pashizky 1976). For a surface with a low Miller index these forces can usually be neglected. Many crystal structures of the first class have been obtained and investigated by Naumov and Fedorus (1977) and their coworkers and have been described in the review of Bolshov et al (1977). The dipole interaction is also the definitive force for adatoms of noble gases on the metal substrate because these adatoms become strongly polarised.

The monolayers of the second class are formed with atomic or molecular oxygen adsorbed on tungsten or molybdenum surfaces (Buchholz and Lagally 1975) and oxygen, molecular hydrogen, nitrogen and deuterium adsorbed on graphite or grafoil (Nielsen et al 1977). Adatoms of the second class do not lose their electrons and in this case the Van-der-Waals forces and repulsion of inner electron shells predominate. The phase diagrams of these second-class systems are usually more complicated than those of the first class. The common feature for both classes is the existence of commensurate plain lattices at small concentrations of adatoms and incommensurate lattices at sufficiently large concentrations. These lattices differ considerably as far as the temperature behaviour of the Debye-Waller factor is concerned (Naumov and Fedorus 1977, Nielsen et al 1977). The Debye-Waller factor of commensurate lattices remains unchanged up to the phase transition (usually between 100 and 300 K) and decreases very sharply at the phase transition temperature. However, it changes gradually without any jumps in the case of an incommensurate structure. In figure 1 the experimental curves

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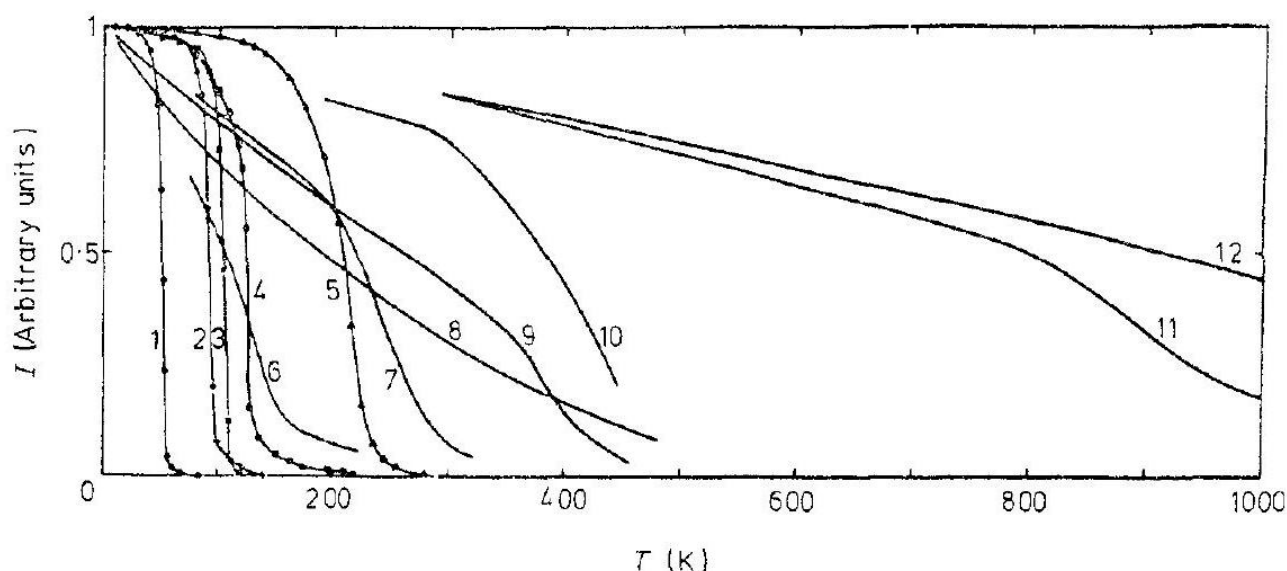


Figure 1. The temperature dependence of the electron-diffraction peak intensities (Naumovez and Fedorus 1977): 1 Sr -Mo (011), $c = 1/9$; 2Li - W(011), $c = 1/6$; 3Li - W(011), $c = 1/4$; 4Na - W(011), $c = 1/4$; 5Li - W(011), $c = 1/3$; 6Cs - W(011), $c = 0.48$; 7Na - W(011), $c = 0.80$; 8Sr - Mo(011), $c = 0.75$; 9Sr - Mo(011), $c = 0.64$; 10Sr - W(011), $c = 0.70$; 11La - W(011), $c = 0.75$; 12La - W(011), $c = 0.80$; where c is the concentration of adatoms.

of the electron-diffraction peak intensities are shown. The graphs are taken from the work by Naumovez and Fedorus (1977). Similar though less clear results have been obtained by Nielsen et al (1977).

In this work we investigate the ground state of the incommensurate lattice and its influence on the scattering picture. Meanwhile the experimental investigation of commensurate crystal structures and the comparison of them with the theoretical predictions may give information on the character of interatomic forces. Here the commensurate crystal structures for adatoms interacting as dipoles are established.

We shall call the lattice of adatoms the secondary lattice to distinguish it from the substrate lattice.

19.0.2 2. Incommensurate structures

The main difference between the commensurate and the incommensurate structures lies in the form of the oscillation spectra. The substrate surface may be considered as a periodical potential relief. The atoms (or ions) of commensurate structures are situated at the bottom of periodical potential wells. There is no translational invariance in this case. Therefore only the optical branches of oscillations exist. The frequency ω_0 of optical oscillations are defined either with the properties of a single well, provided it is sufficiently deep, or with the well and interatomic forces together, but never with interatomic forces only, otherwise the commensurate lattice would not exist. The Hohenberg-Mermin-Wagner theorem stating the absence of long-range order in two-dimensional continually degenerate systems (Hohenberg 1967, Mermin and Wagner 1966) is founded substantially on the existence of a gapless (Goldstone) mode in a system. Therefore it does not hold for commensurate structures, and long-range order may exist in these systems.

From the naïve point of view the incommensurate lattice of adatoms can be shifted with respect to the substrate lattice by an arbitrary vector without change of energy. The translational symmetry is restored in these systems. According to the general theorems of lattice

dynamics it implies the existence of two acoustic branches of oscillations. They influence in a quite decisive way the different static as well as dynamic properties of monolayers.

Certainly the words 'commensurate' and 'incommensurate' have a restricted physical meaning. Evidently meaningless is an attempt to commensurate lattices with too high precision, for instance, more than the distance between grain boundaries. The other restriction is connected with temperature: the interaction between the most distanced atoms in the elementary cell has to be more than temperature. Otherwise the large cell would melt. On the other hand one cannot be sure that an apparently incommensurate structure is not really commensurate with a large period. If the basic cell of a possibly commensurate structure contains more than N adsorbed atoms, the corresponding binding energy per atom (or the gap) is much less than $\sim V_0$, where V_0 is the depth of the well (by the order of magnitude). This small gap is significant provided the temperature T is less than $V_0^{N-N+1}\epsilon_0$, where ϵ_0 is the characteristic interaction energy.

The systems with restored translational invariance obey the Hohenberg-Mermin-Wagner theorem. Long-range order is not theoretically possible in an infinitely large system. However, the real systems are finite and fluctuations of the order parameter are very small compared with its mean value. Indeed the mean square of the amplitude of atomic displacement can be written in the usual way:

$$\langle u^2 \rangle = \frac{\hbar v_0}{M} \int \left(n_q + \frac{1}{2} \right) \frac{2}{\omega_q} \frac{d^2 q}{(2\pi)^2} \quad (1)$$

where $n_q = (\exp(\hbar\omega_q/T) - 1)^{-1}$, v_0 is the area of the elementary cell; M is the mass of the atoms. For the sake of simplicity the two acoustic branches are assumed to be identical. Small wavenumbers give the main contribution to the integral in equation (1). Fluctuations are classical and obey the Rayleigh-Jeans distribution. The integral diverges logarithmically and has to be cut off by $q \sim R^{-1}$ from below (R is the characteristic length of the system). The upper cut-off momentum q_0 is defined by $\hbar\omega_q/T \sim 1$. It depends on temperature and increases from T/s (s being the sound velocity) at low temperature to $1/a$ at a temperature of the order of the Debye temperature. Consequently

$$\langle u^2 \rangle \approx \frac{T v_0}{\pi M s^2} \ln(R q_0) \quad (2)$$

The value of $M s^2$ varies from 1 – 10 eV for a dipole interaction at large concentrations to about 0.01 eV for argon atoms. We shall neglect the change of q_0 and substitute it with the inverse atomic constant. Then R/a is about 10^7 in the experiments of Naumov and Fedorus (1977) and about 100 in the experiments of Nielsen et al (1977). It is clear that $\langle u^2 \rangle$ is much smaller than v_0 in both cases. These ideas were proposed independently by Naumov and Fedorus (1977) and by Nielsen et al (1977).

In the work by one of the authors (Pokrovsky 1977) the incommensurate structure was shown really to have the acoustic branch of the oscillation spectrum. Here a brief outline of that work will be given (see also the earlier work by Ying 1971) and the new results will be added.

The model considered is a one-dimensional system of strongly interacting atoms with a fixed concentration c in a weak periodic potential $V(x) = V_0 \cos q_0 x$. The simplifying assumptions on dimensionality and form of the potential can be easily removed. In the zero-approximation with respect to V_0 the atoms form a regular lattice. The elastic energy of this lattice can be represented with the quadratic form of displacement of atoms:

$$H_e = \frac{1}{2} \sum_q \epsilon_q^0 \hat{u}_q \hat{u}_{-q} \quad (3)$$

Here $\hat{u}_q$ is the Fourier-transform of displacement of the n th atom u_n from its zero-approximation equilibrium position $x_n^0 = n$ (we put $a = 1$)

$$\hat{u}_q = \frac{1}{\sqrt{N}} \sum_n u_n \exp(iqn)$$

and N is the total number of atoms. ϵ_q^0 is a periodic function of q with period 2π . At small wavenumbers it depends quadratically on q : $\epsilon_q^0 = kq^2$, k being the elastic constant. The total Hamiltonian is equal to the sum of the elastic and potential energy:

$$H = H_e + V_0 \sum_n \cos(n + u_n) q_0 \quad (4)$$

The stationary state of the Hamiltonian (4) corresponds to the non-zero u_n :

$$u_n = (V_0 q_0 / \epsilon_0) \sin q_0 n \quad (5)$$

where $\epsilon_0 = \epsilon_{q_0}^0$. The quantity $q_0/2\pi$ is assumed to be an irrational number. Expanding the total energy up to the second power of the displacements v_n of atoms from their stationary positions $x_n = n + (V_0 q_0 / \epsilon_0) \sin q_0 n$, we obtain the new quadratic form:

$$\begin{aligned} H &= E_0 + \frac{1}{2} \sum_q \left(\epsilon_q^0 + \frac{V_0^2 q_0^4}{2\epsilon_0} \right) \hat{v}_q \hat{v}_{-q} - \frac{V_0 q_0^2}{2} \sum_n \cos(q_0 n) v_n^2 \\ E_0 &= -\frac{1}{4} N V_0 (V_0 q_0^2 / \epsilon_0) \end{aligned} \quad (6)$$

Here $\hat{v}_q$ is the Fourier-transform of v_n . The diagonalisation of the quadratic form (6) results in the following form for the spectra in the second approximation with respect to V_0 :

$$\epsilon_q = \epsilon_q^0 + \frac{V_0^2 q_0^4}{4} \left(\frac{2}{\epsilon_0} - \frac{1}{\epsilon_{q+q_0}^0 - \epsilon_q^0} - \frac{1}{\epsilon_{q-q_0}^0 - \epsilon_q^0} \right). \quad (7)$$

It has the sound-like form for small wavenumbers. The elastic constant k , however, is renormalised

$$k_{\mathbf{R}} = k - \frac{V_0^2 S_0^2 q_0^4}{2\epsilon_0^3} \quad (8)$$

where

$$S_0^2 = \left[\left(\frac{\partial \epsilon^0}{\partial q} \right)^2 + \epsilon_0 \left(k - \frac{\partial^2 \epsilon}{\partial q^2} \right) \right]_{q=q_0}$$

Thus the acoustic branch exists provided $k > V_0^2 q_0^4 S_0^2 / 2\epsilon_0^3$. The existence of an acoustic branch is the consequence of the invariance of the system under the quasi-translations. It means that the energy does not depend on ζ provided the displacements have the form

$$u_n = \xi + (V_0 q_0 / \epsilon_0) \sin(q_0(n + \xi)).$$

This symmetry spontaneously breaks at $V_0^2 q_0^4 S_0^2 / 2\epsilon_0^3 k = 1$. The structures arising at large values of V_0 will be considered in §§3 and 4.

So far we have considered lattices with fixed concentrations of the adatoms. It is true for the real case of the repulsive interaction between adatoms located in a limited area. If adatoms attract each other they form a condensed phase with a concentration determined by

details of the interaction only. For the mathematical description of these systems the tensor of deformation $\mathbf{u}_{ik}$ will be introduced. It can be reduced to the scalar value δ in the one-dimensional case. The equilibrium distance between adatoms in the deformed chain is equal to $(1 + \delta)$. The energy of the deformed lattice can be found as the sum of the elastic part of the deformation energy $\frac{1}{2}k\delta^2$ and the expression (6) for E_0 , where the momentum q_0 and 'energy' have to be substituted with:

$$\begin{aligned} q'_0 &= (1 + \delta)q_0 \\ \epsilon'_0 &= (1 + \delta)^2 \left(\epsilon_0 + \left(\partial \epsilon^0 / \partial q \right)_{q=q_0} \delta q_0 \right) \end{aligned}$$

Minimising the energy value over δ one can find its equilibrium value:

$$\delta_0 = -\frac{V_0^2 q_0^2}{4k\epsilon_0^2} \left(\frac{\partial \epsilon^0}{\partial q} \right)_{q=q_0}$$

The oscillation spectrum changes only in the next order of the parameter $(V_0/\epsilon_0)^2$. In two- and three-dimensional cases the energy of the ground state and generated deformations depend on the mutual orientation of secondary and substrate lattices. The orientational dependence of energy was first investigated by Novaco and McTague (1977). The sound velocity obviously depends on the direction of propagation. Thus the mutual orientation of the lattices and deformations depend on the temperature even in the harmonic approximation.

Note that the oscillation spectrum of the incommensurate lattice has gaps if $q = \frac{1}{2}(mq_0 + b)$ where m is an integer and b is a reciprocal-lattice vector. This is similar to the appearance of gaps caused by Bragg scattering in the well known spectrum of particles placed in a periodic potential. Reducing all wavevectors $\{q\}$ to the first Brillouin zone of the initial adatom lattice one can find that the spectrum splits at any point. The sum of the gaps does not exceed V_0 , and the value of a gap decreases as V_0^m . Particularly the gaps in the long-wave range are very small and do not essentially influence the character of this part of the spectrum. The analogous peculiarities of the one-dimensional Schrödinger equation were examined by Dinaburg and Sinai (1976). Of course very small gaps will be smeared by quantum and temperature fluctuations. However we expect the existence of a rather fantastic oscillation spectrum.

The neutron experiments by Nielsen et al (1977) revealed explicitly the existence of optic branches in commensurate structures. It would be interesting to find experimentally the acoustic branch of the spectrum of incommensurate structures.

19.0.3 3. Commensurate structures. One-dimensional case

We start with the one-dimensional case as a very simple model displaying properties which are useful for further investigation. Besides this, the one-dimensional case is interesting in itself due to the possible application to electronic superlattices in the onedimensional crystals TTF-TCNQ.

The problem is to minimise the interaction energy

$$E = \frac{1}{2} \sum_{x_i, x_j} u(|x_i - x_j|) \quad (9)$$

with the proper distribution of adatoms among the sites of a one-dimensional lattice x_i . Here $u(x)$ is the pair interaction energy which is assumed to be: (i) positive at any x (repulsion) (ii) monotonically decreasing with distance x , (iii) tending to zero as $x \rightarrow \infty$ more rapidly than x^{-1} and (iv) convex.

With these premises the structure is defined only for a given concentration of adatoms c . c is defined as the ratio of the number of adatoms to the number of sites. The solution of the

problem will first be formulated and then will be explained. Only concentrations of adatoms c smaller than $\frac{1}{2}$ may be considered; otherwise the concentration of holes $(1 - c)$ has to be considered instead. The concentration c has to be expanded into a continual fraction

$$c = \frac{1}{p_1 \pm \frac{1}{p_2 \pm \frac{1}{p_3 + \dots}}} \quad (10)$$

where all p_i are positive integers and all partial fractions r_i , defined with the system of equalities

$$1/r_{i-1} = p_i \pm r_i \quad (11)$$

are smaller at absolute value than $1/2$. These requirements define the expansion (10) unambiguously. If c is a rational number $c = m/n$, where m and n are integers without common multipliers and $m < n$, it can be proved that the denominators of r_i decrease with the index i so that expansion (10) is finite. The elementary cell has length n and contains m adatoms. The distance between nearest neighbours may be equal to p_1 or $p_1 \pm 1$ (the sign is the same as in fraction (10) after p_1). The intervals of length $p_1 \pm 1$ are separated with p_2 or $p_2 \pm 1$ intervals of length p_1 .

One can consider intervals of length $p_1 \pm 1$ as some new particles (first-order particles), the intervals of length $(p_2 \pm 1)p_1$ between first-order particles as second-order particles etc. In such a way the elementary cell is fully constructed. In the general case the meaning of p_i remains the same as before. The quantities r_i are the concentrations of the i th order particles. It is worthwhile to emphasise that in the case of irrational c the structure is not random and conserves at least very strong correlations.

In order to explain our result consider first the energy of interaction of nearest neighbours only:

$$E_1 = \sum_k u(x_{k+1} - x_k) \quad (12)$$

Introducing the probabilities $w(n)$ for the distance between neighbouring atoms to be equal to n , the energy E_1 can be rewritten as

$$E_1 = N \sum_{n=1}^{\infty} w(n)u(n) \quad (13)$$

where N is the total number of atoms. The requirements of normalisation and fixed concentration c have to be imposed:

$$\sum_{n=1}^{\infty} w(n) = 1; \quad \sum_{n=1}^{\infty} nw(n) = 1/c \quad (14)$$

The minimum of a linear function with linear restrictions imposed can be situated only on the boundary of the region of possible values of arguments. The arguments of the function E_1 (equation (13)) are the quantities $w(n)$. They are restricted by (14) and the inequalities $w(n) \geq 0$. Consequently, the maximally possible number of quantities $w(n)$ have to turn to zero at the minimum. The minimal number of non-zero probabilities $w(n)$, compatible with the conditions (14) is two. When only two of $w(n)$ are not zero they can be found explicitly. Let m and n be values of n corresponding to non-zero probabilities and $m < 1/c < n$. Then

Then

$$w(m) = \frac{n - (1/c)}{n - m} = 1 - w(n)$$

$$\frac{E_1}{N} = \frac{[n - (1/c)]u(m) + [(1/c) - m]u(n)}{n - m} \quad (15)$$

One can easily prove that E_1 is minimal at $m = [1/c]$ and $n = [1/c] + 1$ where $[x]$ is the entier of x and $w(m), w(n)$ are equal to the first partial fraction r_1 and $1 - r_1$ (see equation (11)). One of the integers $[1/c]$ or $[1/c] + 1$, which is nearer to $1/c$ than the other has to be accepted as p_1 (see the definition after equation (10)).

The next step is to consider the interaction of next-nearest neighbours. It is governed with the two-point probability $w(k, l)$ of two consequent distances between atoms:

$$E_2 = \frac{N}{2} \sum_{k,l} w(k, l) u(k + l) \quad (16)$$

with the normalisation conditions imposed

$$\sum_l w(k, l) = w(k), \quad \sum_k w(k, l) = w(l) \quad (17)$$

The maximally possible number of zeros among $w(m, n)$ and $w(n)$ which is compatible with conditions (14) and (17) can be obtained by putting all the $w(n)$ except two $w(m)$ and $w(n)$ equal to zero as before, and all $w(k, l)$ except $w(m, m), w(m, n) = w(n, m)$ and $w(n, n)$ equal to zero. After that one can check that the minimum of E_2 may be reached provided m and n have the former values p_1 and $p_1 \pm 1$ and $w(p_1 \pm 1, p_1 \pm 1) = 0$. Simultaneously the energy of the nearest-neighbour interaction becomes minimal. The problem of minimising E_2 is now reduced to the former problem by substituting the intervals $p_1 \pm 1$ as new particles, the intervals p_1 as new holes and $w(p_1, p_1)$ and $w(p_1, p_1 \pm 1)$ as new probabilities. This process may be repeated any number of times to give the full proof of our solution.

Certainly, this mathematical problem has some unphysical features. One can not expect the very complicated structure to exist for at least two reasons. One of them is the temperature restrictions discussed earlier. The other is the fact that at the low temperatures which are necessary for the existence of complicated structures diffusion processes proceed very slowly and thermodynamical equilibrium in practice may prove unreachable.

On the other hand the change of density does not produce the phase transition at any rational concentration if the temperature is finite. One can estimate the largest size of an elementary cell which can exist at a given temperature T (after an arbitrarily long time) as $n \sim (1/c) (\epsilon_d/T)^{2/3}$, where ϵ_d is the dipole-dipole interaction between atoms situated at neighbouring sites of the lattice.

The problem is purely geometrical (or number-theoretical) only in the case of repulsion, while the attraction results in more complicated structures with phase separation etc. Even the change of sign $u''(x)$ implies the decisive transformation of the solution, which becomes more sensitive to the details of the interaction.

As far as we know the solution described above has not been obtained up to now. The different aspects of the solution of the one-dimensional problem were discussed in the work by Bolshov et al (1973).

19.0.4 4. Structures in two dimensions

The structures in the two-dimensional lattice are much more difficult to investigate. Even the simplest case $c = 1/p$, where p is an integer, has not been considered up to now. Here

we shall restrict ourselves to the detailed consideration of this experimentally most interesting case. Other cases will be considered only in a rather general form, without details. The method for constructing complicated lattices is actually an unsolved problem.

The basic vectors of the substrate and secondary lattices are denoted $\mathbf{a}_0\mathbf{b}_0$ and $\mathbf{a}$ and $\mathbf{b}$ and

$$\mathbf{a} = k_0\mathbf{a}_0 + l_0\mathbf{b}_0; \quad \mathbf{b} = m_0\mathbf{a}_0 + n_0\mathbf{b}_0. \quad (18)$$

Here k_0, l_0, m_0 and n_0 are integers. The following restrictions may be imposed without loss of generality:

$$k_0 \geq n_0, \quad k_0 > m_0, \quad n_0 > l_0; \quad k_0 > 0, \quad n_0 > 0 \quad (19)$$

The concentration c may be expressed as follows

$$c = (k_0n_0 - l_0m_0)^{-1} \quad (20)$$

The conditions (19) restrict strongly the absolute values of k_0 and n_0 at a given concentration i.e. the inequality

$$k_0 + n_0 \leq (1/c) + 1 \quad (21)$$

follows strictly from (19) and (20).

The general lattice vector of the secondary lattice has the form $\mathbf{r} = k\mathbf{a} + l\mathbf{b}$ with k and l being integers. In this and the next sections we shall consider only the power-like repulsion interaction

$$U(\mathbf{r} - \mathbf{r}') = \frac{g}{|\mathbf{r} - \mathbf{r}'|^{2s}}, \quad (s > 1) \quad (22)$$

where g and s are constants. For the dipole interaction $s = 3/2$. The lattice is obviously simple for $c = 1/p$ and p is an integer. In this case the area of the basic cell of the secondary lattice is equal to p . The potential energy of the lattice is equal to

$$E = \frac{g}{2} \sum_{\mathbf{r}, \mathbf{r}'} |\mathbf{r} - \mathbf{r}'|^{-2s} = \frac{gN}{2} \sum'_{k,l} |k\mathbf{a} + l\mathbf{b}|^{-2s} \quad (23)$$

where the term with $k = l = 0$ in the sum has to be omitted. Using the simple transformations and exploiting the requirement of a given concentration the sum (23) can be reduced to the form:

$$E = Ngc^s f(\xi, \phi) \\ f(\xi, \phi) = (\sin \phi)^s \left\{ \sum_{k=1}^{\infty} \sum_{l=1}^{\infty} \left[\left(\xi k^2 + \frac{1}{\xi} l^2 + 2kl \cos \phi \right)^{-s} + \left(\xi k^2 + \frac{1}{\xi} l^2 - 2kl \cos \phi \right)^{-s} \right] \right. \\ \left. + \zeta(3) (\xi^s + \xi^{-s}) \right\} \quad (24)$$

Here the following notation has been used: N is the number of adatoms, ζ is the ratio a/b and ϕ is the angle between basic vectors $\mathbf{a}$ and $\mathbf{b}$, $\zeta(x)$ is the Riemann zeta-function ($\zeta(3) = 1.202056$). The function $f(\xi, \phi)$ has the following properties:

- (i) $f(\xi, \phi)$ is positive at any non-zero ϕ and ξ
- (ii) $f(\xi, \phi) = f(1/\xi, \phi)$;
- (iii) $f(\xi, \phi) = f(\xi, \pi - \phi)$.

The function $f(\xi, \phi)$ is also invariant under the following transformation:

$$\begin{aligned}\xi'^2 &= \xi^2 + 1 \pm 2\xi \cos \phi \\ \xi' \cos \phi' &= 1 \pm \xi \cos \phi\end{aligned}\tag{25}$$

The function has a singularity of the form $\zeta(2s)(\sin \phi)^s \xi^{-s}$ as $\xi \rightarrow 0$ for any fixed ϕ . The other singularity of the function $f(\xi, \phi)$ is situated at $\phi = 0$ and any fixed ξ . This singularity is much more complicated. Asymptotically the function $f(\xi, \phi)$ behaves as $A(\xi)\phi^{-s}$. The coefficient $A(\xi)$ depends on ξ in a quite irregular manner jumping at every rational value ξ . As $\xi \rightarrow 1$ for $1 - \xi \gg \phi$ the coefficient $A(\xi)$ tends to $\zeta(2s)$. Some details of the properties of the function $f(\xi, \phi)$ may be found in the appendix.

The analysis of special situations becomes much easier using the inequalities (19) and (21) and noting that the additional restrictions $k_0 \geq 1, n_0 \geq 1, l_0 \geq 0, m_0 \geq 0, k_0 n_0 \geq 1/c$, may also be imposed without loss of generality. All these inequalities define the region in the k_0, n_0 plane, depicted in figure 2. The problem is reduced to the consequent consideration of these points and possible values of l_0, m_0 and insertion of corresponding quantities ξ and ϕ into function $f(\xi, \phi)$ in order to find the minimal value.

For example, consider the case $c = 1/5$. Possible pairs of vectors $\mathbf{a}$ and $\mathbf{b}$ are given in table 1.

Table 1.

k_0	l_0	m_0	n_0	ξ	$\cos \phi$
5	0	0	1	1/5	1/2
5	0	1	1	$\sqrt{3}/5$	$\sqrt{3}/2$
5	0	2	1	$\sqrt{7}/5$	$5/2\sqrt{7}$
5	0	3	1	$\sqrt{13}/5$	$7/2\sqrt{13}$
5	0	4	1	$\sqrt{21}/5$	$9/2\sqrt{21}$
4	1	3	2	$\sqrt{19}/13$	$35/2\sqrt{399}$
3	2	2	3	1	37/38
3	1	1	2	$\sqrt{7}/13$	$9/2\sqrt{21}$

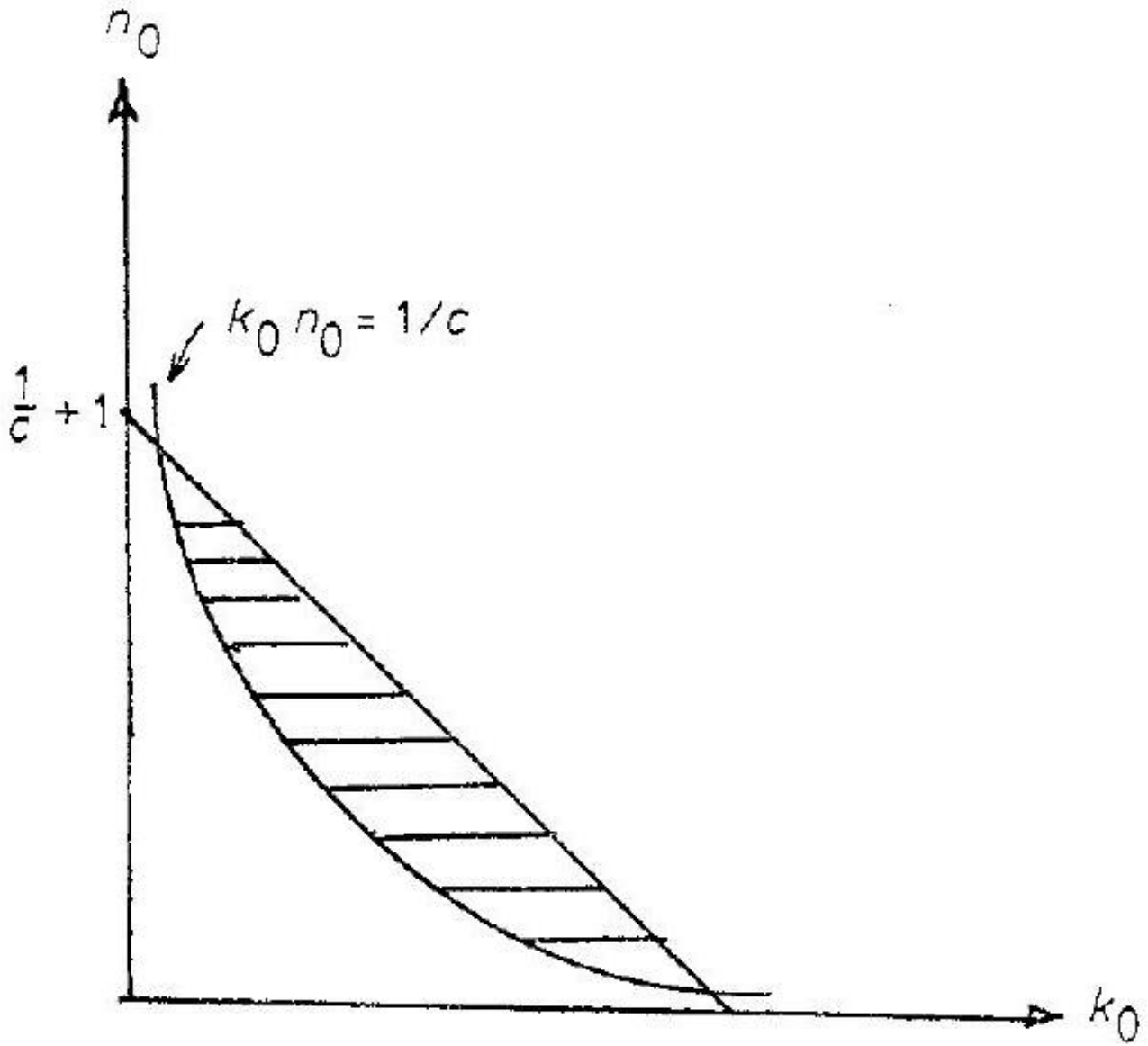


Figure 2. Region of the k_0, n_0 plane defined by inequalities (see text).

The substrate lattice has been assumed to be a simple triangular one. The following formulae were exploited:

$$a = (k_0^2 + l_0^2 + k_0 l_0)^{1/2}, \quad b = (m_0^2 + n_0^2 + m_0 n_0)^{1/2}$$

$$\cos \phi = (ab)^{-1} \left[k_0 m_0 + l_0 n_0 + \frac{1}{2} (k_0 n_0 + l_0 m_0) \right].$$

Inserting quantities from table 1 into the function $f(\xi, \phi)$ and comparing the values obtained we find the most energetically favourable basic cell:

$$a(5, 0), \quad b(1, 1).$$

Table 2 contains the basic vectors $\mathbf{a}$ and $\mathbf{b}$ for concentrations $c = 1/p$ where p runs from 3 to 12.

Table 2.

p	a	b	ξ	$\cos \phi$	$f(\xi, \phi)$
3	3,0	1,1	0.5774	0.8660	4.417
4	2,0	0,2	1	0.5	4.417
	3,1	1,2	0.7338	0.8910	4.784
5	5,0	1,1	0.3464	0.8660	4.773
	3,0	0,2	0.6667	0.5	4.634
6	3,0	1,2	0.8819	0.7559	4.634
	3,1	0,2	0.5547	0.6934	4.631
7	4,1	1,2	0.5774	0.8660	4.417
	4,0	1,2	0.6614	0.7559	4.473
8	5,1	2,2	0.6222	0.9333	4.463
9	3,0	0,3	1	0.5	4.417
	4,2	1,3	0.6814	0.9011	4.568
10	5,0	1,2	0.5292	0.7559	4.571
	5,0	2,2	0.6928	0.8660	4.570
	4,1	1,3	0.7868	0.8171	4.670
11	5,2	2,3	0.6980	0.9368	4.688
	6,1	1,2	0.8690	0.9747	4.687
12	6,0	2,2	0.5774	0.8660	4.417

Table 2 describes the different types of adatom superstructures on the triangular substrate lattice. In the experimental research of Naumovez and Fedorus (1977) the secondary lattices were investigated on the (110) surface of tungsten and molybdenum. This substrate surface represents a triangular lattice with an angle between the basic vectors equal to $\arccos 1/3$. The theoretical predictions for the different energetically favourable lattices on this substrate are given in the table 3. Experimentally the cases $p = 3, 4, 6, 9, 10, 12$ and 21 were investigated (Naumovez and Fedorus 1977). The experimental observations of the structures agree with the theory. However, in the cases

Table 3.

p	a	b	ξ	$\cos \phi$	$f(\xi, \phi)$
3	3,0	1,1	0.544	0.816	$4 \cdot 453$
4	2,0	0,2	1	0.333	4.442
	2,0	1,2	1.258	0.662	4.475
5	3,1	1,2	0.726	0.841	4.618
6	3,0	1,2	0.839	0.662	4.477
7	4,1	1,2	0.567	0.806	4.448
8	5,1	2,2	0.603	0.905	$4 \cdot 430$
9	3,0	0,3	1	0.333	4.442
	3,0	1,3	1.155	0.577	$4 \cdot 442$
10	5,0	2,2	0.653	0.816	4463
11	4,1	1,3	0.781	0.738	4.528
	4,0	1,3	0.866	0.577	4.441
12	7,1	2,2	0.442	0.883	4480
13	5,2	1,3	0.580	0.806	$4 \cdot 443$
14	6,2	2,3	0.595	0.886	$4 \cdot 415$
15	7,2	3,3	0.620	0.931	$4 \cdot 461$
	4,0	0,4	1	0.333	4.442
	4,0	1,4	$1 \cdot 109$	0.526	4.428
16	4,0	2,4	1.258	0.662	$4 \cdot 475$
	4,0	3,4	1.436	0.754	4486
	6,1	2,3	0.644	0.921	$4 \cdot 454$
	5,3	1,4	0.669	0.838	$4 \cdot 490$
17	7,2	2,3	0.522	0.870	$4 \cdot 430$
	5,2	1,4	$0 \cdot 743$	0.768	4.530
	6,0	2,3	0.687	0.728	$4 \cdot 482$
18	6,3	2,4	0.667	0.895	$4 \cdot 527$
	7,1	3,3	0.663	0.883	4.508
19	5,1	1,4	0.819	0.666	$4 \cdot 478$
	7,1	2,3	0.558	0.809	$4 \cdot 451$
	5,0	1,4	0.887	0.526	4.432
20	5,0	2,4	1.007	0.662	$4 \cdot 485$
	8,2	2,3	0.465	0.859	$4 \cdot 492$
	6,3	1,4	0.587	0.806	4.440
21	8,1	3,3	0.584	$0 \cdot 876$	4.409

$p = 4, 9, 12, 21$ the theory predicts the energy of two different structures to be very close to each other. Experimentally observed structures for these cases belong to only one of the predicted structures. We cannot explain so far why the other structures were not observed. Perhaps, the difference between them is more essential at finite temperature because the oscillation free energy has to be taken into consideration.

Now the case of rational $c = m/n$ will be considered. The integers m and n are positive having no general multipliers and $m < n$. We expect the basic cell to have an area equal to n and contain m atoms, as in the one-dimensional case. Their positions have to be chosen to minimise the interaction energy

$$E = \frac{1}{2}g \sum_{r,r'} |r - r'|^{-2s} \quad (26)$$

where r and r' are radius vectors of the lattice sites. They are now labelled with the integer vector of a cell (k, l) as well as with the number, j , of atoms in the cell ($j = 1, 2 \dots m$). The general form of the square of a distance between two atoms in the lattice is as follows:

$$|\mathbf{r} - \mathbf{r}'|^2 = k^2 a^2 + l^2 b^2 + 2kl\mathbf{a}\mathbf{b} + \rho^2 + 2k\rho\mathbf{a} + 2l\rho\mathbf{b} \quad (27)$$

where k and l are integers and the vector ρ connects any two atoms in a basic cell. There are $m(m-1)/2$ different pairs.

Now the energy E may be expressed in terms of two functions $f(\xi, \phi)$ and $h(\xi, \eta, \phi, \psi)$:

$$E = \frac{1}{2}gn^s \left[mf(\xi, \phi) + \frac{1}{2} \sum_{i,j} h(\xi, \eta_{ij}, \phi, \psi_{ij}) \right] \quad (28)$$

where $f(\xi, \phi)$ is defined by equation (24) and

$$h(\xi, \eta, \phi, \psi) = (\sin \phi)^s \sum_{k=-\infty}^{+\infty} \sum_{l=-\infty}^{+\infty} \left[\xi k^2 + \frac{1}{\xi} l^2 + 2kl \cos \phi + \eta^2 + 2k\sqrt{\xi}\eta \cos \psi + 2l\frac{\eta}{\sqrt{\xi}} \cos(\phi - \psi) \right] \quad (29)$$

The new variable η_{ij} is the ratio $\rho_{ij}/\sqrt{ab}$, where ρ_{ij} is the distance between the i th and j th atoms in the basic cell; ψ_{ij} is the angle between ρ_{ij} and $\mathbf{a}$. Now it becomes a question of computational analysis to separate possible values of $\mathbf{a}$, $\mathbf{b}$ and ρ and to compare the corresponding values of E .

19.0.5 4. The Debye-Waller factor

The exponent of the Debye-Waller factor $\exp(-W)$ is tightly connected with the mean square displacement:

$$W = \frac{1}{2} \langle (\mathbf{Q}\mathbf{u})^2 \rangle \quad (30)$$

where $\mathbf{Q}$ is the momentum transfer. Usually $\mathbf{Q}$ is almost equal to some lattice vector $\mathbf{b}$ of the inverse lattice. In the following it will be put equal to $\mathbf{b}$. The temperature dependence of the Debye-Waller factor can be established neglecting the anisotropy and putting $\langle u_x^2 \rangle = \langle u_y^2 \rangle = \frac{1}{2} \langle u^2 \rangle$.

Then we obtain

$$W = \frac{1}{4} b^2 \langle u^2 \rangle. \quad (31)$$

The spectra of oscillation of a commensurate structure can be described with the Einstein model. Then W is exponentially small at low temperatures with the exponent $\hbar\omega_0/T$ where ω_0 is the smallest optic frequency.

Incommensurate structures display quite different behaviour of W . Assuming the approximation (31) to be valid and exploiting the calculations of §1 (see equation (2)) one can obtain

$$W = \frac{b^2}{4\pi M s^2} T \ln Rq_0. \quad (32)$$

The correction to equation (32), proportional to T^2 , arises mainly due to dispersion of sound and becomes essential for $T > \Theta$, where Θ is the Debye temperature. In order to compare the theoretical prediction (32) with the experimental data we investigate the quantity W/T . Values extracted from the experimental data of Naumovez and Fedorus (1977) are shown as a function of $\ln T$ in figure 3. Theoretically this would be a straight line at low temperatures $T \ll \Theta$.

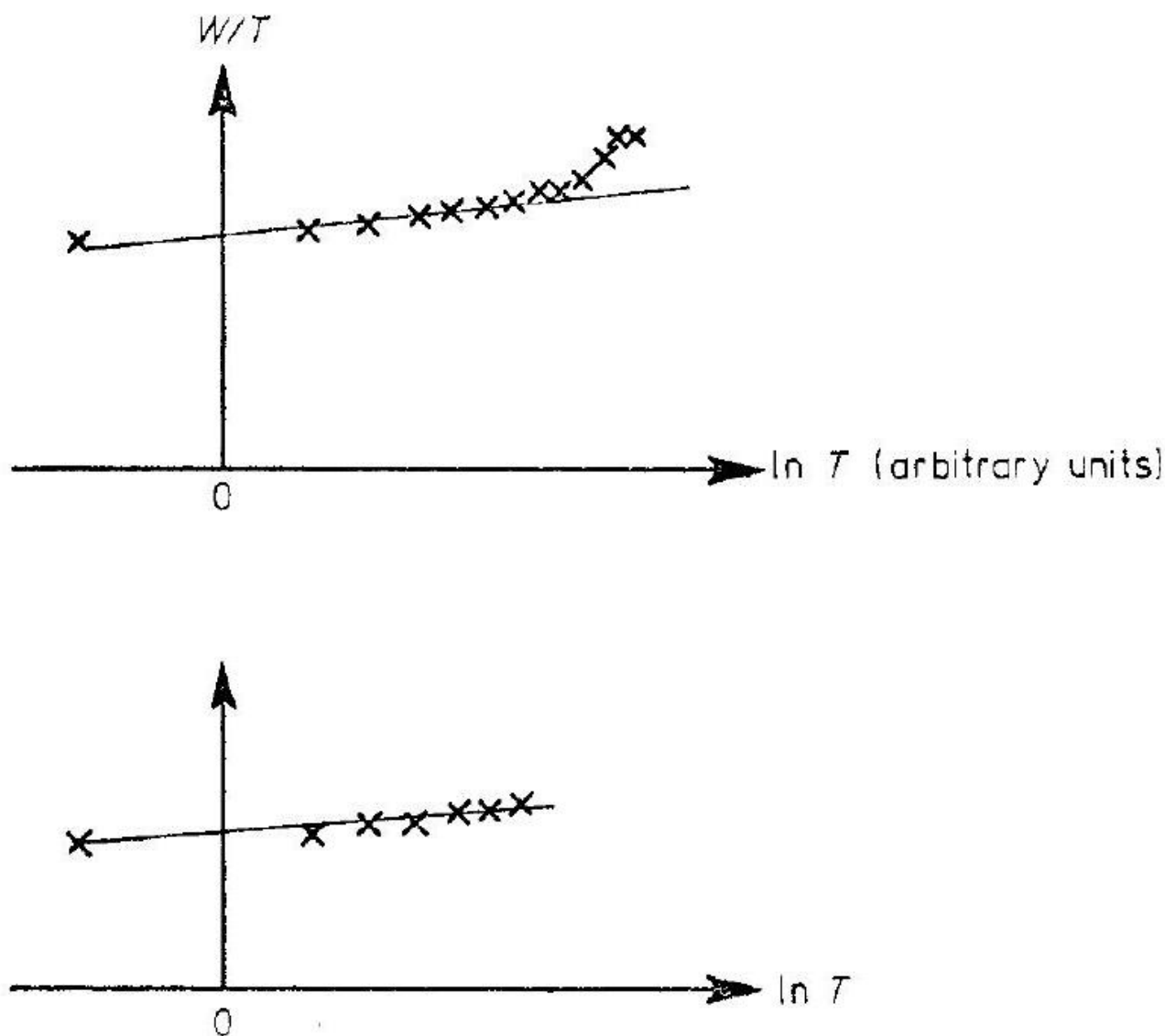


Figure 3. W/T as a function of $\ln T$. W is the exponent of the Debye-Waller factor. From the experimental data of Naumovez and Fedorus (1977).

The sound velocity for a given structure is proportional to the square root of the space derivative of forces, neglecting the influence of the substrate. In the special case of the dipole interaction the sound velocity is proportional to the density of adatoms neglecting the change of dipole momentum. At present it is too early to compare this theoretical prediction with experiments because there are only two curves related to the same adatoms and substrates at different concentrations (Sr-Mo, $c = 0.64, 0.70$). The quantity W/T was actually a gradual function of temperature which fits rather well with the linear function $\ln T$. The slope of the logarithmic curve is theoretically predicted to be proportional to the inverse concentration. This is fulfilled rather well for the two logarithmic straight lines available so far. Further experiments are necessary for a detailed check of the theory.

19.0.6 5. Conclusions

A very simple physical model is sufficient to explain the behaviour of the DebyeWaller factors of commensurate and incommensurate structures. A theory, based on the assumption that the dipole interaction is predominant is able to explain the experimentally observed crystal structures.

Many problems are not yet solved. Firstly, there is the problem of substrate distortions, which have not been taken into consideration at all. The second is the problem of the almost coincident energies of different configurations. Certainly, more detailed experiments on the structure of secondary crystals at different concentrations would be very illuminating.

19.0.7 Appendix. Some properties of the function $f(\xi, \phi)$

Consider the rational value $\xi = p/q$, where p and q are positive integers; $p < q$ and they have no common multipliers. The terms of the series in the right-hand side of formula (24) with $k = mq$ and $l = mp$ take the values $(4pqm^2 \sin^2 \phi/2)^{-s}$ at any integer m . Therefore the contribution of these terms to $f(\xi, \phi)$ is equal to

$$\left(\frac{\sin \phi}{4 \sin^2 \phi/2} \right)^s \frac{\zeta(2s)}{(pq)^s} \quad (\text{A1})$$

It diverges at $\phi \rightarrow 0$ and the coefficient $(pq)^{-s}$ jumps at any rational ξ . Nevertheless the function $f(\xi, \phi)$ is continuous and differentiable at any given ϕ except for $\phi = 0$. Consider the value of ξ near some rational value $\xi_0 = p/q$:

$$\xi = \xi_0 + \epsilon \quad (\epsilon \ll \xi_0).$$

The same set of terms in the series, representing function $f(\xi, \phi)$ gives now the following contribution:

$$\left[\frac{\sin \phi}{4 (\sin^2 \phi/2 + \epsilon^2/\xi_0^2)} \right]^s \frac{\zeta(2s)}{(pq)^s}. \quad (\text{A2})$$

It differs from (A1) with the term ϵ^2/ξ_0^2 in the denominator, which can be neglected provided $\epsilon \ll \xi_0 \sin \phi/2$. For example, if $\xi_0 = 1$ the singularities of the type (A1) can be neglected provided $\epsilon \lesssim \phi/2$ and $pq \gg 1/\phi$.

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20 Landau theory of charge-density waves in transition-metal dichalcogenides by McMillan (1975)

Abstract

A Landau theory is proposed for charge-density waves (CDW) in transition-metal dichalcogenides with the charge density as an order parameter. The theory predicts the sequence of phases, normal-state-incommensurate-CDW-commensurate-CDW with decreasing temperature, separated by first-order phase transitions. The peaks in charge density lie at "lattice sites" of a hexagonal crystal and for the incommensurate case the theory predicts phononlike distortions of the CDW "lattice" as well as dislocations. Impurities pin the charge density wave, broaden the phase transitions, and stabilize the incommensurate state relative to the commensurate state.

20.0.1 I. Introduction

Recently the anomalous properties of TaSe_2 and similar materials have been attributed to chargedensity-wave (CDW) formation.¹⁻³ In the octahedrally coordinated structure, $1T - \text{TaSe}_2$ exhibits an incommensurate-charge-density wave (ICDW) above 473°K and a commensurate-charge-density wave (CCDW) below 473°K . In the trigonal prismatic coordinated structure, $2H - \text{TaSe}_2$ is a normal metal above 120°K and forms a CDW state below 120°K . These materials are essentially two-dimensional metals with the transition-metal ions on a planar hexagonal lattice. The band structure⁴ has sixfold symmetry in the basal plane and the two-dimensional ICDW's form in the ΓM directions. The three possible ICDW's are found to coexist. Electron diffraction, resistivity, and susceptibility measurements have been made on a number of compounds and binary alloys.

Wilson et al.³ have shown that CDW's in these materials are Fermi-surface-driven instabilities and are therefore related to spin-density waves in chromium,^{5,6} to the spiral structures in rare-earth metals,⁷ and to long-period ordering in alloys.⁸ Overhauser⁹ has proposed a CDW ground state for alkali metals but this has not been confirmed. Overhauser⁹ and Chan and Heine¹⁰ discuss CDW formation from a microscopic point of view, but the microscopic theory is not well developed.

The purpose of this paper is to write down a phenomenological Landau theory¹¹ for charge-density waves in the layered compounds and to develop its consequences. We will work with a two-dimensional model of charge-density waves in one layer. The transition temperatures are characteristic of the layer type and are insensitive to the nature of the neighboring layers; this indicates that the dominant interactions are intralayer and that interlayer interactions play only a secondary role. Interlayer interactions do determine the relative phase of CDW's on neighboring layers and provide a three-dimensional stiffness to the structure; the CDW is not two dimensional in the Kosterlitz-Thouless¹² sense. We will choose the electron density as the order parameter and write down the free energy as a power-series expansion in the order parameter and gradients of the order parameter. We include an impurity potential to describe impurity effects. This is accomplished in Sec. II, and the rest of the paper is devoted to calculation of the properties of CDW's using the Landau theory. We first study the phase transitions and show that for the observed triple CDW, the transitions are first order and the

phases occur in the order normal-incommensurate-commensurate with decreasing temperature. Impurity effects are then studied, and we find that the impurity potential drives the charge-density wave and smears out the phase transitions. Each impurity is dressed with a cloud of charge-density wave, even in the normal state, and the impurity-impurity interaction is calculated. The incommensurate wave is flexible and can distort in the impurity potential to lower its energy. This stabilizes the incommensurate wave relative to the commensurate wave and depresses that transition temperature. The fluctuation modes are then examined and two hydrodynamic modes (small energy at long wavelength) are found for the ICDW corresponding to the transverse and longitudinal "phonons" of the twodimensional CDW "lattice." Finally, a "dislocation" in the ICDW "lattice" is discussed, which is the analog of the vortex in superfluid helium and super conductors.

20.0.2 II. Landau Theory

The natural order parameter for charge-density waves is the electronic charge density of the d -band conduction electrons. This charge density is coupled linearly to the longitudinal lattice distortion and the amplitude of the periodic lattice distortion is simply proportional to the amplitude of the charge-density wave. The charge density is a real scalar quantity and one can construct a free-energy functional of the charge density to describe the triple charge-density wave. With this approach, the gradient terms in the free energy are complicated, as is the fourth-order term. It turns out to be simpler to use three complex order parameters, one for each charge-density wave. We write for the electronic charge density

$$\rho(\vec{r}) = \rho_0(\vec{r})[1 + \alpha(\vec{r})], \quad (1)$$

where $\alpha(\vec{r})$ is the real order parameter and $\rho_0(\vec{r})$ is the d -electron conduction-band charge density in the normal state. Then we write $\alpha(\vec{r})$ in terms of three complex order parameters $\psi_i(\vec{r})$.

$$\alpha(\vec{r}) = \text{Re} [\psi_1(\vec{r}) + \psi_2(\vec{r}) + \psi_3(\vec{r})]. \quad (2)$$

The next step is to write down an expansion of the free energy in powers of α (or ψ_i) and gradients of α (or ψ_i). We will discuss the various terms individually. For the free energy of one layer, we write the expansion in powers of the order parameter as

$$F_1 = \int d^2r [a(\vec{r})\alpha^2 - b(\vec{r})\alpha^3 + c(\vec{r})\alpha^4 + d(\vec{r}) (|\psi_1\psi_2|^2 + |\psi_2\psi_3|^2 + |\psi_3\psi_1|^2)] \quad (3)$$

where $a(\vec{r})$, $b(\vec{r})$, $c(\vec{r})$, and $d(\vec{r})$ exhibit the periodicity of the crystal lattice. We will write, for example,

$$c(\vec{r}) = c_0 + c_1 \sum_i e^{i\vec{k}_i \cdot \vec{r}}, \quad (4)$$

where the six $\vec{K}_i$ are the six shortest reciprocal lattice vectors characteristic of the planar hexagonal transition-metal lattice. The constant terms such as c_0 are sufficient to discuss ICDW's, but the umklapp terms such as c_1 are necessary to discuss CCDW's. The unusual form of the fourth-order term in Eq. (3) is chosen to permit description of both single and triple CDW's (see Sec. III).

We next include the random potential $U(r)$, due to impurities for the alloy case. $U(r)$ could also be an external potential.

$$F_2 = \int d^2r U(\vec{r}) \rho_0(\vec{r}) \alpha(\vec{r}). \quad (5)$$

The gradient terms are chosen so that the free energy of the three charge-density waves is at a minimum when they lie in the right direction and have the right wavelength,

$$F_3 = \int d^2r \left[e(\vec{r}) \sum_i \left| \left(\vec{q}_i \cdot \vec{\nabla} - i q_i^2 \right) \psi_i \right|^2 + f(\vec{r}) \sum_i \left| \vec{q}_i \times \vec{\nabla} \psi_i \right|^2 \right], \quad (6)$$

where

$$|\vec{q}_1| = |\vec{q}_2| = |\vec{q}_3| = 2\pi/\lambda,$$

and λ is the wavelength of the ICDW, and the three $\vec{q}_i$ vectors lie in ΓM directions 120° apart (Fig. 1). e_0 and f_0 are the elastic constants for the CDW. The total free energy is the sum of three terms

$$F = F_1 + F_2 + F_3. \quad (7)$$

We make the usual Landau theory assumption that the parameters a_0, b_0 , etc., are smooth functions of temperature and can be expanded in powers of $T - T_{NI}$ near the onset temperature. Since a_0 must change sign near T_{NI} , we assume that

$$a_0 = a'(T - T^*), \quad (8)$$

and that the other parameters are temperature independent. In doing this, we have assumed that the transition is mean-field-like and that critical fluctuations are unimportant.

20.0.3 III. Phase Transitions

The Landau theory is capable of describing a variety of situations depending on the magnitudes of the parameters. Here we investigate several phases of the clean metal with $U = 0$. We proceed by solving for the order parameters $\psi_i(\vec{r})$, which minimize the free energy. When there are several

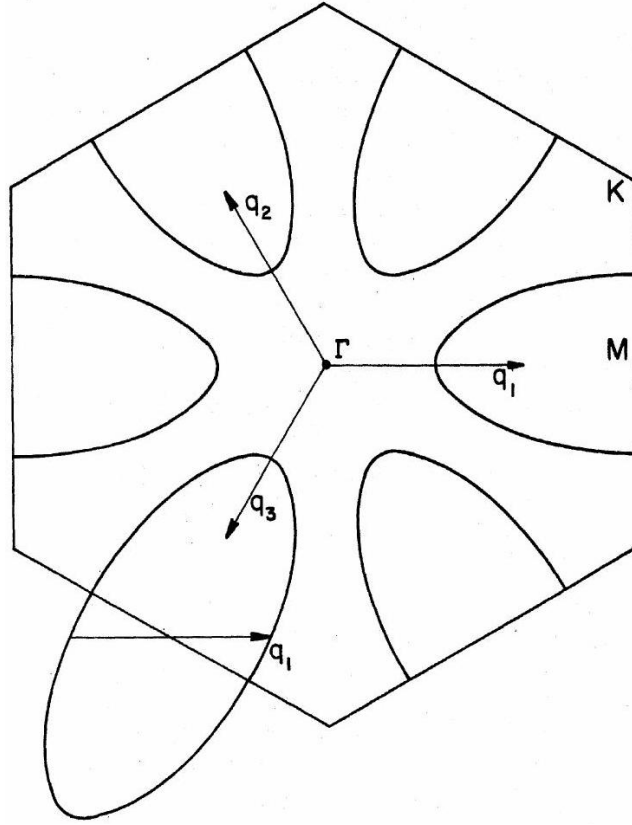


FIG. 1. Sketch of the Fermi surface of $1T-\text{TaS}_2$ (Ref. 4) in the basal plane of the first Brillouin zone. The q vectors of the three charge-density waves in the incommensurate state are shown; q_1 is shown as a spanning vector of the Fermi surface. The vector from Γ to M is one half the first reciprocal-lattice vector.

minima of the free energy, that is several possible states of the system, the state with the lowest free energy is thermodynamically stable. Throughout the paper, we will compute the free energy per unit area for one layer.

A. Single ICDW

For the single incommensurate CDW, we write

$$\psi_1(\vec{r}) = \phi_0 e^{i\vec{a}_1 \cdot \vec{r}}, \quad \psi_2 = \psi_3 = 0. \quad (9)$$

After integrating over a plane of unit area, we find for the free energy per unit area for one layer

$$F = \frac{1}{2}a_0\phi_0^2 + \frac{3}{8}c_0\phi_0^4. \quad (10)$$

Minimizing F with respect to ϕ_0 , we find

$$\phi_0 = \begin{cases} 0, & T > T^* \\ [2a'(T^* - T)/3c_0]^{1/2}, & T < T^* \end{cases} \quad (11)$$

so that the phase transition from the incommensurate to the normal phase is second order with transition temperature $T_{IN} = T^*$. The free energy in the incommensurate phase is

$$F_{1I} = -a_0^2/6c_0. \quad (12)$$

B. Single CDW

If the wave number of the incommensurate wave is near one-third of a reciprocal-lattice vector, the commensurate phase may be stable. For the single commensurate CDW, we write

$$\psi_1(r) = \phi_0 e^{i \vec{K}_1 \cdot \vec{r} / 3}, \quad \psi_2 = \psi_3 = 0, \quad (13)$$

and find

$$F = \left[\frac{1}{2} a_0 + e_0 q_1^2 \left(q_1 - \frac{1}{3} K_1 \right)^2 \right] \phi_0^2 - \frac{1}{4} b_1 \phi_0^3 + \frac{3}{8} c_0 \phi_0^4. \quad (14)$$

Forcing the wave to be commensurate has cost elastic energy from the gradient terms in the free energy but has gained umklapp energy or "lock-in" energy from the cubic term. The free energy gained is approximately

$$F_{1C} - F_{1I} \approx e_0 q_1^2 \left(q_1 - \frac{1}{3} K_1 \right)^2 \phi_{0I}^2 - \frac{1}{4} b_1 \phi_{0I}^3, \quad (15)$$

where ϕ_{0I} is the amplitude of the CDW in the incommensurate phase

$$\phi_{0I} = [2a' (T_{IN} - T) / 3c_0]^{1/2}. \quad (16)$$

If $F_{1C} - F_{1I}$ is positive, the incommensurate phase is stable, whereas if $F_{1C} - F_{1I}$ is negative, the commensurate phase is stable. At the phase transition from the incommensurate phase to the commensurate phase $F_{1C} - F_{1I} = 0$ and this condition determines the transition temperature

$$T_{CI} = T_{IN} - \frac{3c_0}{2a'} \left(\frac{4e_0 q_1^2 (q_1 - \frac{1}{3} K_1)^2}{b_1} \right)^2 \quad (17)$$

The transition energy is given by

$$\begin{aligned} \Delta S_{CI} &= \frac{dF_{1C}}{dT} - \frac{dF_{1I}}{dT} \Big|_{T=T_{CI}} \\ &= a' e_0 q_1^2 \left(q_1 - \frac{1}{3} K_1 \right)^2 / 3c_0 \end{aligned} \quad (18)$$

and the phase transition is first order. The order parameter is larger in the commensurate phase by

$$\Delta \phi_0 = e_0 q_1^2 \left(q_1 - \frac{1}{3} K_1 \right)^2 / 3c_0 \phi_0. \quad (19)$$

In the presence of a periodic lattice distortion and charge-density wave, there is an energy gap in the band structure at the Fermi energy over the nested portion of the Fermi surface. Since the energy gap is proportional to the order parameter, the energy gap is larger in the commensurate phase and the susceptibility smaller. The single CDW is a simple example of a commensurate-incommensurate phase transition driven by umklapp terms in the free energy. This case is not observed in practice, and we turn now to the triple CDW.

C. Triple ICDW

We give the three CDW's identical amplitudes

$$\psi_i(\vec{r}) = \phi_0 e^{i\vec{a}_i \cdot \vec{r}}, \quad (20)$$

and compute the free energy

$$F = \frac{3}{2}a_0\phi_0^2 - \frac{3}{2}b_0\phi_0^3 + \frac{3}{8}(15c_0 - 8d_0)\phi_0^4. \quad (21)$$

Note the presence of a new cubic term (proportional to b_0) and a fourth-order cross term, which were absent for the single CDW case. In order to take advantage of the cubic term in reducing the free energy, we choose the relative phases of the three waves so that the cubic term is attractive. Thus the cubic term acts as a "phasing energy." With b_0 positive, as assumed here, the three CDW's add, as shown in Fig. 2, to give peaks in electron density at lattice sites of a two-dimensional hexagonal lattice with CDW "lattice spacing" equal to K_1/q_1 times the crystal-lattice spacing. We will show below that the triple ICDW exhibits other properties of a two-dimensional "lattice," namely CDW "phonons" and CDW "dislocations." With b_0 negative, the signs of ψ_i are reversed and the CDW "lattice" is a hole lattice rather than an electron lattice; henceforth, we assume $b_0 > 0$.

There are two types of fourth-order terms in the theory, a direct term $\frac{1}{8}(3c_0)(|\psi_1|^4 + |\psi_2|^4 + |\psi_3|^4)$ and a cross term $\frac{1}{8}(12c_0 - 8d_0)(|\psi_1\psi_2|^2 + |\psi_2\psi_3|^2 + |\psi_1\psi_3|^2)$. With $d_0 = \frac{3}{2}c_0$, the cross term vanishes and there is no (fourth-order) interaction energy among the three CDW's; the free energy is 3 times that of the single CDW case. For $d_0 < \frac{3}{2}c_0$, the cross term is repulsive and the free energy of the triple CDW state is increased relative to the single CDW state.

To compute the free energy of the triple CDW state, we minimize F with respect to ϕ_0 and find

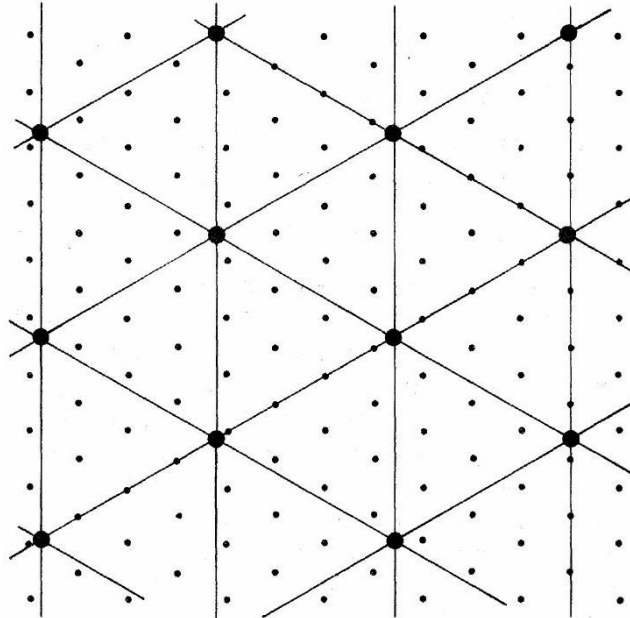


FIG. 2. Dots represent transition-metal atoms on the hexagonal crystal lattice, and the lines represent maxima in the charge density of each of the three CDW's. At the intersection of the lines, the charge densities of each of the three CDW's add up, and there is a peak in electron density represented by the filled circles. These peaks in electron density occur at lattice sites of the CDW "lattice."

$$\phi_0 = \frac{3b_0}{2(15c_0 - 8d_0)} + \left[\left(\frac{3b_0}{2(15c_0 - 8d_0)} \right)^2 - \frac{2a_0}{15c_0 - 8d_0} \right]^{1/2}, \quad (22)$$

and a phase transition which is first order with transition temperature

$$T_{IN} = T^* + b_0^2/a' (15c_0 - 8d_0), \quad (23)$$

and transition entropy

$$\Delta S = 3a'b_0/(15c_0 - 8d_0). \quad (24)$$

With b_0 small, the phase transition is only weakly first order. We now want to compare the free energy of the triple ICDW with the single ICDW to find out which is stable. We temporarily neglect b_0 and find

$$F_{3I} = -3a_0^2/2(15c_0 - 8d_0), \quad (25)$$

which is below F_{1I} provided $d_0 > \frac{3}{4}3c_0$. The amplitudes of the three CDW's are independent if $d_0 = \frac{3}{2}3c_0$; this would be the case if the part of the Fermi surface utilized by one CDW was not affected by the energy gaps of the other two CDW's. One expects a repulsive interaction of CDW's so that $d_0 < \frac{3}{2}3c_0$; since one observes the triple CDW, not the single CDW, we must have $\frac{3}{4}3c_0 < d_0 < \frac{3}{2}3c_0$.

D. Triple CDW in trigonal prismatic layers

In $2H - \text{TaSe}_2$ and related materials, $\vec{q}_1$ is very close to $\frac{1}{3}\vec{K}_1$, and the CDW locks in with $\vec{q} = \frac{1}{3}\vec{K}_1$.

To treat this commensurate case, we choose

$$\psi_i(r) = \phi_0 e^{i\vec{K}_i \cdot \vec{r}/3}. \quad (26)$$

The free energy per unit area for one layer is

$$F = \left(\frac{3}{2}a_0 + 3e_0q_1^2 \left(q_1 - \frac{1}{3}K_1 \right)^2 \right) \phi_0^2 - \left(\frac{3}{2}b_0 + \frac{3}{4}b_1 \right) \phi_0^3 + \frac{3}{8}(15c_0 - 8d_0) \phi_0^4. \quad (27)$$

To first order in e_0 and b_1 the free energy difference between the commensurate and incommensurate phases is

$$F_{3C} - F_{3I} \approx 3e_0q_1^2 \left(q_1 - \frac{1}{3}K_1 \right)^2 \phi_{0I}^2 - \frac{3}{4}b_1\phi_{0I}^3, \quad (28)$$

with ϕ_{0I} given by Eq. (22). Forcing the wave to be commensurate has lost elastic energy from the gradient terms in the free energy but has gained unklapp energy from the cubic term. Proceeding as in Sec. III B, we find (neglecting b_0 for simplicity)

$$T_{CI} = T_{IN} - \frac{15c_0 - 8d_0}{2a'} \left(\frac{4e_0q_1^2 (q_1 - \frac{1}{3}K_1)^2}{b_1} \right)^2 \quad (29)$$

$$\Delta S_{CI} = \frac{3a'e_0q_1^2 (q_1 - \frac{1}{3}K_1)^2}{15c_0 - 8d_0} \quad (30)$$

$$\Delta\phi_0 = \frac{e_0q_1^2 (q_1 - \frac{1}{3}K_1)^2}{(15c_0 - 8d_0)\phi_0} \quad (31)$$

E. Triple CCDW in octahedral layers

In $1T-\text{TaSe}_2$, $\vec{q}_1$ is not close enough to $\frac{1}{3}\vec{K}_1$, and it costs too much elastic energy to lock in with $\vec{q} = \frac{1}{3}\vec{K}_1$. Instead, the CDW rotates $13^\circ 54'$ away from the ΓM direction so that $3\vec{p}_1 - \vec{p}_2 = \vec{K}_1$, and $\vec{p}_1, \vec{p}_2$ and $\vec{p}_3$ are 120° apart and $|p_1| = |p_2| = |p_3| \approx |q_1|$. The wavelength of the charge-density wave is almost unchanged, and it costs little longitudinal elastic energy (proportional to e_0); however, the large angle of rotation costs transverse elastic energy (proportional to f_0), and for this rotation to occur, f_0 must be small. The umklapp energy now comes from the fourth-order term. We write

$$\psi_i(\vec{r}) = \phi_0 e^{i\vec{p}_i \cdot \vec{r}}, \quad (32)$$

and find

$$F = \left[\frac{3}{2}a_0 + 3e_0 (\vec{q}_1 \cdot \vec{p}_1 - q_1^2)^2 + 3f_0 (\vec{q}_1 \times \vec{p}_1)^2 \right] \phi_0^2 - \frac{3}{2}b_0\phi_0^3 + \frac{3}{8}(15c_0 + 4c_1 - 8d_0)\phi_0^4 \quad (33)$$

Forcing the wave to be commensurate has cost elastic energy to change the wavelength (αe_0) and elastic energy to rotate the direction of the wave (αf_0), but has gained fourth-order umklapp energy (αc_1). We assume $c_1 < 0$ and neglect b_0 for simplicity. The free energy in the commensurate phase is

$$F_{3C} = -\frac{3}{2} \frac{\left[a_0 + 2e_0 (\vec{q}_1 \cdot \vec{p}_1 - q_1^2)^2 + 2f_0 (\vec{q}_1 \times \vec{p}_1)^2 \right]^2}{15c_0 - 8d_0 + 4c_1}. \quad (34)$$

The transition temperature is

$$T_{CI} = T_{IN} - \frac{15c_0 - 8d_0}{a'|c_1|} \left[e_0 (\vec{q}_1 \cdot \vec{p}_1 - q_1^2)^2 + f_0 (\vec{q}_1 \times \vec{p}_1)^2 \right] \quad (35)$$

and we find

$$\Delta S_{CI} = \frac{4a' \left[e_0 (\vec{q}_1 \cdot \vec{p}_1 - q_1^2)^2 + f_0 (\vec{q}_1 \times \vec{p}_1)^2 \right]}{15c_0 - 8d_0}, \quad (36)$$

$$\Delta\phi = \frac{2 \left[e_0 (\vec{q}_1 \cdot \vec{p}_1 - q_1^2)^2 + f_0 (\vec{q}_1 \times \vec{p}_1)^2 \right]}{(15c_0 - 8d_0)\phi_0}. \quad (37)$$

This theory should describe the phase transition at 473°K in $1T - \text{TaSe}_2$. The incommensurate-normal metal transition is not observed in these materials because the

crystal structure converts to trigonal prismatic at $\approx 600^\circ\text{K}$. $1T - \text{TaS}_2$ undergoes a phase transition at 350°K from an ICDW state to a complex phase which has not been characterized yet. The experimental situation on the $2H$ phases, to which the theory of Sec. III D should apply, is not yet clear.

The theory predicts that the onset transition from normal metal to ICDW state is at least weakly first order and that the ICDW-CCDW transition is first order with an increased energy gap. The normal order of the phases with decreasing temperature is normal-ICDW-CCDW.

20.0.4 IV. Alloys

In this section, we calculate the effects of the impurity potential $U(r)$ on the charge-density wave. The other parameters of the Landau theory will change in a continuous way with impurity concentration, and we are not interested in this effect. The random impurity potential couples directly to the charge-density wave and qualitatively changes the nature of the phase transitions and the fluctuation modes; it is these effects that we wish to describe.

To treat the impurity potential correctly, we should take an ensemble of systems, each with a particular distribution of impurities and a particular impurity potential $U_i(\vec{r})$. We should compute the physical quantity of interest for each system and then take an ensemble average. It is often impossible to carry out a calculation in this order, and one must ensemble average at an intermediate step in the calculation. This introduces an approximation which one should then discuss.

We will discuss impurity effects (i) in the normal phase, (ii) on the incommensurate-normal phase transition, and (iii) on the commensurate-incommensurate phase transition. We will carry out the calculations for the single CDW case; the physics of the impurity effects is clear from this calculation, and the algebra is simpler than that for the triple CDW. We will indicate, where possible, the extensions to the triple CDW case. We will also discuss the charge density near one impurity, as well as impurity-impurity interactions.

A. Normal phase

We consider only one CDW and write the order parameter as the product of a plane wave times a smoothly varying part $\phi(\vec{r})$.

$$\psi_1(\vec{r}) = \phi(\vec{r})e^{i\vec{a}_1 \cdot \vec{r}}, \quad \psi_2 = \psi_3 = 0 \quad (38)$$

$$\phi(\vec{r}) = \sum_{\vec{q}} \phi_{\vec{q}} e^{i\vec{q} \cdot \vec{r}}. \quad (39)$$

In the normal phase, there are only thermal fluctuations and impurity driven fluctuations of $\phi(r)$, and $\phi(r)$ is small. We also Fourier transform the impurity potential in the same way,

$$U(\vec{r})\rho_0(\vec{r}) = \sum_{\vec{q}} U_{\vec{q}} e^{i(\vec{q}+\vec{q}_1) \cdot \vec{r}} + \text{c. c.} \quad (40)$$

Since each of the ϕ_q is small, we can expand the free energy to second order in ϕ_q .

$$\begin{aligned} F = \sum_{\vec{q}} \left[\frac{1}{2} a_0 + e_0 (\vec{q}_1 \cdot \vec{q})^2 + f_0 (\vec{q}_1 \times \vec{q})^2 \right] \phi_{\vec{q}}^* \phi_{\vec{q}} \\ + \frac{1}{2} \sum_{\vec{q}} (U_{\vec{q}}^* \phi_{\vec{q}} + U_{\vec{q}} \phi_{\vec{q}}^*). \end{aligned} \quad (41)$$

Minimizing F with respect to ϕ_q^* , we find

$$\phi_{\vec{q}} = -U_q/2\epsilon_{\vec{q}}^0, \quad (42)$$

$$\epsilon_{\vec{q}}^0 = \frac{1}{2}a_0 + e_0 (\vec{q}_1 \cdot \vec{q})^2 + f_0 (\vec{q}_1 \times \vec{q})^2. \quad (43)$$

Since the impurity potential has random phase, the ensemble average of U_q vanishes,

$$\langle U_{\vec{q}} \rangle = 0, \quad \langle \phi_{\vec{q}} \rangle = 0. \quad (44)$$

However, the structure factor average S_q is nonvanishing.

$$S_{\vec{q}} \alpha \langle \phi_{\vec{q}}^* \phi_{\vec{q}} \rangle = \frac{\langle U_{\vec{q}}^* U_{\vec{q}} \rangle}{4 (\epsilon_{\vec{q}}^0)^2} = \frac{N u_0^2}{4 (\epsilon_{\vec{q}}^0)^2}, \quad (45)$$

where u_0 is the space integral of the potential of one impurity, and N is the impurity density. We see that the impurity potential drives the charge-density wave. The effect on the structure factor can be stronger than thermal fluctuations and can produce a visible pretransition effect in electron diffraction well above the phase transition; this effect has been observed in $2H\text{-TaSe}_2$.³

For one impurity at the origin $U_q = u_0$, and we have

$$\phi(\vec{r}) = -\frac{1}{2}u_0 \sum_{\vec{q}} \frac{e^{i(\vec{q} + \vec{q}_1) \cdot \vec{r}}}{\epsilon_{\vec{q}}^0}. \quad (46)$$

We find for the charge density (using $e_0 = f_0$ to simplify the integral),

$$\rho(r) = \rho_0(r) \left(1 - \frac{u_0 \cos(\vec{q}_1 \cdot \vec{r}) f(r/\xi)}{4\pi e_0 q_1^2} \right), \quad (47)$$

where $\xi = (2e_0 q_1^2 / |a_0|)^{1/2}$ is the correlation length, and

$$f(r/\xi) \equiv \int_1^\infty dy e^{-yr/\xi} (y^2 - 1)^{-1/2} \quad (48)$$

This function is asymptotically

$$f(r/\xi) \sim \begin{cases} \ln(1.12\xi/r), & r/\xi \ll 1 \\ (\pi\xi/2r)^{1/2} e^{-r/\xi}, & r/\xi \gg 1. \end{cases} \quad (49)$$

Thus, in the normal state, there is a charge-density wave localized on the impurity whose amplitude falls off as $\ln(\xi/r)$ for $r < \xi$ and exponentially for $r > \xi$. Expression (47) is only valid for $r q_1 > 1$. For the triple CDW, one merely replaces $\cos(\vec{q}_1 \cdot \vec{r})$ by $\sum_i \cos(\vec{q}_i \cdot \vec{r})$.

A second impurity a distance $\vec{R}$ from the first is attracted to the charge density of the first, and the impurity-impurity interaction energy is

$$U_{I-I} = -\frac{u_0^2}{4\pi e_0 q_1^2} f\left(\frac{R}{\xi}\right) \sum_i \cos(\vec{q}_i \cdot \vec{R}). \quad (50)$$

Thus, even in the normal state, impurities feel a strong potential attracting them to the "lattice sites" of the triple CDW. The impurity interaction is nothing new; it has been invoked to explain ordering in alloys where one does not observe a CDW but where Fermi-surface effects are believed to be important.

B. Commensurate-incommensurate phase transition

We consider now the ordered phases where the higher-order terms in the free energy are important. We write

$$\psi_1(\vec{r}) = \phi(\vec{r})e^{i\vec{p}_1 \cdot \vec{r}}, \quad (51)$$

$$\phi(\vec{r}) = \phi_0 + \sum_{\vec{q}} \phi_{\vec{q}} e^{i\vec{q} \cdot \vec{r}}, \quad (52)$$

where $\vec{p}_1 = \frac{1}{3}\vec{K}_1$ for the commensurate phase ($\vec{K}_1$ is a reciprocal-lattice vector), and $\vec{p}_1 = \vec{q}_1$ for the incommensurate phase; ϕ_0 is real. ϕ_0 is the uniform charge-density wave amplitude and the ϕ_q are the amplitudes of the thermal or impurity driven fluctuations.

Then, the free energy is

$$\begin{aligned} F = & \epsilon_0^0 \phi_0^2 + \frac{1}{8} 3c_0 \phi_0^4 + \frac{1}{2} \sum_q (U_q^* \phi_q + U_q \phi_q^*) + \sum_q \epsilon_q^0 \phi_q^* \phi_q + \frac{1}{8} 3c_0 \phi_0^2 \sum_q (\phi_q \phi_{-q} + \phi_q^* \phi_{-q}^* + 4\phi_q^* \phi_q) \\ & + \frac{1}{8} 3c_0 \left[\sum_p \phi_p^* \phi_{-p}^* \sum_q \phi_q \phi_{-q} + 2 \left(\sum_q \phi_q^* \phi_q \right)^2 \right] - \frac{1}{4} b_1 \left(\phi_0^3 + \frac{1}{2} 3\phi_0 \sum_q (\phi_q \phi_{-q} + \phi_q^* \phi_{-q}^*) \right) \delta_{\vec{p}_1, \vec{q}_1} \end{aligned} \quad (53)$$

where

$$\alpha_{q+-} = - (U_q \pm U_{-q}^*) / 2\sqrt{2}\epsilon_{q+-}, \quad (60)$$

$$\epsilon_q^0 = \frac{1}{2} a_0 + e_0 [\vec{q}_1 \cdot \vec{q} - \vec{q}_1 \cdot (\vec{q}_1 - \vec{p}_1)]^2 + f_0 (\vec{q}_1 \times \vec{q})^2. \quad (54)$$

The last term in (53) is the umklapp term, which is present only for the commensurate phase. Minimizing F with respect to ϕ_0 , we find

$$\begin{aligned} 0 = & 2\epsilon_0^0 \phi_0 + \frac{1}{2} 3c_0 \phi_0^3 + \frac{1}{2} 3c_0 \phi_0 (2\lambda_1 + \lambda_2) \\ & - \frac{1}{4} 3b_1 (\phi_0^2 - \lambda_2) \delta_{\vec{p}_1, \vec{q}_1}, \end{aligned} \quad (55)$$

where

$$\lambda_1 = \sum_q \phi_q^* \phi_q, \quad (56)$$

$$\lambda_2 = \sum_q \phi_q \phi_{-q}. \quad (57)$$

Minimizing F with respect to ϕ_q^* , we find

$$\begin{aligned} 0 = & \frac{1}{2} U_q + \left(\epsilon_q^0 + \frac{1}{2} 3c_0 (\phi_0^2 + \lambda_1) \right) \phi_q \\ & + \left(\frac{1}{4} 3c_0 (\phi_0^2 + \lambda_2) - \frac{1}{4} 3b_1 \phi_0 \delta_{\vec{p}_1, \vec{q}_1} \right) \phi_{-q}^*. \end{aligned} \quad (58)$$

We find that ϕ_q and ϕ_{-q}^* are coupled in the ordered phases. Then, changing variables

$$\alpha_{q+-} = (1/\sqrt{2}) (\phi_q \pm \phi_{-q}^*), \quad (59)$$

we find

$$\begin{aligned} \epsilon_{q+-} = & \epsilon_q^0 + \frac{1}{2} 3c_0 (\phi_0^2 + \lambda_1) \\ & \pm \left(\frac{1}{4} 3c_0 (\phi_0^2 + \lambda_2) - \frac{1}{4} 3b_1 \phi_0 \delta_{\vec{p}_1, \vec{q}_1} \right) \end{aligned} \quad (61)$$

which is the energy of magnitude (+) and phase (-) fluctuations. We must now determine the three constants ϕ_0 , λ_1 , and λ_2 self-consistently. At this point in the calculation, we must ensemble average expressions (56) and (57) for λ_1 and λ_2 . This yields

$$\lambda_1 = \sum_q \langle \phi_q^* \phi_q \rangle = \frac{NU_0^2}{8} \sum_q \left(\frac{1}{\epsilon_{q+}^2} + \frac{1}{\epsilon_{q-}^2} \right), \quad (62)$$

$$\begin{aligned} \lambda_2 &= \sum_q \langle \phi_q \phi_{-q} \rangle = \sum_q \langle \phi_q^* \phi_{-q}^* \rangle \\ &= \frac{NU_0^2}{8} \sum_q \left(\frac{1}{\epsilon_{q+}^2} - \frac{1}{\epsilon_{q-}^2} \right). \end{aligned} \quad (63)$$

Writing

$$\epsilon_{q+-} = \beta_{+-} + e_0 [\vec{q}_1 \cdot \vec{q} - \vec{q}_1 \cdot (\vec{q}_1 - \vec{p}_1)]^2 + f_0 (\vec{q}_1 \times \vec{q})^2, \quad (64)$$

$$\beta_{+-} = \frac{1}{2} a_0 + \frac{1}{2} 3c_0 (\phi_0^2 + \lambda_1) \pm \left(\frac{1}{4} 3c_0 (\phi_0^2 + \lambda_2) - \frac{1}{4} 3b_1 \phi_0 \delta_{\vec{p}_1, \vec{q}_1} \right) \quad (65)$$

we perform the integrals in (62) and (63) and find

$$\lambda_{1,2} = \frac{1}{2} C (1/\beta_+ \pm 1/\beta_-), \quad (66)$$

$$C = NU_0^2 / (4\pi)^2 (e_0 f_0)^{1/2} q_1^2. \quad (67)$$

Substituting (66) into (55) and (65), we find three equations for β_+ , β_- , and ϕ_0 which must be solved self-consistently:

$$\begin{aligned} \beta_+ &= \frac{1}{2} a_0 + \frac{1}{4} 9c_0 \phi_0^2 + \frac{1}{4} 3c_0 C (3/\beta_+ + 1/\beta_-) - \frac{1}{4} 3b_1 \phi_0 \delta_{\vec{p}_1, \vec{q}_1}, \\ \beta_- &= \frac{1}{2} a_0 + \frac{1}{4} 3c_0 \phi_0^2 + \frac{1}{4} 3c_0 C (1/\beta_+ + 3/\beta_-) + \frac{1}{4} 3b_1 \phi_0 \delta_{\vec{p}_1, \vec{q}_1}, \end{aligned} \quad (68)$$

The solution of these three equations will occupy the rest of this section. There are two types of solutions: (i) $\phi_0 = 0$, $\lambda_1 = \lambda_2$, normal state; and (ii) $\phi_0 \neq 0$, ordered state. The phase transition from the normal to the incommensurate phase will be taken up in Sec. IV C. Here we study the commensurate-incommensurate phase transition and assume that it occurs well below the transition to the normal state.

We first examine the solutions for the pure metal ($C = 0$). For the incommensurate phase, we find

$$\phi_0^2 = 2|a_0|/3c_0; \quad \beta_+ = |a_0|; \quad \beta_- = 0. \quad (71)$$

From (64), the energy spectrum for amplitude fluctuations ϵ_{q+} exhibits a gap ($= |a_0|$), whereas the energy spectrum for phase fluctuations ϵ_{q-} vanishes as $q \rightarrow 0$. For the commensurate phase, the amplitude fluctuations are essentially unchanged, but the phase fluctuation spectrum has a gap of

$$\beta_- = \frac{1}{8}9b_1(2|a_0|/3c_0)^{1/2} - e_0q_1^2 \left(q_1 - \frac{1}{3}K_1 \right)^2 > 0. \quad (72)$$

In the commensurate phase, the CDW is pinned to the crystal lattice, and this introduces a gap in the phase fluctuation spectrum as well.

We turn now to the dirty material where C is finite. If we try to use straightforward perturbation theory for small C we get into trouble. In zeroth order $\beta_- = 0$ for the incommensurate phase and the integral of $1/\epsilon_q^2$ - diverges. We can, however, use a self-consistent perturbation scheme, being careful to treat the long-wavelength phase fluctuations correctly. We first eliminate the ϕ_0^2 term from (68) and (69) using (70). Then using

$$\beta_+ \approx |a_0|, \quad (73)$$

we find

$$\beta_- = \frac{1}{2}g + \left(\frac{1}{4}g^2 + \frac{1}{4}3c_0C \right)^{1/2}, \quad (74)$$

$$g = -3c_0C/4|a_0| + [-e_0q_1^2(q_1 - p_1)^2 + \frac{1}{8}9b_1(2|a_0|/3c_0)^{1/2}] \delta_{a_1, p_1} \quad (75)$$

The free-energy difference between the commensurate and incommensurate phases is

$$F_C - F_I = \Delta S^p (T - T_{CI}^p) + \frac{33}{32}C^2c_0 \left(\frac{1}{\beta_{-C}^2} - \frac{1}{\beta_{-I}^2} \right) + \frac{1}{2}C \ln \frac{\beta_{-C}}{\beta_{-I}}, \quad (76)$$

where ΔS^p is the transition entropy for the pure metal, and T_{CI}^p is the transition temperature. For small C , we have

$$\beta_{-I} \approx \left(\frac{1}{4}3c_0C \right)^{1/2} \quad (77)$$

$$\beta_{-C} \approx g_0 = \frac{1}{8}9b_1(2|a_0|/3c_0)^{1/2} - e_0^2q_1^2 \left(q_1 - \frac{1}{3}K_1 \right)^2, \quad (78)$$

and

$$F_C - F_I \approx \frac{1}{4}C \left(\ln \frac{4g_0^2}{3c_0C} - \frac{11}{2} \right) + \Delta S^p (T - T_{CI}^p), \quad (79)$$

and the transition temperature of the dirty metal is

$$T_{CI}^d \approx T_{CI}^p - \frac{C}{4\Delta S^p} \left(\ln \frac{4g_0^2}{3c_0C} - \frac{11}{2} \right). \quad (80)$$

The principal effect of the impurities is to pin the long-wavelength phase fluctuations in the incommensurate phase and introduce a gap $(\frac{1}{4}3c_0C)^{1/2}$ in the excitation spectrum. The phase fluctuations of the commensurate phase are already pinned to the lattice and are essentially unmodified. Another way of saying this is that the incommensurate CDW is flexible and can adjust itself to take advantage of the impurity potential, whereas the commensurate CDW is inflexible. The expansion parameter used above is $(3c_0C/4g_0^2)^{1/2}$, which is the ratio of the gaps. When this parameter is large, we have

$$F_C - F_I \approx \frac{1}{8}9C (4g_0^2/3c_0C)^{1/2} + \Delta S^p (T - T_{CI}^p), \quad (81)$$

$$T_{CI}^d \approx T^p - (9C/8\Delta S^p) (4g_0^2/3c_0C)^{1/2}. \quad (82)$$

The free energy is singular at $C = 0$, and this is why straightforward perturbation theory fails. Within the approximations used, the phase transition is first order and sharp. We have, however, performed the ensemble average at an intermediate step in the calculation, and this is physically equivalent to taking into account the average effects of impurities on the excitation spectrum but omitting fluctuations in impurity density. Since the transition temperature is a strong function of impurity concentration, fluctuations in concentration will broaden the phase transition. The correlation length for phase fluctuations is finite in the dirty case and is

$$\xi_{ph} \approx \left[2e_0q_1^2 / (3c_0C)^{1/2} \right]^{1/2}. \quad (83)$$

The sharp reduction in T_{CI} is observed in the isoelectronic alloy $\text{Ta}_{1-x}\text{Nb}_x\text{Se}_2$.³

C. Incommensurate-normal-state transition

In the normal state near the phase transition, we must use the full nonlinear Eqs. (68)-(70) but with $\phi_0 = 0$; this implies $\beta_+ = \beta_-$, and we find

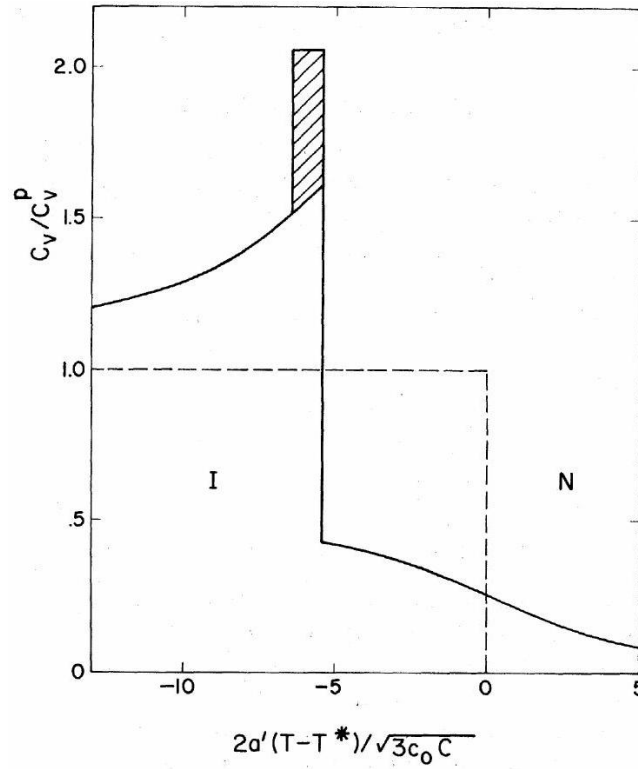


FIG. 3. Detail of the heat capacity near the incommensurate-normal-metal transition according to the approximate theory for the clean (dashed-line) and dirty (solid-line) case. The cross hatched area is the transition entropy for the alloy case which is weakly first order. The approximation used for the alloy neglects fluctuations of impurity concentration and yields a spurious first-order transition; this phase transition should be smeared out.

$$\beta_+ = \frac{1}{4}a_0 + \left[\left(\frac{1}{4}a_0 \right)^2 + 3c_0C \right]^{1/2}. \quad (84)$$

At the pure-metal transition temperature ($a_0 = 0$), there is an energy gap in the fluctuation spectrum of $(3c_0C)^{1/2}$, and the correlation length is finite.

$$\xi \approx \left[e_0 q_1^2 / (3c_0C)^{1/2} \right]^{1/2}; \quad T = T^*. \quad (85)$$

In the incommensurate state near the phase transition, we must solve Eqs. (68)-(70) numerically. We first define dimensionless variables

$$\bar{\beta}_{\pm} = 2\beta_{\pm} / (3c_0C)^{1/2} \quad (86)$$

$$\bar{\phi}_0 = \phi_0 / (2|a_0|/3c_0)^{1/2} \quad (87)$$

and the dimensionless coupling constant

$$\bar{g} = (3c_0C/4a_0^2)^{1/2}. \quad (88)$$

Equations (68)-(70) now read

$$\bar{\beta}_+ = 1/\bar{g} - (3/\bar{\beta}_+ + 1/\bar{\beta}_-), \quad (89)$$

$$\bar{\beta}_- = 1/\bar{\beta}_+ - 1/\bar{\beta}_-, \quad (90)$$

$$\bar{\phi}_0^2 = 1 - \bar{g} (3/\bar{\beta}_+ + 1/\bar{\beta}_-), \quad (91)$$

and the free energy is

$$\begin{aligned} c_0 F/a_0^2 = & -\frac{1}{3}\bar{\phi}_0^2 + \frac{1}{6}\bar{\phi}_0^4 + \frac{2}{3}\bar{g}^2 (\ln \bar{\beta}_+ + \ln \bar{\beta}_-) - \frac{1}{3}\bar{g} (1/\bar{\beta}_+ + 1/\bar{\beta}_-) \\ & + \frac{1}{3}\bar{g}\bar{\phi}_0^2 (3/\bar{\beta}_+ + 1/\bar{\beta}_-) + \frac{1}{6}\bar{g}^2 \left[(1/\bar{\beta}_+ - 1/\bar{\beta}_-)^2 \right. \\ & \left. + 2 (1/\bar{\beta}_+ + 1/\bar{\beta}_-)^2 \right]. \end{aligned} \quad (92)$$

By minimizing F with respect to $\bar{\beta}_+$, $\bar{\beta}_-$, and $\bar{\phi}_0$, one can rederive (89)-(91). To solve the equations, we choose a value for $\bar{\beta}_-$ and solve (90) for $\bar{\beta}_+$, then we solve (89) for $\bar{g}$ and find $\bar{\phi}_0$ from (91); the free energy is then found from (92). We must compare free energies of the normal and incommensurate states to decide which state is stable at a particular temperature. From the free energy, one can compute the heat capacity, and this is shown in Fig. 3. There is a pretransition heat capacity in the normal phase due to the buildup of CDW driven by the impurity potential. The transition temperature is suppressed somewhat, and the transition to a finite ϕ_0 is weakly first order, with ϕ_0 at the phase transition being 0.8 of the pure-metal value. In the ordered phase, the fourth-order interaction suppresses the ϕ_q driven by the impurity potential. The fact that one finds a sharp first-order phase transition is undoubtedly an artifact arising from the way that the impurity averaging is done. Fluctuations in impurity concentration will smear the "phase transition" and remove the sharp details. Thus, one must be cautious in accepting at face value the results of this type of effective-potential method. The mechanism for the depression of the commensurate-incommensurate transition appears to be physically correct. Spatial fluctuations in impurity density will cause spatial fluctuations in the energy gap for phase fluctuations but will not qualitatively affect the free-energy difference.

20.0.5 V. Fluctuation Modes

In this section, we study the order-parameter fluctuation modes for the triple ICDW in pure material. In Sec. IV, we found the energies of these modes for single ICDW's and CCDW's. For the commensurate state, we found an amplitude fluctuation mode with an energy gap $|a_0|$ at long wavelength and a phase fluctuation mode with an energy gap given by (72). For the incommensurate state, we found an amplitude fluctuation mode with an energy gap $|a_0|$ and a phase fluctuation mode with no energy gap (a hydrodynamic mode). The energy of the phase fluctuation mode is

$$\epsilon_q^- = e_0 (\vec{q}_1 \cdot \vec{q})^2 + f_0 (\vec{q}_1 \times \vec{q})^2 \quad (93)$$

for the incommensurate wave. This last mode is Overhauser's phason.¹³

For the triple ICDW case, we omit the impurity potential, while the umklapp terms drop out. We write

$$\psi_i(\vec{r}) = \phi_i(\vec{r}) e^{i\vec{q}_i \cdot \vec{r}}, \quad (94)$$

$$\phi_i(\vec{r}) = \phi_0 + \sum_q \phi_{iq} e^{i\vec{q} \cdot \vec{r}}, \quad (95)$$

where the $\phi_i(\vec{r})$ is slowly varying. The free energy is then
The minimum in the free energy is for $\phi_{iq} = 0$ and

$$F = \int d^2r \left(\frac{1}{2} a_0 \sum_i |\phi_i|^2 - \frac{1}{4} 3b_0 (\phi_1 \phi_2 \phi_3 + \phi_1^* \phi_2^* \phi_3^*) \right)$$

ϕ_0 given by (22). Near that minimum, we can expand F in powers of ϕ_{iq} and keep only second-order terms. We find

$$\begin{aligned} F = F(\phi_0) + \sum_{iq} \left[\frac{1}{2} a_0 + \frac{1}{2} 3c_0 \phi_0^2 + (3c_0 - 2d_0) \phi_0^2 + e_0 (\vec{q}_i \cdot \vec{q})^2 + f_0 (\vec{q}_i \times \vec{q})^2 \right] \phi_{iq}^* \phi_{iq} \\ + \frac{1}{8} 3c_0 \phi_0^2 \sum_{iq} (\phi_{iq} \phi_{i-q} + \phi_{iq}^* \phi_{i-q}^*) - \frac{1}{4} 3b_0 \phi_0 (\phi_{1q} \phi_{2-q} + \phi_{1q}^* \phi_{2-q}^* + \text{permutations}) \end{aligned} \quad (97)$$

In order to find the eigenmodes, we first transform to amplitude (+) and phase (-) variables

$$\alpha_{iq}^{+-} = (1/\sqrt{2}) (\phi_{iq} \pm \phi_{i-q}^*), \quad (98)$$

and find

$$F = F(\phi_0) + F^+ + F^- \quad (99)$$

$$\begin{aligned} F^- = \sum_{iq} \left[\frac{1}{4} 3b_0 \phi_0 + e_0 (\vec{q}_i \cdot \vec{q})^2 + f_0 (\vec{q}_i \times \vec{q})^2 \right] \alpha_{iq}^{-*} \alpha_{iq}^- \\ + \frac{1}{4} 3b_0 \phi_0 \sum_q (\alpha_{1q}^{-*} \alpha_{2q}^- + \alpha_{2q}^{-*} \alpha_{1q}^- + \text{permutations}) \end{aligned} \quad (100)$$

with a similar expression for F^+ . The amplitude fluctuations have a large energy gap $3|a_0|c_0/(15c_0 - 8d_0)$ at long wavelength and are uninteresting. We now diagonalize the 3×3 matrix of Eq. (100) and find one phase fluctuation mode with an energy gap $\frac{1}{4} 9b_0 \phi_0$ involving relative motion of the three CDW's and two hydrodynamic modes (i.e., zero gap), with energies

$$\bar{\epsilon}_q^1 = \left(\frac{1}{4} e_0 q_1^2 + \frac{3}{4} f_0 q_1^2 \right) q^2 \quad (101)$$

$$\bar{\epsilon}_q^2 = \left(\frac{3}{4} e_0 q_1^2 + \frac{1}{4} f_0 q_1^2 \right) q^2 \quad (102)$$

with $\vec{q}$ along a symmetry axis. These modes involve long-wavelength distortions of the chargedensity lattice and are the transverse and longitudinal "phonons" of the ICDW "lattice." These modes are probably overdamped (due to the resistivity of electron motion relative to the crystal lattice), but we do not yet have a dynamical theory to describe the motion. The thermally excited "phonons" will induce diffuse scattering near the CDW Bragg scattering peak, with intensity proportional to

$$\langle |\phi_q|^2 \rangle = \sum_i kT / \bar{\epsilon}_q^i. \quad (103)$$

20.0.6 VI. Dislocations

We have seen that the triple ICDW has peaks of electron density at the "lattice" sites of a hexagonal "crystal" and that the long-wavelength distortions of the ICDW are the "phonons." One wonders if there may be other imperfections or distortions analogous to crystalline imperfections or distortions. Vacancies or interstitials are not possible because the units making up the ICDW "lattice" are not discrete. However, "dislocations" are possible, and we will now describe a "dislocation" in the charge-density wave. We emphasize that the host crystal is assumed to be perfectly uniform and that only the charge-density wave is distorted into a "dislocation." It will be apparent that the ICDW "dislocation" is perfectly analogous to the vortex line in superfluid helium and superconductors. Following (94), we write a trial solution for the order parameter with a "dislocation" at the origin.

$$\phi_1(\vec{r}) = f(r)e^{-i(\theta-\pi/2)}, \quad (104)$$

$$\phi_2(\vec{r}) = f(r)e^{i(\theta-\pi/2)}, \quad (105)$$

$$\phi_3(\vec{r}) = f(r), \quad (106)$$

$$f(r) = \phi_0 (1 - e^{-\alpha r}), \quad (107)$$

where θ is the angle between $\vec{r}$ and $\vec{q}_1$. Using (1), one can compute the electron density and show that (104)-(107) represent an edge dislocation with Burger's vector in the $\vec{q}_3$ direction. Substituting (104)-(107) into the free-energy expression, we find

$$F \approx F(\phi_0) + (4\pi/\alpha^2) |F(\phi_0)| + 8\pi e_0 q_1^2 \phi_0^2 \ln(\alpha R), \quad (108)$$

where we have used the isotropic approximation ($e_0 = f_0$), and R is the radius of the crystal or half the distance to the nearest dislocation of opposite sign. The two terms are the condensation energy of the core region (core radius $\approx 1/\alpha$) and the distortion energy of the ICDW outside the core. In the core, ϕ is small and this region is normal. Minimizing F with respect to α , we find

$$\alpha^2 = 3|a_0|/4e_0 q_1^2 = 3/2\xi^2, \quad (109)$$

so that the core radius is approximately equal to one correlation length. This describes the twodimensional properties of a "dislocation" in one layer. As regards the three-dimensional structure, it is possible, in principle, to have a "dislocation" pair in one layer with the other layers uniform. It is also possible to have a dislocation proceeding vertically through a number of layers. In order to discuss these possibilities, it is necessary to consider interlayer interactions in some detail, and we will not pursue the matter here.

20.0.7 VII. Conclusions

We have written down a conventional but rather complicated Landau theory to describe charge-density waves in layered compounds. We have discussed the nature of the phase transitions between the normal incommensurate and commensurate phases and concluded that the phases should appear in this order with decreasing temperature and that the phase transitions should be first order. The peaks of electron density occur at lattice sites of a hexagonal "crystal," and we calculate the behavior of two other crystalline properties, "phonons" and "dislocations." Impurities distort the charge-density wave and pin it. Since the incommensurate wave is more flexible, it can distort more readily and gain more energy from the impurity potential than can the commensurate wave. This reduces the commensurate-incommensurate transition temperature for the alloy.

There are a number of things that we have not done in this paper.

(i) We have not considered interlayer interac-

(ii) At this point, the Landau theory is entirely phenomenological, and the parameters must be determined from experiment. It will be of great interest to derive the Landau parameters from a microscopic theory once a quantitative microscopic theory is developed. There is a small parameter in the problem, $kT_c/(d \text{ bandwidth})$, and one anticipates that, as in superconductivity, the behavior may be mean-field-like over a wide temperature range.

(iii) We have not considered the dynamic behavior of this system. Perhaps the next step is to develop a dynamical Landau theory.

(iv) The most interesting properties of the CDW's are the transport properties, and one would like to have a microscopic transport theory, as well as accurate measurements of resistivity and thermal conductivity.

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Part VI

Special Effects: Useful, Selected Articles

21 Origin of Distinct Insulating Domains in the Layered Charge Density Wave Material 1T-TaS₂ by Yang

21.1 Article

Vertical charge order shapes the electronic properties in layered charge density wave (CDW) materials. Various stacking orders inevitably create nanoscale domains with distinct electronic structures inaccessible to bulk probes. Here, the stacking characteristics of bulk 1T-TaS₂ are analyzed using scanning tunneling spectroscopy (STS) and density functional theory (DFT) calculations. It is observed that Mott-insulating domains undergo a transition to band-insulating domains restoring vertical dimerization of the CDWs. Furthermore, STS measurements covering a wide terrace reveal two distinct band insulating domains differentiated by band edge broadening. These DFT calculations reveal that the Mott insulating layers preferably reside on the subsurface, forming broader band edges in the neighboring band insulating layers. Ultimately, buried Mott insulating layers believed to harbor the quantum spin liquid phase are identified. These results resolve persistent issues regarding vertical charge order in 1T-TaS₂, providing a new perspective for investigating emergent quantum phenomena in layered CDW materials.

Introduction

Layered materials exhibit unique electronic properties governed by the atomic and electronic characteristics of their constituent building blocks, as well as their interlayer couplings, including Coulomb interactions, orbital hybridization, charge transfer, and van der Waals forces [1, 51, 3]. Given the susceptibility of these interlayer interactions to various stimuli, such as atomic defects [4] and hydrostatic pressure [5], distinct domains with various stacking configurations naturally coexist in layered materials. To understand the electronic properties of these diverse structures and the emergence of exotic quantum phenomena at their interfaces, it is crucial to systematically investigate domain configurations and their electronic structures.

1T-TaS₂ is an extensively studied two-dimensional correlated system, renowned for its rich phase diagram [5, 16, 7, 8, 9, 10, 30, 12, 64]. The atomic layer is composed of a plane of Ta atoms encapsulated by S atoms with an octahedral coordination. Upon cooling, it undergoes a metal-insulator transition with a charge density wave (CDW) reconstruction [14]. The CDW phase is accompanied by a $\sqrt{13} \times \sqrt{13}$ periodic lattice distortion, comprising clusters that resemble the Star of David (SD). Each SD contains 13 Ta atoms, with 12 forming pairs to create a CDW band gap, while the unpaired electron of the central Ta atom contributes to a narrow metallic band [16]. Due to strong on-site Coulomb interactions, intralayer electron hopping is strongly suppressed at low temperatures. Since the localized spins of the correlated insulator are frustrated by the triangular lattice, this material is an ideal platform to realize the quantum spin liquid phase (QSL)[15, 14].

In bulk 1T-TaS₂, the electronic structure is significantly influenced by the vertical stacking order [17], resulting in the ground state with a dimerized configuration. Interlayer electron hopping promotes a dispersive metallic band along the stacking direction [18]. However, at

low temperatures, it exhibits insulating electronic properties with commensurate CDWs. Theoretical calculations associate this with the formation of a dimerized insulating layer where the SD is vertically aligned without a lateral shift [46, 20]. This dimerized configuration is energetically stable because of the energy gain from bonding-antibonding hybridization of the unpaired electrons; otherwise, it would be prohibited due to Coulomb repulsion. Dimerized band insulating layers are stacked with a lateral shift in the bulk. This is similar to the Peierls' CDW metal-insulator transition in one-dimensional half-filled metallic systems [21].

Cleaving this layered material produces two distinct insulating surfaces: Type-I with a dimerized layer termination and Type-II with an undimerized layer termination. The two distinct surface terminations can be distinguished by their energy band gaps [20, 43, 23], with Type-I exhibiting a larger band gap compared to Type-II. They also exhibit distinct spectral responses to electron doping, featuring a rigid band shift and a spectral weight transfer for Type-I and Type-II surfaces [44], respectively. In contrast, subsequent scanning tunneling microscopy and spectroscopy (STM/STS) studies have shown a larger gap spectrum on the surface terminated with a single layer rather than a smaller gap [25]. Moreover, the larger gap domain has been suggested to host a QSL phase, as evidenced by the band shift in a magnetic field [26, 27, 28]. These results strongly imply that subsurface stacking configurations, which include stacking faults induced by undimerized layers, are crucial for reconciling the discrepancy in the measured tunneling spectra [23]. However, experimental verification of subsurface stacking faults, their distribution and impact on the electronic structure of the surface remains limited.

In this work, we employ STM and STS measurements to visualize distinct insulating domains which form as a result of the change in stacking configurations across the surface of bulk 1T-TaS₂. Our observations reveal the coexistence of Type-I and Type-II domains near a monolayer step on the topmost layer [43, 44]. Interestingly, in proximity to the monolayer step, both the upper and lower layers are predominantly occupied by the Type-I termination, suggesting that it is more energetically favorable for the stacking fault to reside beneath the surface. Furthermore, spatially resolved STS measurements over a large area reveal three distinct Type-I domains separated by both surface and subsurface domain walls. These distinct Type-I domains show a rigid band shift and band edge broadening, highlighting the interplay between subsurface stacking configurations and the electronic properties of the surface state. Finally, by combining our high-resolution STS data with density functional theory (DFT) calculations, we demonstrate how different subsurface stacking orders can lead to the observed electronic structures of the surface.

Results and Discussion

Our data are acquired in the commensurate CDW phase, characterized by the presence of a triangular SD superlattice (Figure 21.1a). A representative STM image (Figure 21.1b) shows the SD clusters as bright protrusions (inset). The dark spots in the STM image acquired at -400 mV are intrinsic defects related to sulfur (S) vacancies [29, 30] whose features are more enhanced at the lower bias due to their in-gap states (Figure S1 in Supplementary Information). Figure 21.1c shows a representative differential conductance (dI/dV) spectrum acquired at a region away from intrinsic defects. The spectrum displays two prominent peaks located near ± 200 meV, which show upward band bending near intrinsic defects or CDW domain walls. These insulating spectral features have been commonly observed in STS measurements [43, 44, 52]. Notably, our high-resolution STS spectra enable us to finely resolve the band edges as spectral peaks (see red arrows in Figure 21.1c) with negative differential resistance, which have usually been resolved as shoulders in the tunneling spectra. We attribute the peculiar characteristics to resonant tunneling between localized states of the sample and an atomically

sharp STM tip [32]. These enhanced spectral features allow us to distinguish domains that have subtle differences in the edges of their electronic bands. The origin of the edges will be discussed in the subsequent section.

We first present STM results acquired near a monolayer step to examine the electronic structure on both Type-I and Type-II surface terminations. The STM image (Figure 21.2a) shows bright and dark regions corresponding to the upper and lower terraces, respectively. A subsequent STM image at a reduced bias voltage of +170 mV (Figure 21.2b) displays a uniform electronic structure across the lower terrace, characterized by a consistent superstructure and absence of domain walls. In contrast, the upper terrace exhibits two types of domains with different electronic structures, separated by surface domain walls. The step height is consistent with the thickness of a single layer 1T-TaS₂, but is slightly higher at the step edge (Figure S2 in Supplementary Information). This implies that a higher conductance domain locally forms close to the step edge and rearranges the vertical charge order across the domain wall to maintain a similar electronic structure to the lower terrace [23].

The dI/dV map (Figure 21.2c), simultaneously acquired with the STM image (Figure 21.2b), clearly illustrates the presence of two distinct types of domains with varying contrasts on the upper terrace: a dark triangular center domain and bright adjacent domains. Notably, the contrast of the bright domains on the upper terrace matches that of the lower terrace. A series of dI/dV spectra (Figure 21.2d), taken along the black arrow in Figure 21.2c, indicates that the bright domains on both terraces indeed share identical electronic structures. Furthermore, it reveals that while both the bright and dark domains are insulating, their spectra exhibit significant differences in terms of bandgap values and peak intensities (Figure 21.2e): the peak-to-peak bandgaps for the two domain types are around 0.39 eV and 0.2 eV, respectively. Since the contrast in the dI/dV map highlights the relative difference in the electronic structures, the domain walls with in-gap states in larger gap domains are more prominent than those in smaller gap ones (See Experimental Section). A collection of dI/dV maps obtained near the step edge (Figure S3 in Supplementary Information) demonstrates that the larger gap spectrum is dominant across the surface, with the smaller gap spectrum confined to small domains near the step edge.

According to previous DFT calculations [23] and many-body theoretical calculations [20], the larger bandgap of 0.39 eV results from interlayer hybridization in the dimerized layer (Type-I) and the smaller gap of 0.2 eV arises from the correlated Mott gap in the undimerized surface layer (Type-II). The latter, a half-filled layer, exhibits correlated insulating behavior with strong on-site Coulomb repulsion, otherwise, it shows metallic behavior. This correlated insulating layer is expected to have a smaller gap than the band insulating layer with an appropriate Coulomb energy, which stabilizes the dimerized configuration. From the characteristic dI/dV spectra of the two different domains (Figure 21.2e), we can identify the areas with higher and lower dI/dV intensities in Figure 21.2c as Type-I and Type-II domains, respectively (See Experimental Section).

The crossover from Type-I to Type-II domains within a terrace is incompatible with the dimerization scenario for the insulating ground state in the layered CDW material. Prior STM studies have demonstrated that the undimerized layer is a Mott insulator with a smaller gap [43] and exhibits doping-induced spectral weight transfer instead of a rigid band shift [44]. However, subsequent STM results have shown surfaces with the larger gap spectrum, even when the terraces are separated by a monatomic step [25, 54]. These observations have attracted renewed attention to the underlying physics of the ground state. Importantly, it was predicted that the undimerized layer (Type-II) is less stable than the dimerized layer at the surface, leading to the surface reconstruction of the CDWs [23]. In systems with undimerized layers at the surface, CDW phase shifts occur via the lateral bond-relaxation of the SD clusters in the second layers. This reconstruction relocates the undimerized layer from the top to the

third layer, leaving a dimerized layer on the surface (Type-I with a subsurface fault). We can interpret this unique reconstruction as the vertical bond relaxation driven by the lateral bond relaxation. The unstable Type-II surface can only manifest in small domains near surface steps, where electronic structures at the domain boundaries can overcome the surface energy instability within the domain. Our observations, in which most of the surface is populated by the Type-I domains with the Type-II domains existing primarily near the step edge, fully corroborate these theoretical predictions (Figure S3 in Supplementary Information). It is worth noting that our samples were cleaved at room temperature and subsequently cooled to cryogenic temperatures, ensuring that the vertical configuration of CDW stacking is stabilized during the commensurate CDW formation around 180 K. This strongly implies the presence of buried undimerized layers, which have been identified, within the otherwise fully dimerized ground state configuration.

Although the topmost layer is likely to be dimerized, there can be various deviations from the ground state, forming heterogeneous domain configurations [23, 34]. To demonstrate the presence of distinct stacking orders, we visualize the electronic structure of a large flat terrace without a step edge (Figure 21.3a). By selecting a bias voltage close to the band edge, we highlight the spatial variation of the band edge that can be influenced by subsurface stacking orders (Figure S4 in Supplementary Information). Remarkably, the dI/dV map of the same area (Figure 21.3b) shows three distinct insulating domains (marked by α , α^* and β) with varying intensities, which up to now have not been thoroughly investigated. The bright (dark) lines in Figure 21.3a (Figure 21.3b) represent surface domain walls resulting from CDW phase shifts (Figure S5 in Supplementary Information). Additionally, the consistency of our tunneling spectra with previous studies [46, 43, 44], which indicate dimerization of the first and second layers, leads us to attribute the sharp interfaces lacking CDW phase shifts to subsurface domain walls. These domain walls may exist in the third layer or below, giving rise to domains with different stacking orders. Therefore, these domain configurations and their interfaces strongly support the presence of distinct stacking configurations beneath the surface, resulting in a heterogeneous surface electronic structure.

Figure 21.3c shows the representative dI/dV spectra of the three distinct insulating domains indicated in Figure 21.3b. They exhibit the characteristic Type-I spectrum, implied by the large band gap of about 0.39 eV [46, 20, 43]. Despite each having dimerized layers at the surface, there are some clear differences: First, domain- α^* shows a notable rigid band shift of about 45 meV compared to domain- α without a significant change in the overall spectral shape. Second, domain- β exhibits broader band edges (marked by red arrows in Figure 21.3c) than domain- α , while the two prominent peaks seem identical. It is worth noting that the variations in the surface electronic structure are not local features caused by defects or domain walls (Figure S6 in Supplementary Information), as evidenced by the homogeneous background dI/dV contrast across each domain in Figure 21.3b.

Among the three different Type-I domains, we observed that domain- α and domain- α^* appear most frequently on multiple cleaved surfaces. This implies that domain- α (or domain- α^*) has a lower formation energy compared to domain- β . To identify the stacking configurations, we adopt the notations from a previous work [46] (Figure 21.4a). Our theoretical calculations clearly show that there are distinct Type-I configurations with energies lower than the Type-II (colored red in Figures 21.4b and c). Note that the layered material likely has all-dimerized configurations with diverse stacking orders (colored black in Figures 21.4b and c). In addition, one or more undimerized layers can be found in the bulk [34], leading to a slightly higher formation energy (colored blue in Figures 21.4b and c). A comprehensive set of calculated formation energies for various stacking configurations is provided in Figure S7 in Supplementary Information. Although we cannot precisely determine the number of undimerized layers in the bulk sample, all-dimerized configurations are likely connected to domain- α and domain- α^* ,

while the other Type-I configurations are associated with domain- β , with subsurface faults within a few layers close to the surface.

We now focus on the two distinct tunneling spectroscopic features of the surface density of states (DOS) of domain- α^* and domain- β with respect to domain- α . The most obvious difference is that domain- β has broader band edges compared to domain- α (Figure 21.3c). Our calculated projected density of states (PDOS) spectra reveal that the spectral features are related to the existence of the undimerized layer underneath the surface (red arrows on blue curves in Figure 21.4d). The layer-selective PDOS spectra (See Figure S7 in Supplementary Information) clearly show that the minor peaks at the band edges in the top-layer PDOS can be attributed to the coupling with the principal peaks of the third-layer central Ta atoms. The band gap for the subsurface dimerized layer is estimated to be 0.18 eV. In contrast, the band gap of the subsurface undimerized layer is around 0.11 eV. These results agree with the experimentally observed changes in the gap values of 0.25 eV and 0.16 eV determined by the minor peaks in domain- α and domain- β , respectively.

On the other hand, domain- α^* exhibits spectral characteristics identical to domain- α with an upward band shift (Figure 21.3c). These features are well consistent with the calculated spectra for all-dimerized configurations (black curves in Figure 21.4c). The band shift is attributed to a higher defect density in domain- α^* compared to domain- α (Figure S8 in Supplementary Information). The upward band bending near the intrinsic defects is a typical screening behavior against acceptor-type dopants in the insulating material [30]. Taken together, we conclude that domains with distinct all-dimerized configurations exist and while their defect densities are not crucial in determining their stacking orders, they do influence their Fermi levels (E_F).

Very recently, magnetic field-dependent STM experiments [26] revealed suggestive fingerprints of the QSL phase predicted to exist in 1T-TaS₂. Specifically, certain Type-I spectra exhibited a downward shift in the presence of an external magnetic field, consistent with the theoretical predictions for QSL behavior [27, 28]. However, two issues must be addressed to establish this phenomenon as direct evidence for the QSL phase. First, it conflicts with the conventional understanding that Type-I domains do not host localized spins due to interlayer hybridization. Second, some Type-I spectra do not exhibit the magnetic field response. Our data reconcile these disparate observations by demonstrating the likely presence of Mott insulating layers beneath band insulating surfaces. Thus, the two different behaviors of the Type-I spectra under a magnetic field can be attributed to subsurface stacking faults, emphasizing that Type-I domains cannot be characterized solely by a single electronic structure.

Conclusion

In conclusion, we have identified multiple distinct insulating domains in a wide field of view on the surface of bulk 1T-TaS₂ with our high-resolution STS measurements and DFT calculations. We find that the material prefers to maintain a dimerized surface via surface reconstruction and that the subsurface stacking configuration can be altered due to surface reconstruction. The spatial variations in the surface DOS, identified by the reduction of the CDW gap, broadening of the band edges and a rigid band shift, are revealed to be determined by the differences in stacking configurations and the defect concentration, respectively. These findings provide important insights into reconciling the discrepancies in spectroscopic measurements and identifying this layered CDW material as a platform for a QSL phase. Since our results are related to vertical charge orders, they are envisaged to be highly relevant to many other layered CDW systems, helping to resolve long-standing open issues about competing phases and ground state formation.

Experimental Section

Synthesis and STM Measurements

1*T*-TaS₂ crystals (HQ graphene) were synthesized by chemical vapor transport (CVT) with iodine as a transport agent. The 1*T*-phase was confirmed by low-temperature micro-Raman spectroscopy (Figure S9 in Supplementary Information). Measurements of STM and STS were conducted using a commercial low-temperature STM (UNISOKU) at a temperature of 4.2 K in an ultra-high vacuum environment of 1×10^{-10} Torr. Mechanically sharpened Pt / Ir (90/10) wires were used for STM tips after characterizing them on a gold (Au) or lead (Pb) (111) surface. Bulk 1*T*-TaS₂ samples were cleaved at room temperature and then transferred to the STM head, which had been cooled to 4.2 K. A standard lock-in technique was used for dI/dV measurements, with an ac voltage (a voltage modulation amplitude of 5 mV and a frequency of 613 Hz) added to the dc sample bias. Occasionally, dI/dV maps display a reverse contrast to a topographic image, which maps the height of the STM tip with feedback to keep the tunneling current constant. As the STM tip moves away from the surface due to the higher conductance, dI/dV signal gets weaker when it is acquired simultaneously with a topographic image [35].

Density Functional Theory Calculations

DFT investigations were carried out using the Vienna Ab Initio Simulation Package (VASP) [36, 37]. The computational approach involved the projector augmented wave method [38], the generalized gradient approximation for the exchange-correlation potential [39], and the DFT + *U* formalism as formulated by Dudarev et al. [40], setting the Hubbard *U* parameter to 1.25 eV for Ta 5*d* orbitals. Van der Waals forces were taken into account by applying the Tkatchenko-Scheffler method [41]. Electronic wave functions were described with a plane-wave basis set, with cutoff energies of 323 eV for bulk and 259 eV for surface calculations. Reciprocal space integration was conducted using a $4 \times 4 \times 8$ k-point mesh within the Brillouin zone of the $\sqrt{13} \times \sqrt{13} \times 1$ supercell. For surface models, a periodic slab geometry with seven or eight layers of TaS₂ and a vacuum separation of 20 Å was employed. The relaxation of all atomic positions was continued until the forces on each atom were below 0.01 eV/Å.

Raman Scattering Measurements

Raman spectroscopic experiments were carried out using a $\lambda = 561$ nm laser (Oxxius) with the sample mounted onto the cold finger of a He-flow cryostat (Oxford MicroStat). The laser was focused onto the sample with a spot diameter of 2 μ m and a laser power of less than 0.1 mW. Raman-scattered light was dispersed through a Princeton Instruments Trivista spectrometer onto a charge-coupled device detector (PyLoN eXcelon).

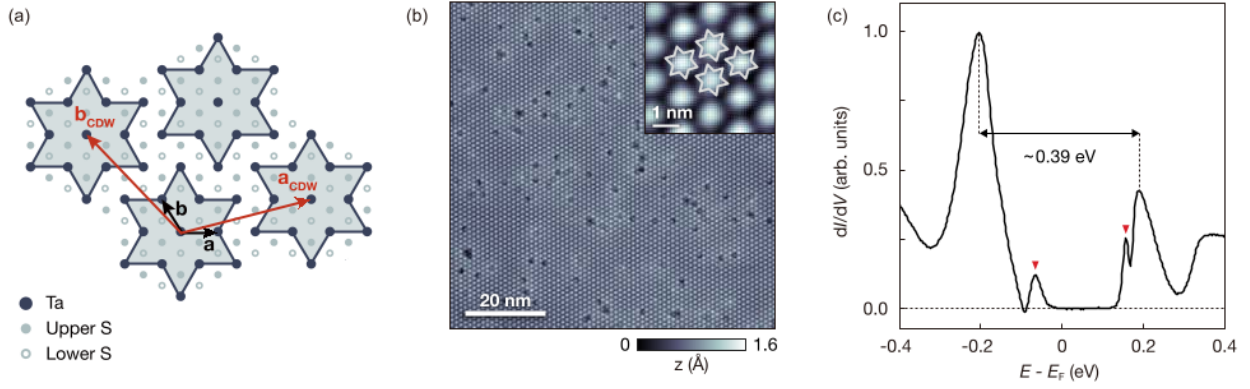


Figure 21.1: Insulating commensurate CDW phase of $1T$ -TaS₂. a) A schematic representation of the atomic structure of $1T$ -TaS₂ with the Star of David (SD) superstructure. The black and red arrows correspond to the unit vectors of the 1×1 and the $\sqrt{13} \times \sqrt{13}$ lattices, respectively. b) An STM image of the commensurate CDW phase in $1T$ -TaS₂ ($V_{\text{set}} = -400$ mV, $I_{\text{set}} = 50$ pA). Each bright protrusion represents an SD (inset). c) The representative dI/dV spectrum acquired on the surface of a Type-I domain ($V_{\text{set}} = -400$ mV, $I_{\text{set}} = 50$ pA, $V_{\text{mod}} = 5$ mV). The band gap, approximately 0.39 eV, is marked by a black arrow. Our spectrum exhibits enhanced band edge features marked by red arrows.

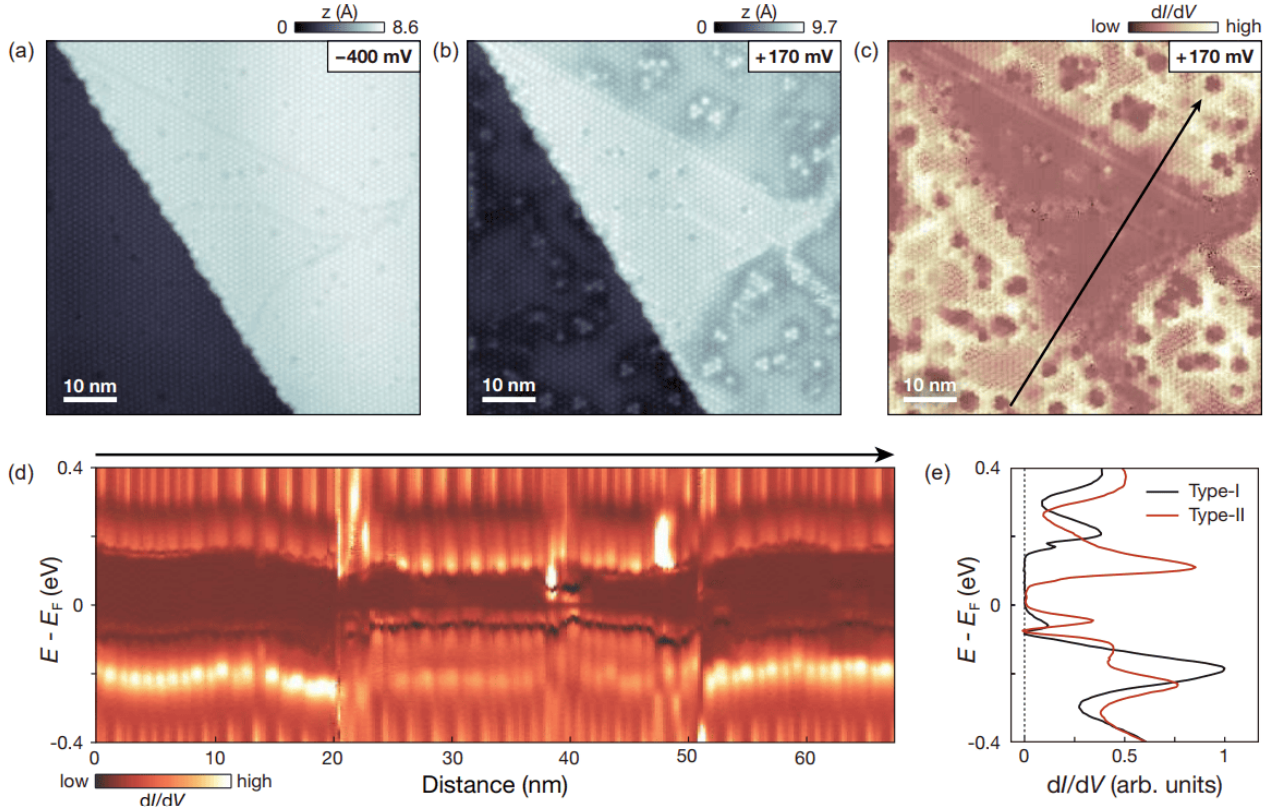


Figure 21.2: Coexistence of dimerized (Type-I) and undimerized (Type-II) layer terminations on the upper terrace of a step edge. a-b) STM images of the surface of bulk $1T$ -TaS₂ with the upper and lower terraces separated by a monolayer step obtained at different bias voltages (a $V_{\text{set}} = -400$ mV, $I_{\text{set}} = 100$ pA and b $V_{\text{set}} = +170$ mV, $I_{\text{set}} = 100$ pA, $V_{\text{mod}} = 5$ mV). c) The dI/dV map was acquired simultaneously with the STM image shown in b (See Methods). d) Line dI/dV spectra acquired along the line marked by the arrow shown in c. e) Averaged dI/dV spectra of the Type-I (black) and Type-II (red) domains acquired from defect-free areas ($V_{\text{set}} = -400$ mV, $I_{\text{set}} = 200$ pA, $V_{\text{mod}} = 5$ mV).

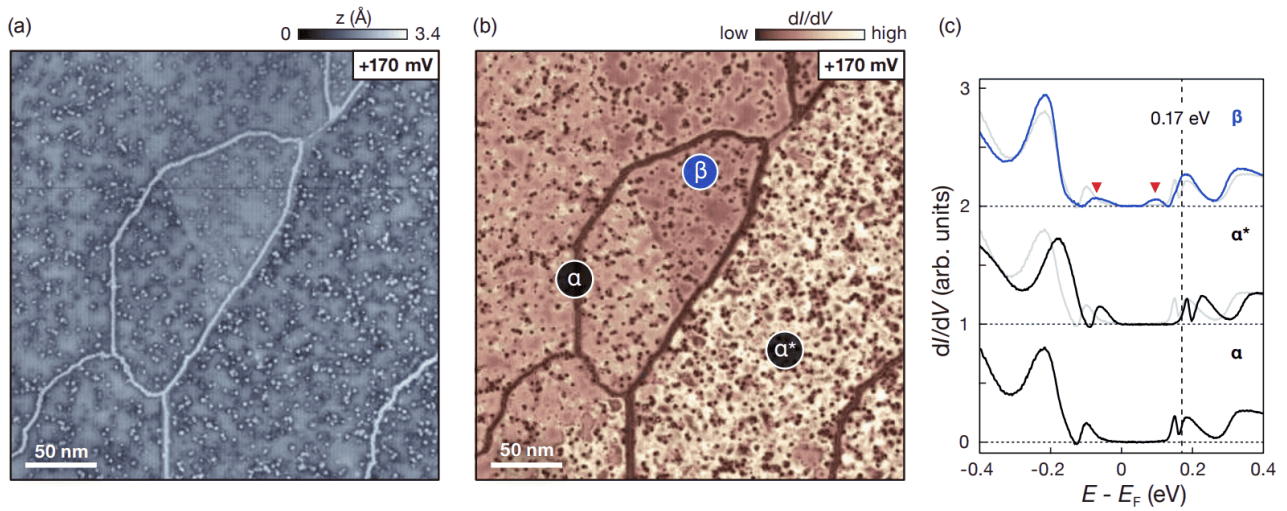


Figure 21.3: Three different Type-I insulator domains on a flat surface. a-b) Three different domains shown by both the STM image (a) and the dI/dV map (b) ($V_{\text{set}} = +170$ mV, $I_{\text{set}} = 50$ pA, $V_{\text{mod}} = 5$ mV). c) dI/dV spectra of the three domains (α , α^* and β) indicated in b averaged over areas not affected by local defects ($V_{\text{set}} = -400$ mV, $I_{\text{set}} = 50$ pA, $V_{\text{mod}} = 5$ mV). Each spectrum is vertically shifted with equal spacing for clarity. The vertical dashed line indicates the energy for the maps shown in (a) and (b). The higher dI/dV intensity in the tunneling spectra corresponds to the lower contrast in the dI/dV map (b), which is simultaneously acquired with the topographic image (a) (see Experimental Section) For comparison, the spectrum of domain- α is superimposed as a faint gray line. There is an upward band shift for domain- α^* and a band edge broadening (marked by red arrows) for domain- β .

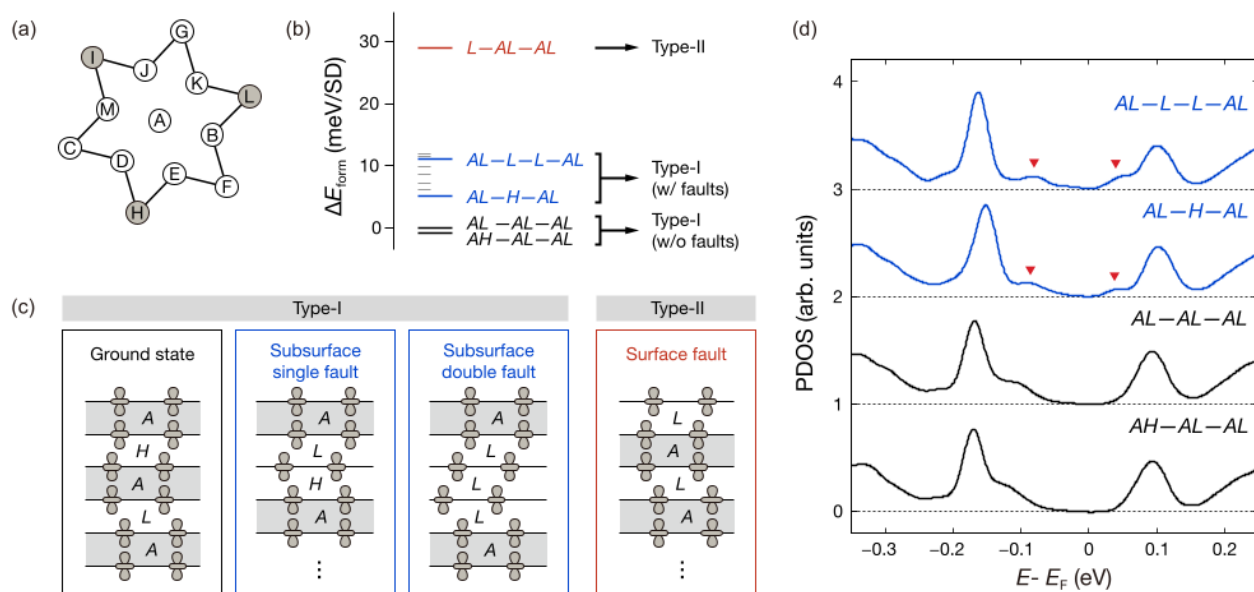
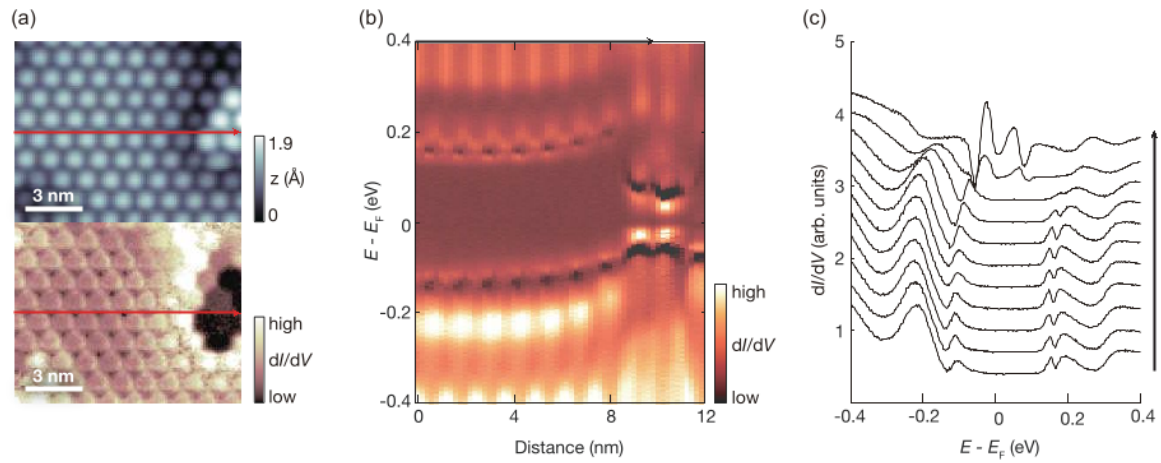


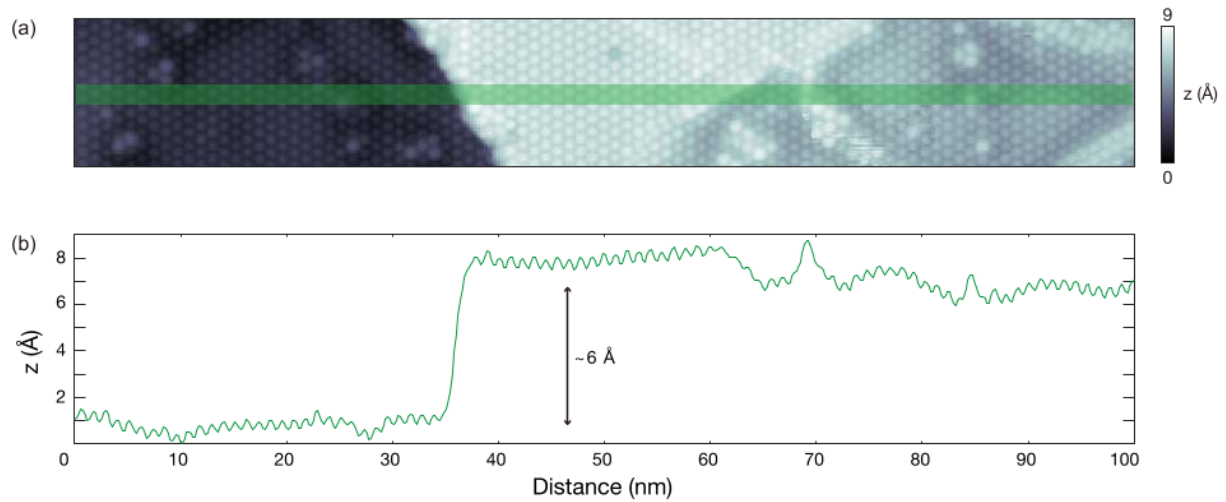
Figure 21.4: Formation energies and electronic structures of the various stacking configurations. a) A schematic representation of the SD supercell with 13 Ta atoms, each labelled in line with previous studies which have identified L , I and H (identical by three-fold rotational symmetry, shaded in gray) as the most stable sliding configurations among the 12 possibilities (B-M) [46]. b) Direct comparison of the formation energies of two different types of stacking configurations and their variations: fully dimerized (black), subsurface undimerized (blue) and surface undimerized configurations (red). Formation energies of other possible stacking configurations, marked by short gray lines, and their corresponding PDOS spectra are presented in Figure S7. c) A visual representation of four distinct stacking configurations discussed in (b). Each object denotes the position of the supercell center on individual layers, with the shaded regions (gray) indicating dimerization between adjacent layers. d) The calculated PDOS spectra of the four different Type-I stacking configurations identified in (b). Each spectrum is vertically shifted with equal spacing, in order of their formation energies, with the lowest at the bottom. The red arrows point to the wider band edges caused by undimerized subsurface layers.

References

Supplementary Information

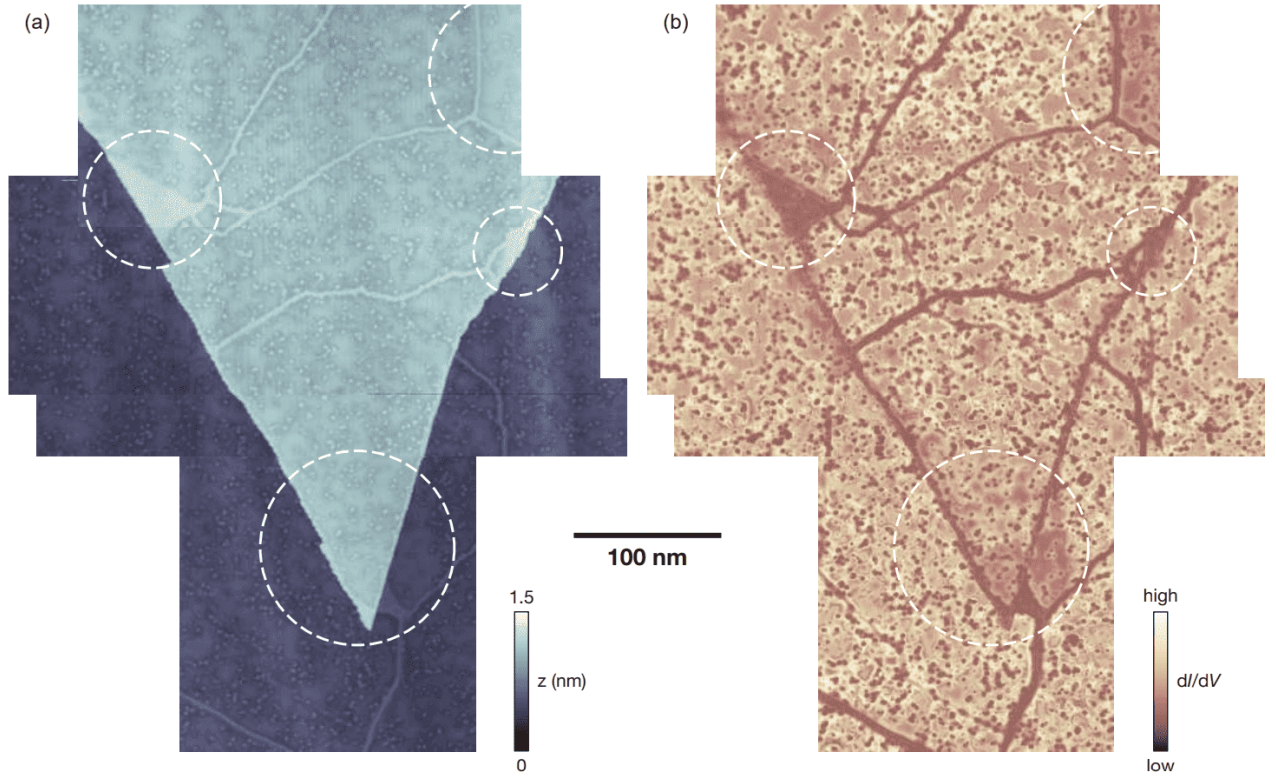


Supplementary Fig. 1: Defect spectra. a) STM image and dI/dV map containing defects ($V_{\text{set}} = +200$ mV, $I_{\text{set}} = 50$ pA). b) dI/dV spectra taken across the red arrows in (a). c) A waterfall plot of the dI/dV spectra along the black arrow in (b) with vertical shifts applied for clarity. Near the defects, the spectra show an upward shift in (b-c), which implies that these are acceptor-type defects. On top of the defects, in-gap states appear near the Fermi level (E_F).



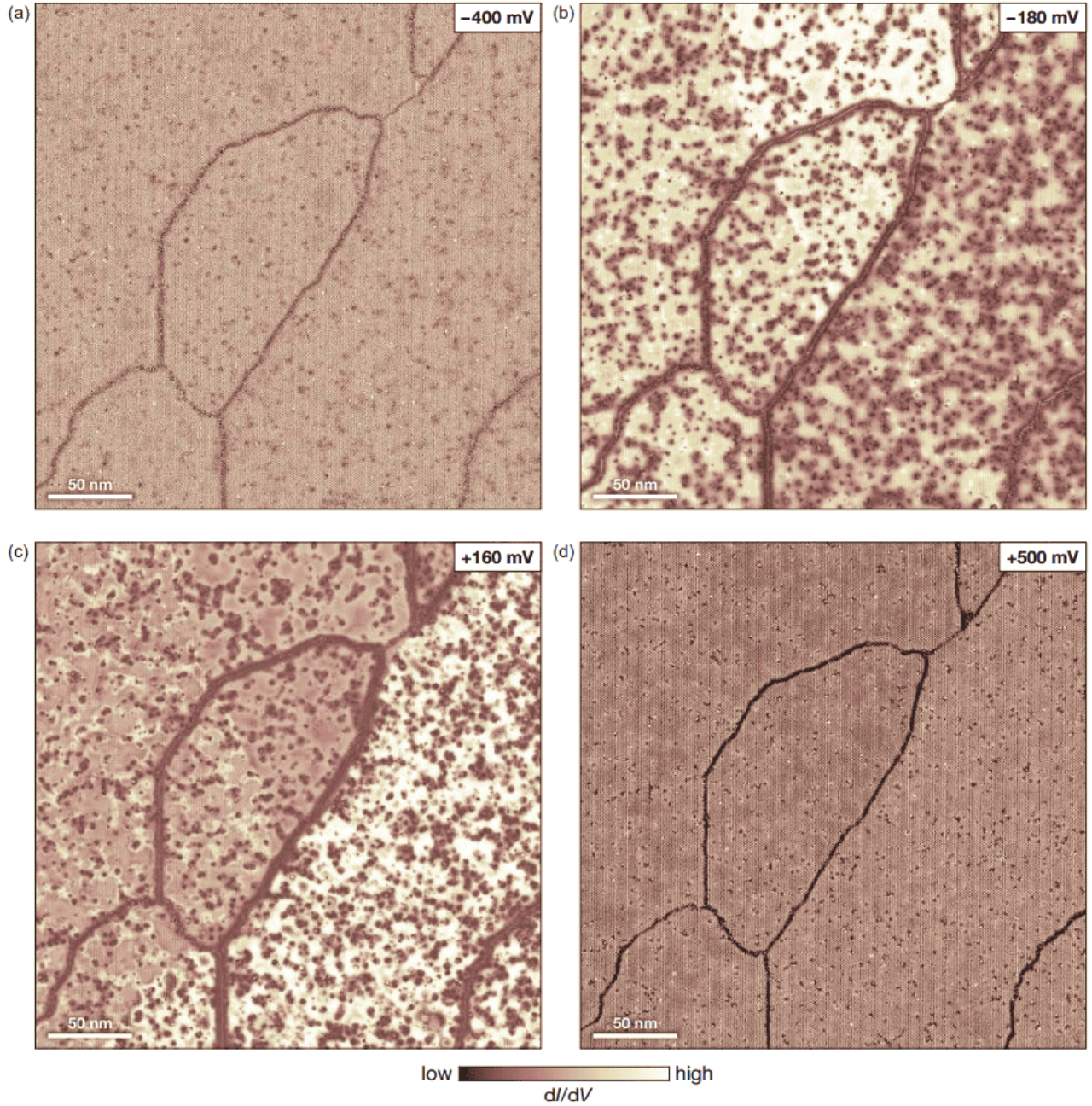
Supplementary Fig. 2: Height of the step edge in Figure 2 of the main text. a) STM image acquired across the step edge shown in Figure 2 of the main manuscript ($V_{\text{set}} = +170$ mV, $I_{\text{set}} = 100$ pA). b) Averaged height profile across the area highlighted in green. A height of around 6 Å is consistent with previous reports of a monolayer step [43, 44]. Type-II surface is slightly higher than the thickness of the monolayer. It undergoes the charge rearrangement accompanied by the surface domain wall (marked by a red arrow), termed surface reconstruction, to become Type-I.

Temperature- and position-dependent Raman measurements confirm the global crystalline structure of the sample. Indeed, both the thermal evolution of Raman-active modes through

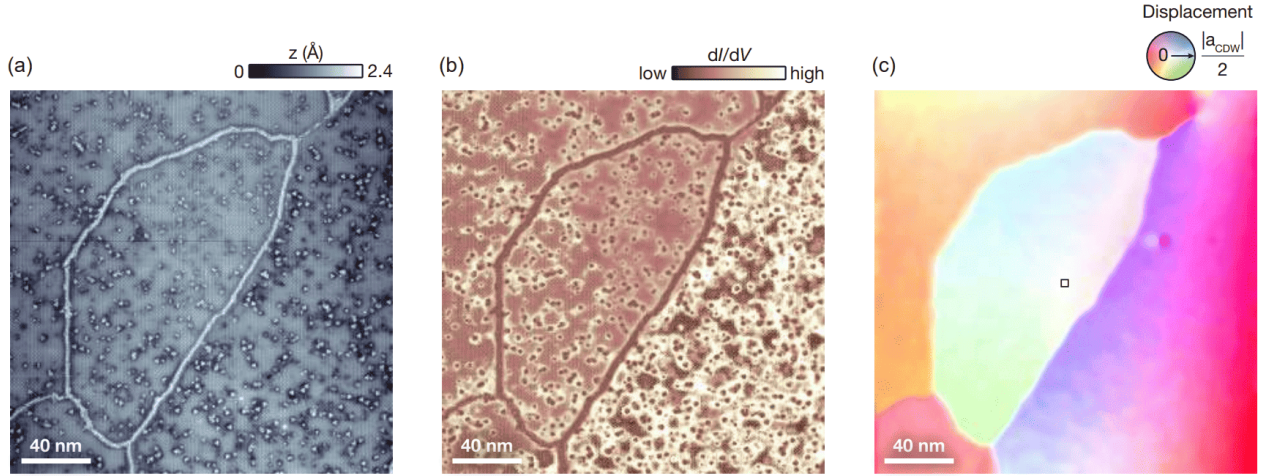


Supplementary Fig. 3: Large field of view of the various insulating states near a monolayer step edge in Figure 2. a-b) Assembled a) STM images and b) dI/dV maps show a larger field of view of the area shown in Figure 2 of the main manuscript. We identify various domains, including Type-II and Type-I* (β), denoted by white dotted circles. However, both the upper and lower terraces are dominated by Type-I domains, which can be seen by the overall homogeneous dI/dV intensities ($V_{\text{set}} = +170$ mV, $I_{\text{set}} = 21$ and 30 pA).

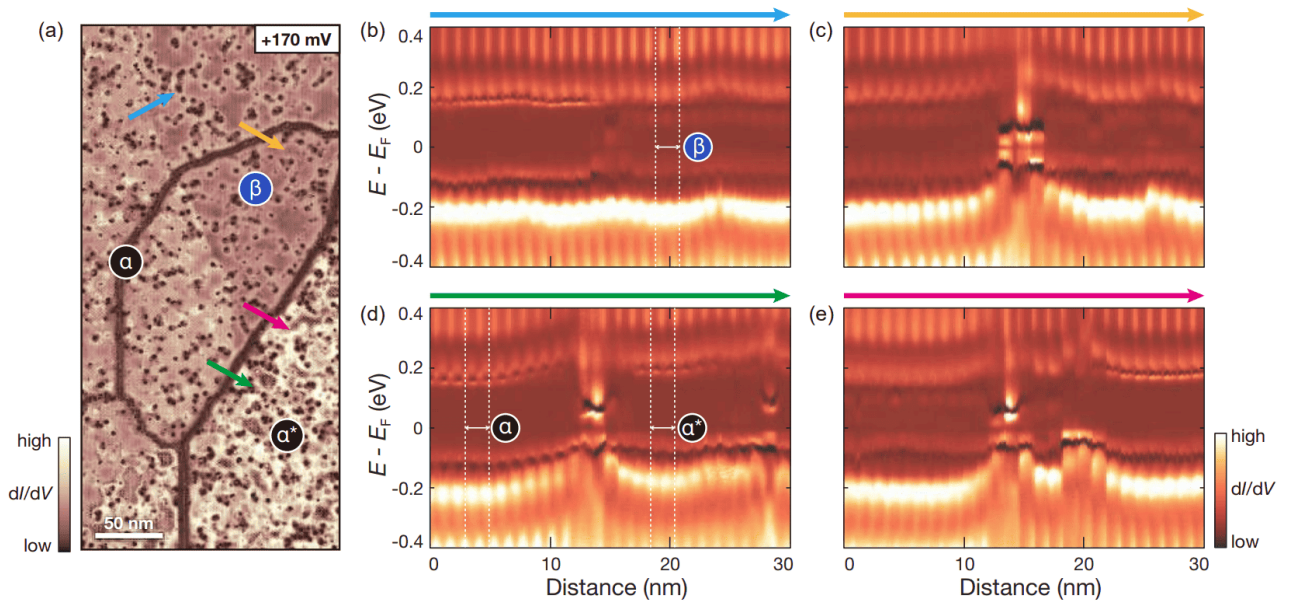
the different CDW phases, as well as Raman spectra taken at ten random spots across the mm-sized sample are in full accordance with the $1T$ phase and clearly distinct from the $4H$ one [43]. We note that with a laser spot diameter of $2\ \mu\text{m}$ each spectrum contains rather mesoscopic information compared to the truly microscopic nature of the STM study. Interestingly, as can be seen in the color contour plot of panel b), we uncover subtle variations in the form of minor phonon shifts depending on the measurement position, which are greater than the spectral resolution limit of our experiment. While the origin of these variations is currently not fully understood, we interpret them as fingerprints of different Type-I : Type-II ratios, which are expected to slightly modify the energy of CDW-induced zone-folded phonons as well as CDW amplitude modes. We envision that future studies focusing on a detailed Raman mapping through various thermal cycling processes can pinpoint the origin and thereby directly link mesoscopic Raman results to microscopic STM data.



Supplementary Fig. 4: Series of dI/dV maps at various bias voltages. a-d) dI/dV maps acquired in the same field of view as Figure 3 in the main text at various bias voltages ($V_{\text{set}} = -400, -180, +160$ and $+500$ mV, $I_{\text{set}} = 50$ pA). The boundaries dividing the domains become more pronounced with lower bias voltages (both positive and negative).



Supplementary Fig. 5: CDW displacement analysis. a-b) Cropped areas of the STM image and dI/dV map shown in Figure 3 of the main manuscript ($V_{\text{set}} = +170$ mV, $I_{\text{set}} = 50$ pA). c) CDW displacement map of the same area. We apply the Lawler-Fujita algorithm to analyze the CDW phases across the domain walls, with the black box at the center taken as reference[43, 42]. We identify the presence of abrupt changes in the CDW phases in (c) as surface domain walls, which are seen as bright and dark lines in (a) and (b), respectively.

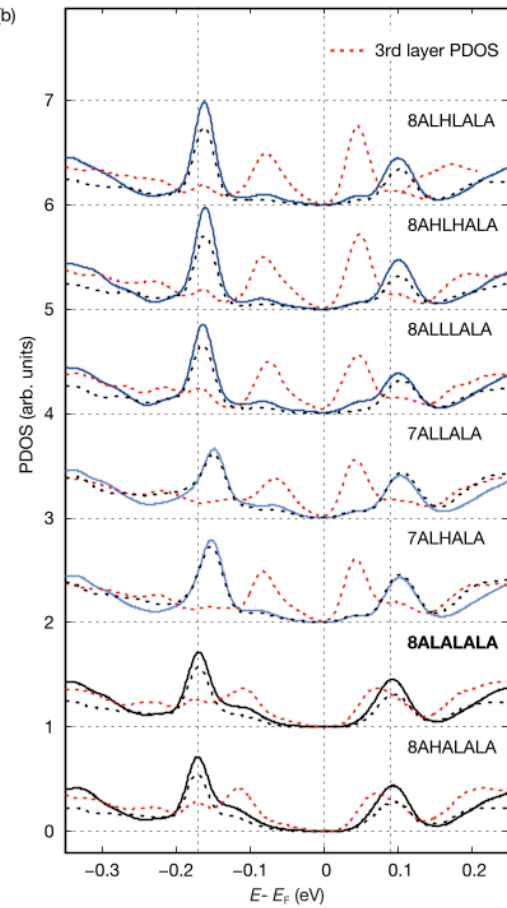


Supplementary Fig. 6: Multiple dI/dV spectra taken across the surface and subsurface domain walls shown in Figure 3 in the main text. a) Cropped dI/dV map of Figure 3b. b-e) dI/dV spectra taken across b) a subsurface domain wall with different electronic structures (blue), c) a surface domain wall with the same electronic structure (yellow), d) a surface domain wall with different electronic structures (green) and e) a surface domain wall with the same electronic structure, continued by a subsurface domain wall with different electronic structures (magenta) ($V_{\text{set}} = -400$ mV, $I_{\text{set}} = 200$ pA). The dI/dV spectra for domains- α , α^* and β in Figure. 3e of the main text are obtained from regions unaffected by local defects and identified in b) and d) as white dotted lines.

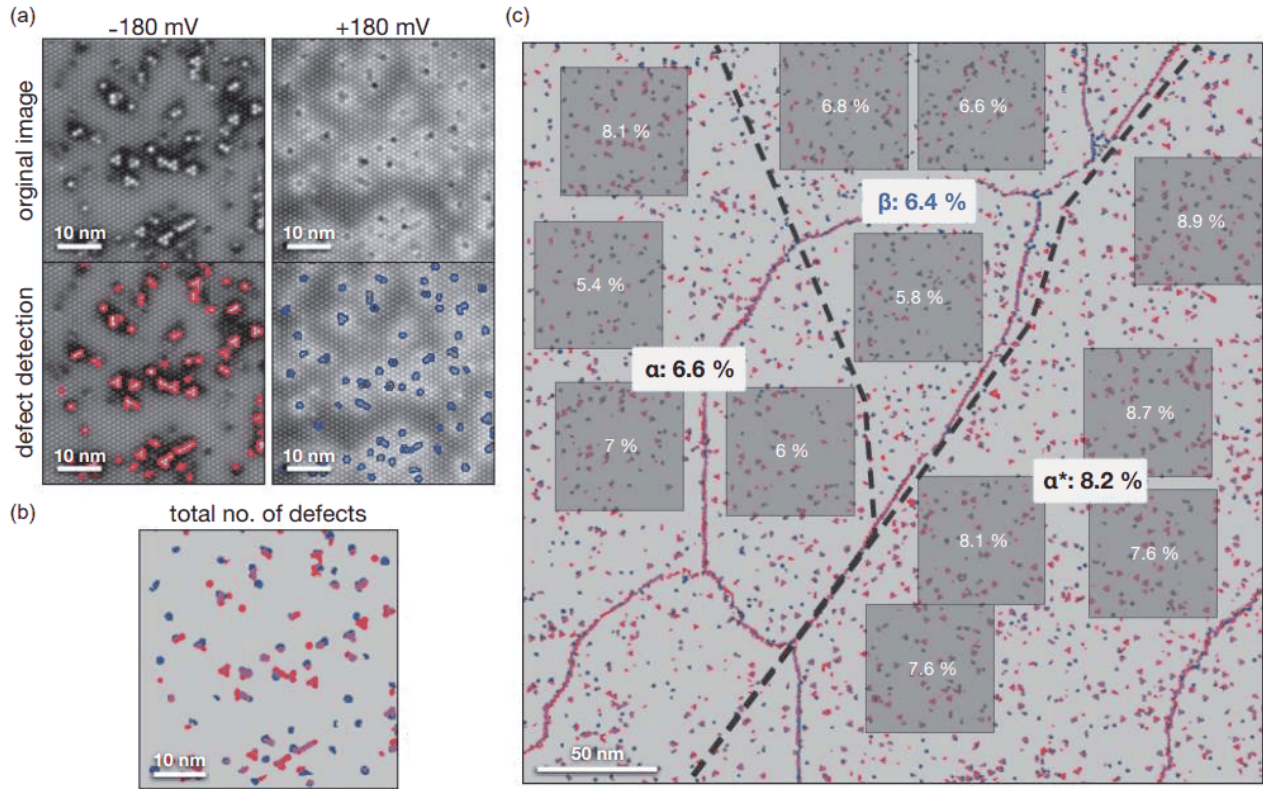
(a)

Stacking	Relative E_{form}	Description
7LALALA	29.1	Surface fault
8ALHLALA	11.7	Subsurface double fault
8AHLHALA	11.6	Subsurface double fault
8ALLLALA	11.0	Subsurface double fault
7ALLALA	11.0	Subsurface single fault
7AIHALA	9.8	Subsurface single fault
7AHHALA	8.6	Subsurface single fault
7AHLALA	7.2	Subsurface single fault
7ALHALA	5.1	Subsurface single fault
8ALALALA	0.0	All-dimerized (reference)
8AHALALA	-0.8	All-dimerized

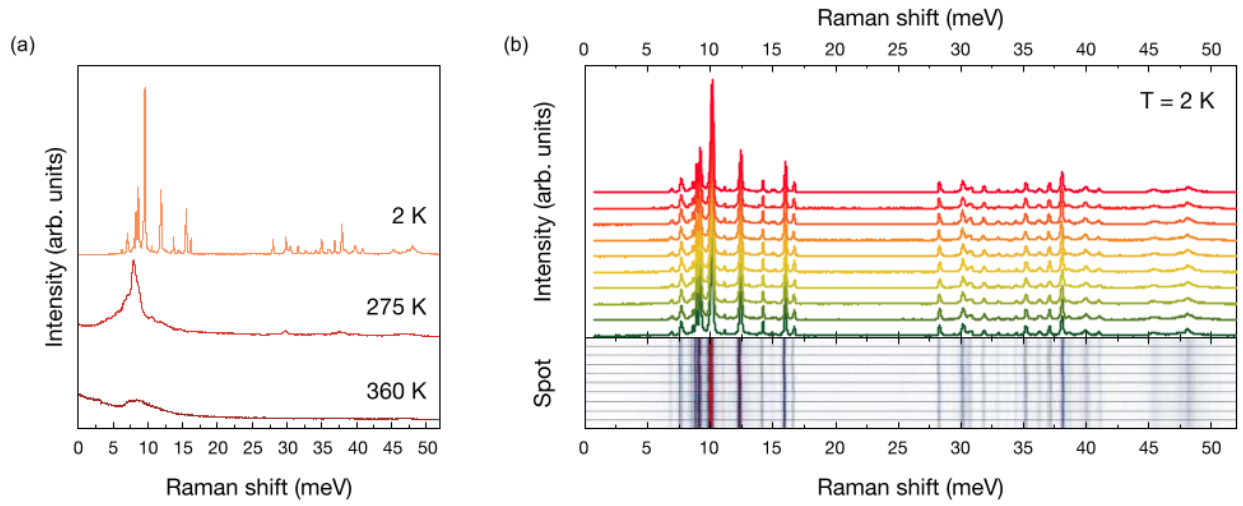
(b)



Supplementary Fig. 7: The formation energies of the favorable stacking configurations and their corresponding surface electronic structures. a) Relative formation energies of various stacking configurations, including all-dimerized layers (gray), subsurface single fault (bright blue), subsurface double fault (dark blue) and surface fault (red) with the 8ALALALA stacking configuration taken as the reference point. b) The PDOS spectra of distinct stacking configurations with the layer selective PDOS for the second (black dashed curves) and third layers (red dashed curves). The solid curves correspond to the surface PDOS acquired by integrating d_{z^2} orbital contributions from 13 Ta atoms in the SD cluster.



Supplementary Fig. 8: Distribution of defects in each domain. a) STM images extracted from the same location as Figure 3(a-b) at negative and positive bias voltages ($V_{\text{set}} = -180$ and $+180$ mV). Defects are highlighted in red and blue for negative and positive bias voltages. At negative bias voltage, defects are usually shown as protrusions in the STM images, whereas at positive bias voltage, they are displayed as depressions. Defect sites in the STM images are identified and marked through image processing techniques. b) Superposition of (red and blue) defects from (a). Some defects are shown only at negative or positive, which are identified as isolated blue or red dots. However, numerous defects are observable at both negative and positive bias voltages, which are shown as purple dots. We quantify the area covered by red, blue and purple to identify defect sites. c) In the individual gray boxes, we note the ratio of defects, while the total averaged values of each domain are shown in the white boxes. Domain- α^* exhibits approximately 1.24 times more defects than the other domains.



Supplementary Fig. 9: Raman spectroscopy data. a) Raman spectra of $1T\text{-TaS}_2$, recorded in the ICCDW phase (360 K), the NCCDW phase (275 K) and the CCDW phase (2 K). b) Raman spectra of $1T\text{-TaS}_2$ in the CCDW phase at $T = 2$ K measured at ten random spots across the mm-sized sample.

22 Dynamic phase transition into a mixed-CDW state in 1T-TaS₂ via a thermal quench by de la Torre et al.

Ultrafast light-matter interaction has emerged as a new mechanism to exert control over the macroscopic properties of quantum materials toward novel functionality. To date, technological applications of non-thermal phases are limited by their ultrashort lifetimes and low-ordering temperatures. The hidden metallic charge density wave (H-CDW) in 1T-TaS₂ is among the most studied photoinduced metastable phases because of its technological promise. However, despite active study, the nature of the photoinduced H-CDW remains the subject of debate and potential applications have been limited because it has so far only been stabilized at cryogenic temperatures. Here, we stabilize the H-CDW phase at thermal equilibrium by accessing a mixed CDW order regime via thermal quenching. Using x-ray high dynamic range reciprocal space mapping (HDRM) and scanning tunneling spectroscopy (STS), we reveal the coexistence of commensurate (C) CDW and H-CDW domains up to 210 K. Our findings show that each order parameter breaks basal plane mirror symmetry with different chiral orientations and induces out-of-plane unit cell tripling in the H-CDW phase. Despite metallic domain walls and a finite density of states at zero bias observed via STS, bulk resistance remains insulating due to CDW stacking disorder. By comparing our data to Landau-Ginzburg theory calculations of the free energy functional, our study establishes the H-CDW as a thermally stable phase and introduces a new mechanism for switchable metallic behavior in thin flakes of 1T-TaS₂ and similar materials with competing phases.

22.0.1 Introduction

The correlated van der Waals material 1T-TaS₂ displays a series of first-order phase transitions associated with the onset of CDW orders with different degrees of commensurability [1, 27, 16]. Lowering from high temperatures, at $T = 550$ K a mirror-symmetry preserving incommensurate (I) CDW onsets from a metallic state [9]. At $T_{\text{I-NC}} \approx 350$ K, 1T-TaS₂ enters into a nearly commensurate (NC) CDW phase. The atomic rearrangement associated with the incommensurate NC-CDW (in-plane ordering wavevector $q_{\parallel} = 0.284$ r.l.u.) leads to disconnected regions displaying a $\sqrt{13} \times \sqrt{13}$ spatial reconstruction in which twelve Ta atoms move towards a central one forming a star-of-David (SOD) pattern [5]. The NC-CDW breaks the mirror symmetries of the lattice basal plane and spontaneously selects one of two chiral domains rotated from the a -axis by $\phi \approx 12^\circ$. Then, at $T_{\text{NC-C}} \approx 175$ K in cooling and $T_{\text{NC-C}} \approx 225$ K in warming, a 3D CDW order emerges from the NC-CDW phase. This low-temperature phase is commensurate (C) with the atomic lattice in-plane ($\phi = 13.9^\circ$ and $q_{\parallel} = 0.277$ r.l.u.) with the in-plane C-CDW atomic reconstruction inheriting the chiral structure from the NC-CDW. On the other hand, in the out-of-plane direction, the C-CDW displays a large stacking disorder between dimerized CDW planes [1, 27].

Experimental probes spanning a large range of length scales find that in the C-CDW phase of 1T-TaS₂ samples lack the chiral twin domains expected across the $T_{\text{NC-C}}$ first-order phase transition [6, 7, 8, 9, 10]. The stabilization of a single chiral domain reflects the kinetics of the cooling across the only first-order phase transition in 1T-TaS₂ that breaks in-plane mirror symmetries, $T_{\text{I-NC}}$ [11, 12]. During synthesis, the metastable 1T phase is stabilized by quenching from $T \approx 1000$ K to $T \approx 273$ K across the polytype transition, $T_{\text{1T-2H}} = 600$ K [1]. During this initial quench, the cooling rate across $T_{\text{I-NC}}$ is effectively slow when compared to the intrinsic timescales of the electronic ($\approx$ fs) and lattice ($\approx$ ps) degrees of freedom and enables

the nucleation of large chiral CDW domains with lateral sizes comparable to the correlation length of the order parameter parameter [13]. The chiral mono-domain structure of the C-CDW in 1T-TaS₂ is stable to cooling through $T_{\text{NC-C}}$ [6, 7, 8, 9, 10] with suggestions that strain fields and defects can pin a single chirality [6, 14]. Still, chirality reversal of single domain samples has been demonstrated by repeated cleaving of a bulk sample [7] or by cycling through $T_{\text{I-NC}}$ [15].

On the other hand, multi-chiral domain samples can be engineered in thin exfoliated flakes by heating and quenching above $T_{\text{T-2H}}$ [16, 17] or upon irradiation with 800 nm laser pulses with fluence $F > 7 \text{ mJ/cm}^2$ [6]. Once created, chiral domain walls are long-lived at low temperatures, but a dominant chiral domain of dimensions comparable to the sample size can be restored by heating above $T_{\text{I-NC}}$ and adiabatically cooling through the mirror symmetry-breaking IC-NC transition [16, 17, 6]. Thus, $T_{\text{I-NC}}$ emerges as the relevant energy scale for chiral CDW domain nucleation in 1T-TaS₂ as the temperature at which the initial mirror-symmetry breaking transition in the CDW phase diagram [1] occurs and the largest specific heat divergence is observed [18]. Moreover, x-ray pair distribution function measurements have revealed that the anisotropic Ta Debye-Waller factor, associated with CDW formations, remains constants across the NC-C CDW transition but dramatically changes across $T_{\text{I-NC}}$ [19].

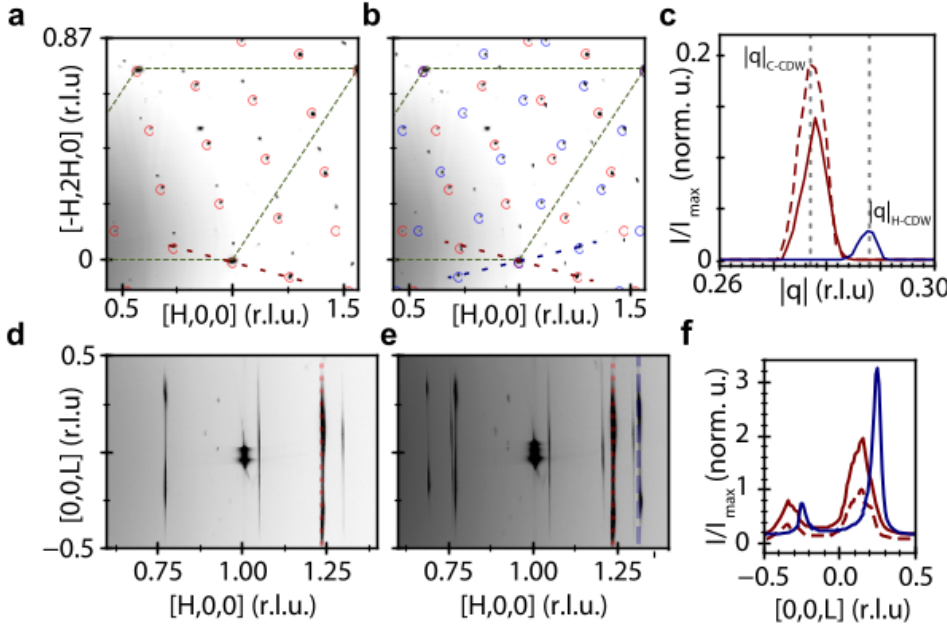


Figure 22.1: Thermal quench into the mixed-CDW phase. **a.** Reciprocal space maps parallel to the $[\text{HK}0]$ plane ($\delta L = .5$, $L = 0$) at $T = 140 \text{ K}$ for an as-grown sample. **b.** Reciprocal space maps parallel to the $[\text{HK}0]$ plane ($\delta L = .5$, $L = 0$) at $T = 80 \text{ K}$ after a quench. Red and blue markers highlight the C-CDW and H-CDW-like satellite peaks, respectively. Green dashed lines highlight the a^* and b^* directions. **c.** Average intensity dependence as a function of $|q|$ across a C-CDW satellite peak in the as-grown sample (dashed red line) and the C-CDW (red line) and H-CDW-like (blue line) after a quench. (Red and blue dashed lines in **b**). Vertical dashed lines correspond to the reported $|q_{||}|$ values for the C-CDW [1] and H-CDW [20] satellite peaks. **d.** Reciprocal space map parallel to the $[\text{H}0\text{L}]$ plane for the as-grown sample. **e.** Reciprocal space map parallel to the $[\text{H}0\text{L}]$ plane for the quench sample. Vertical red and blue dashed lines indicate C-CDW and H-CDW-like satellite peaks, respectively. **f.** Integrated intensity along $[\text{h}0\text{L}]$ for the as-grown sample (red dashed) and after a quenched (red, C-CDW peak and blue, H-CDW peak).

An additional low-temperature metastable metallic CDW phase, the so-called hidden H-CDW phase, has been accessed in 1T-TaS₂ from the insulating C-CDW state via a single

femtosecond laser pulse of fluence larger than a critical value ($F_c > 1$ mJ/cm²) [21, 20, 22] or by exciting 1T-TaS₂ with a ns voltage pulse [23, 24, 25, 26, 27]. The H-CDW phase locally resembles the SOD arrangement but breaks the large C-CDW domains into many nanoscale domains and has a metallic density of states [30, 24, 29]. These domains maintain the chirality of the C-CDW [20] and are related by a relative translation of the SOD pattern by a finite number of atomic lattice vectors [24, 30, 30]. Slight differences between the displacement of the Ta atoms between the H-CDW and the C-CDW distinguish the two. The H-CDW phases result in CDW Bragg peaks rotated by $\phi = 11.9^\circ$ from the a^* -axis with a larger basal plane ordering wavevector, $q_{||} = 0.284$ r.l.u.. The CDW plane stacking also rearranges towards a $l = 1/3$ periodicity along the c-axis [20]. We note that a similar metallic mosaic state can also be induced by cooling thin exfoliated samples ($d < 24$ nm) across T_{I-NC} with a cooling rate faster than 0.2 K/s [26] or by intrinsic strain and defect effects [32, 33, 34].

Despite much study, the origin of the H-CDW state remains controversial, with photodoping [35, 30], incoherent thermal effects [24, 36] or electron-phonon relaxation bottlenecks [29, 37] all possible explanations. Nonetheless, the H-CDW has attracted much interest, not only as an example of the non-thermal control of quantum materials [38] but also as a platform for new functional devices [39, 43, 41]. However, the H-CDW has only been stabilized for ultrashort periods (~ 100 μ s) at temperatures above $T = 50$ K [21, 42, 29] preventing its deployment in efficient and fast memory devices towards novel technological applications [43].

Here, we demonstrate that the H-CDW phase exists in thermal equilibrium in 1T-TaS₂ and extend its thermal stability by a factor of three by accessing a new long-lived mixed-CDW state via a reversible thermal quench across T_{I-NC} . We use x-ray high dynamic range reciprocal space mapping (HDRM) to unequivocally demonstrate the co-existence of the C-CDW and H-CDW states in thermally quenched samples. Each CDW order parameter is linked to a mirror-symmetry breaking chiral domain. The mixed-CDW state emerges from a multi-domain NC-CDW state below $T^{CD} = 180$ K in cooling and $T^{WU} = 210$ K in warming. The mixed-CDW low temperature state can be recovered as long as the system is not heated above T_{I-NC} . Scanning tunneling spectroscopy (STS) shows that the mixed-CDW is characterized by a semi-metallic in-plane density of states. At the same time, bulk resistivity remains insulating due to out-of-plane CDW stacking disorder in mixed CDW bulk samples. Our results and calculations of the free energy landscape within the Ginzburg-Landau theory demonstrate a new thermally accessible state in the phase diagram of 1T-TaS₂, enabling a new mechanism to engineer a semimetallic density of states at temperatures well above liquid nitrogen temperatures.

22.0.2 Results

Accessing a novel mixed-CDW state by quenching through the mirror symmetry breaking transition. In Figure 22.1 a, we show a characteristic [HK0] plane reciprocal space map for the C-CDW phase of 1T-TaS₂, collected after a standard cooling cycle. Red circular markers highlight the CDW reflections at $q_1^C = (\sigma_1^C, \sigma_2^C, l)$ and $q_2^{TH} = (-\sigma_2^C, \sigma_1^C + \sigma_2^C, l)$ with $\sigma_1^C = 3/13$ r.l.u and $\sigma_2^C = 1/13$ r.l.u [1, 27], corresponding to a single C-CDW chiral domain. Additional non-indexable reflections in the reciprocal space map are attributed to a second small crystallite in our sample. Identical reciprocal space maps were obtained across many cooling cycles and samples. We found that the C-CDW domain structure in a given sample depends on the cooling rate through T_{I-NC} and fast thermal quench across T_{I-NC} stabilizes a multi-chiral domain CDW. Fig. 22.1 b shows the [HK0] reciprocal space map after an in-situ quench in our bulk sample across T_{I-NC} down to $T = 140$ K at a rate of 0.2 K/ms near T_{I-NC} (See Methods for a description of the in-situ quench method and calculation of quenching rates using heat diffusion calculations). We found that thermal quenching consistently resulted in a new set of superlattice reflections of opposite chirality to the original set of satellite peaks ($\phi = -12.3^\circ$) (Fig. 22.1 b,

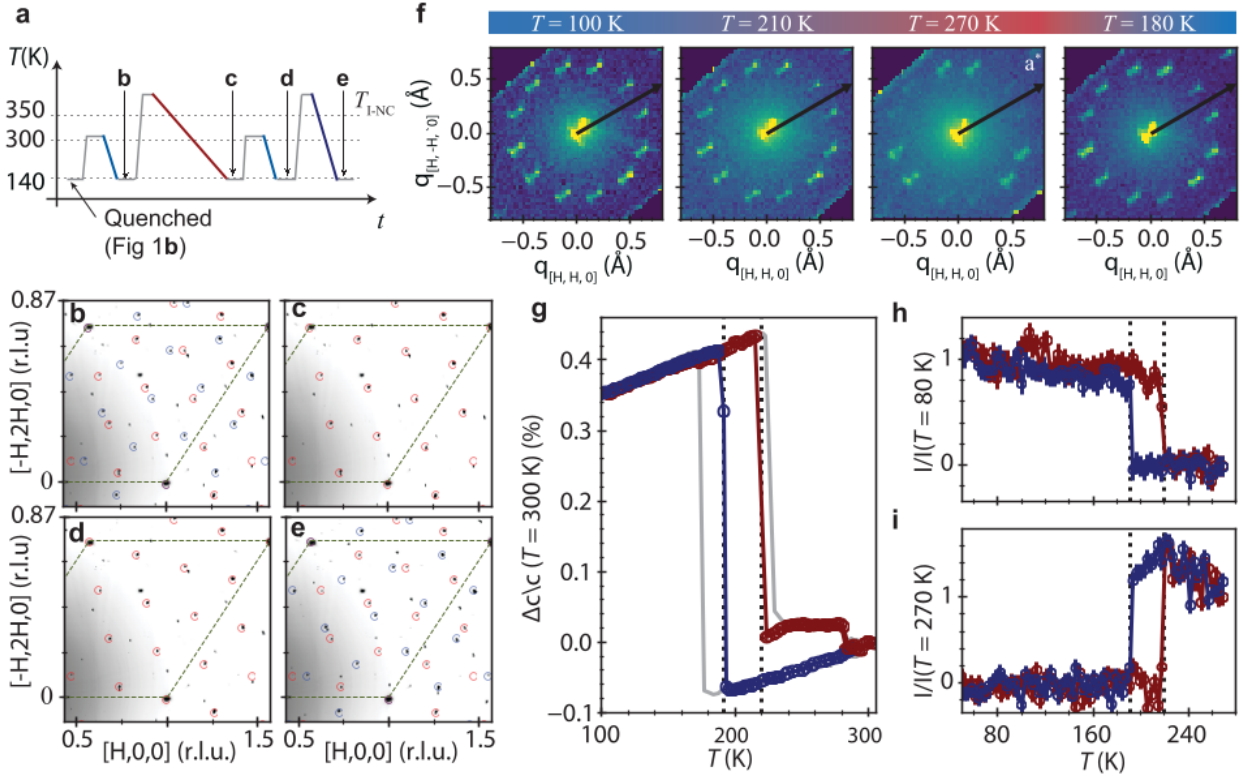


Figure 22.2: **Temperature dependence of the mixed-CDW.** **a** Schematic of the subsequent in-situ thermal cycles undergone by a pre-quenched sample. **b-e** HRDM reciprocal space maps parallel to $[HK0]$ plane ($\delta L = .5$, $L = 0$) at $T = 140$ K after a thermal cycle as indicated in **a**. Red and blue markers highlight the C-CDW and H-CDW-like satellite peaks. Green dashed lines highlight the a^* and b^* directions. **f** Ag K_α reciprocal space maps parallel to the $[HK0]$ ($\delta L = .5$, $L = 10$) as a function of temperature across the C-NC transition. The black arrow encodes the a^* direction. **g** Temperature dependence of the relative change of the c -axis lattice parameter during cooling (blue) and heating (red) for a quenched sample (circular markers). Grey solid lines showcase the same magnitude for an as-grown sample. The quenched crystal shows a narrow hysteresis window for the C-NC transition compared to an as-grown sample. **h** Temperature dependence of a H-CDW-like satellite peak ($L = 9.66, \delta L = .1$) during cooling (blue) and warming (red). The thermal hysteresis follows that of the c -axis. **i** Temperature dependence of a H-CDW-like-precursor satellite peak ($L = 9.33, \delta L = .1$) in the NC phase during cooling (blue) and warming (red). Error bars in **h** and **i** represent one standard deviation.

highlighted by blue markers). The superior reciprocal space resolution of synchrotron single crystal HDRM enables us to resolve differences in the wavevector of the two sets of CDW Bragg peaks with different chirality. The in-plane wavevector magnitude $|q_{||}| = 0.284(3) \text{ \AA}^{-1}$ of the quenched-induced satellite peaks is larger than that of the C-CDW ($|q_{||}| = 0.277(3) \text{ \AA}^{-1}$) and is the same as the light-stabilized H-CDW state [20]. This is shown in Fig. 22.1 c, where we display the integrated intensity across the C-CDW and H-CDW Bragg peaks (dashed lines in Fig. 22.1 a and b) as a function of $|q_{||}|$. Strikingly, each order parameter preferentially selects a chirality orientation, with the C-CDW domains of the mixed-CDW phase maintaining that of the as-grown samples.

We also find that the c -axis periodicity differs between the C-CDW and H-CDW-like domains. Figure 22.1 d and e show $[H0L]$ reciprocal space maps centered at $H = 1$ r.l.u. and $L = 0$ r.l.u. ($\delta k = 0.3$ r.l.u.) before and after the thermal quench, respectively. The as-grown sample displays a broad two-peak structure, with the center of mass at integer values of L . These

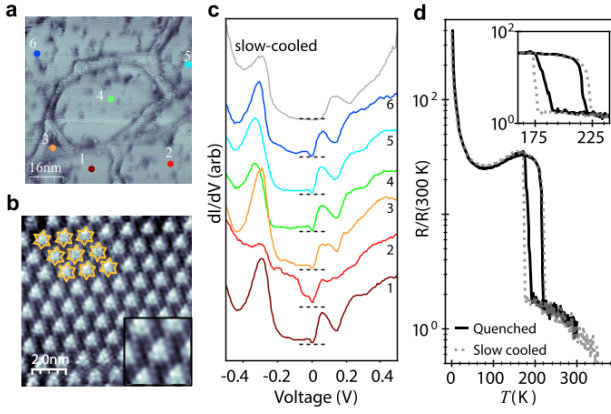


Figure 22.3: **Electronic structure of the mixed-CDW phase** **a -b** Representative topography of the mixed-CDW phase showing domains, atomic resolution and the $\sqrt{13} \times \sqrt{13}$ reconstruction. **c** dI/dV curves at each of the 6 domains seen in **d**. dI/dV data reflects a narrower gap in the electronic structure of $1T\text{-TaS}_2$ compared to the slow-cooled C-CDW phase (grey). Metallic behavior is observed in domain walls as indicated by point 3. **d** Resistivity, normalized to that at $T=300$ K for a mixed-sample (solid line) and as-grown sample (dotted grey). The inset shows a zoom in view around the TH-CDW/C-CDW transition.

short-range out-of-plane correlations are characteristic of the dimerization of CDW layers in the low-temperature C-CDW phase [44]. On the other hand, while retaining a dumbbell-like shape, the H-CDW-like satellite peaks shift towards $l = \pm 1/3$ indicating a collapse of the inter-layer dimerization towards a triple layer CDW stacking as was observed for the light-induced H-CDW [20]. The H-CDW-like satellite peaks are sharper than the C-CDW ones, reflecting a longer correlation length for the quench-induced domains $\xi = 6(6)$ nm (Fig. 22.1 f). Similar sharpening of the out of plane CDW peaks was also observed in light-induced H-CDW $1T\text{-TaS}_2$ [20]. Altogether, our HDRM data in quenched samples demonstrates the coexistence of the C-CDW with a second CDW phase with the same order parameter as the H-CDW phase at much higher temperatures ($T = 140$ K).

Critical temperature and metastability of the quenched mixed-CDW state. We performed a set of in-situ thermal cycles to directly demonstrate that (i) T_{I-NC} is the relevant temperature scale to access the mixed state and (ii) the transition is reversible. Consecutive thermal quenches were performed at different quench rates and starting temperatures, as illustrated in Figure 22.2 a (see Methods and Extended data). We found that after quenching from above T_{I-NC} , the mixed CDW state is thermally stable and insensitive to warming-cooling cycles if temperature kept less than T_{I-NC} [Fig. 22.2 b]. Such thermal stability is in contrast with the light-induced H-CDW phase that was found to be suppressed above $T = 60$ K [21]. However, the C-CDW state can be recovered from the mixed state by warming up and slow-cooling across T_{I-NC} (Fig. 22.2 c). Subsequent thermal quenches from $T = 300$ K do not recover the mixed state (Fig. 22.2 d), which can only be recovered upon heating and quenching from above T_{I-NC} (Fig. 22.2 e). Thus, our data confirms the IC-NC CDW as the necessary energy scale to access the mixed-CDW phase containing both the C-CDW and H-CDW order parameters.

The possibility of recovering the H-CDW phase as part of the stable mixed-CDW phase by keeping the samples below T_{I-NC} enables us to ex-situ form the CDW mixed state (see Methods) and perform additional characterization of this state. We note that the mixed CDW state is stable over months, independent of the number of cleaves, and has been reproduced in quenched samples over multiple growth batches. Detailed temperature-dependent XRD measurements (See Methods) of ex-situ quenched samples display twelve satellite reflections characteristic of the mixed-CDW state at low temperatures (Fig. 22.2 f). For temperatures

above $T_{NC-Mixed}^{WU} = 210$ K during warming up, or below $T_{NC-mixed}^{CD} = 195$ K during cooling down, we observe a transition into the NC-CDW. However, the NC-CDW state in quenched samples is characterized by two sets of CDW Bragg peaks with opposite chiralities. This state is shown in Fig. 22.2 f at $T = 270$ K for ex-situ quenched samples. Equivalent HDRM data at $T = 300$ K is shown in Extended Data 2. We note that the L dependence of the two NC-CDW satellite peaks is different from that of the H-CDW we observe at low temperature (see Extended data 2), ruling out a supercooled NC-CDW phase in our quenched samples [26]. The existence of two chiral domains in the NC-CDW is consistent with previous ultrafast electron diffraction experiments that demonstrated the chirality of the low-temperature C-CDW domains was inherited from the symmetry-breaking at the IC-NC transition [45] and that two NC-CDW domains were stabilized after laser excitation at room temperature [6].

A detailed temperature dependence of the H-CDW-like and NC-CDW Bragg reflections are shown in Fig. 22.2 h and i. Upon stabilizing the mixed state at low temperatures via a quench across T_{I-NC} , the H-CDW peaks directly emerge from NC-CDW peaks of corresponding chirality. This temperature dependence is distinct from the metastable H-CDW phase, which is suppressed above $T = 60$ K. [20, 21, 30]. We found that C-CDW and H-CDW-like Bragg peaks show the same temperature dependence (see Extended data) suggesting the coupled nature of the two order parameters in the mixed-CDW phase. The asymmetrically narrower hysteretic loop of the first-order transition, when compared to as-grown samples, $T_{NC-C}^{CD} = 180$ K and $T_{NC-C}^{WU} = 210$ K, in conjunction with the narrower CDW Bragg peaks along L and the temperature dependence of the [0010] structural Bragg peak shown in Fig. 22.2 c, suggests longer range interlayer correlations and a more 3D nature of the H-CDW phase.

Scanning tunneling microscopy (STM), measurements confirm the multi-domain nature of our quenched samples. Figure 22.3 a shows a characteristic 80×80 nm² area in a quenched sample. Each domain shows the atomic reconstruction of the sulfur layer due to a low-temperature CDW, as shown in Fig. 22.3 c with $V = 380$ mV, $I = 0.35$ nA, scale bar length = 2 nm). We note that the in-plane momentum resolution of our STM experiments prevents us from distinguishing between the C-CDW and the H-CDW-like domains. However, from the Fourier transform of STM images with atomic resolution, we extract a rotated satellite peak $\phi = 12.8(5)^\circ$, that reflects the presence of domains of opposite chirality (related by a mirror operation along one of the high symmetry crystallographic directions) (See extended data). Our STM data resembles the in-plane inhomogeneity observed in optically and electrically driven $1T$ -TaS₂, where multiple domains of opposite phase have been reported [30, 24, 29]. We note that the smaller domain density prevented us from performing a comprehensive in-plane phase configuration analysis of the chiral domains, but we cannot exclude the presence of phase domains (related by a translation operation) [30, 24, 29].

To summarize, intermediate-quenched bulk $1T$ -TaS₂ samples host a mixed CDW state with two distinct order parameters, locked to opposite chiral phases, which emerge from a multi-chiral NC-CDW phase. Moreover, our temperature-dependent data reveals the narrowing of the hysteretic window across the NC-mixed-CDW phase transition. This indicates a stronger out-of-plane electronic correlation in the mixed-CDW phase of $1T$ -TaS₂.

Electronic structure of the bulk quenched samples. We now bring attention to the low-temperature electronic structure of the mixed-CDW phase. While the origin of the insulating nature of the C-CDW remains controversial [46, 47], it is well established that the c-axis stacking of CDW domains strongly influences the electronic structure of $1T$ -TaS₂ [48, 49, 43, 51]. Moreover, recent STM and scanning tunneling spectroscopy (STS) studies of the stacking shift between in-plane domains in consecutive layers have identified interlayer coupling as the key ingredient that determines the band structure of the low-temperature CDW phase in $1T$ -TaS₂ [52, 24, 53, 30, 54]. Thus, we use STS to study the low-temperature electronic state of the quenched samples. dI/dV curves taken at $T = 10$ K within six different domains, Fig.

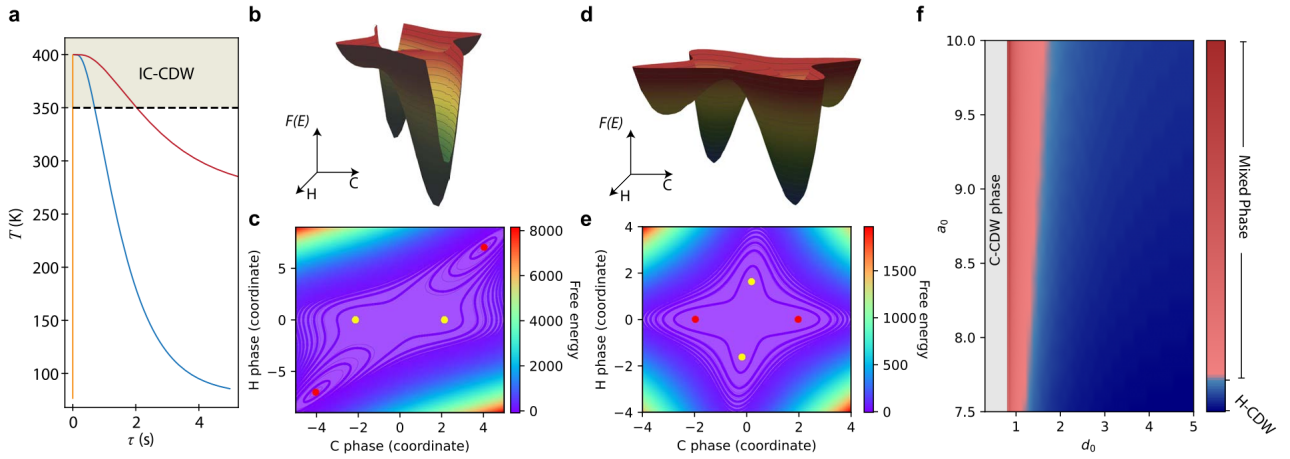


Figure 22.4: Dynamic phase transition with two competing order parameters in 1T-TaS₂. **a** Cooling rate estimates for an optically induced quench (orange) and solutions of the heat diffusion equation for the slow (red) and fast (blue) cooling schemes used in this work (See Methods and Extended data). **b** Meanfield-only free energy functional for the two competing CDW orders, with a competition factor $d_0 = 0.8$, corresponding to an adiabatic quench. **c** 2D projection of the energy functional in **b**. **d** Meanfield-only free energy functional for the two competing CDW orders, with a competition factor $d_0 = 6.1$, corresponding to laser quench. Fast quenches correspond to larger values of d_0 . **e** 2D projection of the energy functional in **d**. The yellow and red markers indicate local and global minima, respectively. **f** Computed phase diagram as a function of the competition factor, d_0 , and mass term, a_0 . The mixed CDW phase can only be stabilized in a narrow range of intermediate-rate quenches. Faster quenches (optical or electrical pulses) lead to the suppression of the C-CDW phase and the emergence of the H-CDW phase

22.3 a, reveal a reduction of the $E_g = 300$ meV gap of the C-CDW [10] towards a state with a reduced but non-zero density of states at the Fermi level (Fig. 22.3 c). While a transition to a semimetallic state is consistent with that observed for the H-CDW [24, 30], the density of states maintains two pronounced peaks at around $V_B = -300$ meV and $V_B = 150$ meV, that have been associated with the lower and upper Hubbard bands [55, 56, 57]. Despite the finite in-plane density of states at E_F and the formation of metallic domain walls (Fig. 22.3 b, curve 3), electrical transport in the mixed-CDW sample resembles that of the as-grown crystals.

We observed that quenched bulk samples display insulating behavior at all temperatures with the same relative resistivity increase with respect to $R(300\text{ K})$ as the C-CDW phase [1] (Figure 22.3 d). The mixed state resistivity exhibits a narrow thermal hysteresis that tracks that of the structural transition (Fig. 22.2 g), reflecting the role of out-of-plane order in the resistivity of 1T-TaS₂. The insulating nature of the mixed-CDW phase is distinct from the substantial $T < 70$ K resistivity drop observed for the light-induced H-CDW phase in thin samples [21]. This difference likely originates from the insulating C-CDW domains that occupy a large volume fraction of the mixed-CDW state and stacking CDW disorder between the two CDW orders with different periodicity along L (Figure 22.2 g-h). Additionally, we find that in-situ thermal cycling above $T_{IC} = 350$ K and slow cooling recovers the characteristic resistivity of bulk 1T-TaS₂ with a hysteretical transition separated by $\Delta T = 50$ K (Figure 22.3 d), consistent with our diffraction measurements in as-grown samples. Thus, our STS, resistivity, and XRD data support an interpretation in which bulk metallic transport is impeded by the stacking disorder along L of two order parameters with different long-range intralayer CDW order [58].

22.0.3 Discussion

In summary, our results demonstrate that a mixed-CDW phase characterized by C-CDW and H-CDW domains of opposite chirality can be stabilized by a thermal quench through T_{I-NC} . The required thermal quench is at an intermediate rate (≈ 120 K/s) based on heat diffusion calculations (see Methods), faster than the initial quench that 1T-TaS₂ crystals experience during growth (≤ 2 K/s) but slower than the changes to the electronic temperature induced by a laser pulse (≥ 1 K/fs) [6, 21] (Figure 22.4) **a**. We note that the chiral splitting (relative rotation) of the two order parameters enables us to clearly resolve the mixed-CDW phase. If the H-CDW and C-CDW phases exhibited the same chirality, the small difference in their ordering wavevectors would lead to overlapping satellite peaks, complicating the observation of this novel state. Our STS data reveals that this mixed state hosts a semimetallic in-plane electronic density of states, while out-of-plane CDW stacking disorder prevents bulk metallic behavior.

It is compelling to compare our observations with theories for dynamical phase transitions [59, 60] and how domain formation influences the competition between coexisting order parameters. Thus, to describe the low temperature state after a quench, we consider a mean-field energy functional [61] within the Landau-Ginzburg theory including, among others (see the Supplementary Information for more details of the calculations), a $d_0\bar{\phi}_C^2\bar{\phi}_H^2$ term in which d_0 parameterized the competition between the C-CDW and the H-CDW phase. The order parameter is the spatial charge modulation, $\alpha(\vec{r}) = \Re(\phi_C e^{i\vec{Q}_C \cdot \vec{r}} + \phi_H e^{i\vec{Q}_H \cdot \vec{r}})$ in which the amplitude of the order parameter for the C-CDW, ϕ_C , corresponds to the global minimum of the free energy landscape for slow cooling protocols, and ϕ_H is the amplitude of the H-CDW order parameter. We note that our model does not include the order parameter for the NC-CDW as the initial quench from T_{I-NC} down to low temperature effectively skips over the intermediate CDW state. Moreover, the H-CDW phase can only be stabilized from the C-CDW phase [21] indicating that the NC-CDW is not necessary to discuss the competition between these two states. Such free energy landscape allows a mixed inhomogeneous phase to be accessed at intermediate but adiabatic quenching rates in which a single temperature can be defined for all the different degrees of freedom in the material. This state is characterized by the coexistence of trapped regions of the two competing orders [62] and enhanced lifetime due to the transiently created domain walls [59].

These behaviors are illustrated in Fig. 22.4**b-c** where the energy functional, $F(E)$, is calculated for $d_0 = 0.8$ with the same mass term, a_0 , for both order parameters, $\frac{a_0}{2} \int dr^2 \alpha(\vec{r})^2 = \frac{a_0}{2} (\bar{\phi}_C^2 + \bar{\phi}_H^2)$. Under these conditions, the mixed state becomes the global minima ($F(E)_{mixed} = -52.17$), and we find a large energy barrier to the next local minima corresponding to a pure C-CDW state ($F(E)_C = -5.66$). On the contrary, a much larger value of $d_0 = 6.1$ leads, Fig. 22.4**d-e**, into a state in which an almost pure H-CDW phase emerges as a local minimum ($F(E)_H = -2.28$), although with a much shallower energy barrier ($F(E)_C = -5.66$). We note that d_0 encodes the number and size of adjacent domains with different order parameters that emerges during the quench and it is proportional to the length of neighboring domain walls of the two competing orders. Thus, large values of d_0 are associated with larger populations of small domains, expected in fast quenches. Small values of d_0 indicate the existence of larger domains, consistent with intermediate quenches. We note that for values of $d_0 < 0.5$, competition is not possible, and there is only a global minimum corresponding to the C-CDW phase within our model. The dependence of the global minima on d_0 and a_0 is shown in Fig. **f**, where the color encodes $F(E)_{mixed}/F(E)_H$.

Our data is consistent with a scenario in 1T-TaS₂ in which a thermal quench stabilizes a mixed phase of H-CDW and C-CDW order parameters up to $T = 180$ K in cooling and $T = 210$ K in warming. We note that coexistence of the H-CDW and C-CDW phase in ultrafast switched samples has also been recently reported [63]. Moreover, all our thermal quenching

attempts were unsuccessful in engineering a sample without signatures of the C-CDW state indicating that sufficiently large values of d_0 were not achieved. It is likely that the quench protocol we describe here results in a nonuniform quench rate that is locally too slow over some regions of the sample to allow for the nucleation of the H-CDW domains. Within this context, previous ultrafast stabilization of the H-phase in thin flakes [21, 20, 22, 23, 24, 25, 26, 27], can be understood as a non-thermal ultrafast quench [59, 60] leading to high domain densities and large values of d_0 . Our results are consistent with proposals in which the absorption of energy by the electronic degrees of freedom suppresses the C-CDW order parameter. The consequent relaxation of the non-thermal electrons via the lattice leads to an ionic displacement from that of the C-CDW state into that of the H-CDW [29] allowing for the correlations of the H-CDW order parameter to grow [59]. Thus, our results and Landau-Ginzburg theory calculations suggest that the minimum of the free energy landscape associated with the H-CDW order parameter already exists at the thermodynamic equilibrium of 1T-TaS₂ and can be accessed with a sufficiently fast adiabatic quench (Figure 22.4 a).

Our quenching protocol and the observation of the mixed-CDW phase opens a new pathway towards the development of new efficient functional devices based on 1T-TaS₂ in which H and C-CDW domain engineering can lead to switchable metallic behavior at temperatures above LN₂ [39, 43, 26]. More generally, our results have implications for the dynamic control of quantum materials [38, 64] by establishing that for macroscopic order parameters, the engineering of free energy landscapes can be achieved without the need for strong laser pulses when a thermally stable phase is already present at equilibrium [65, 66, 67].

22.0.4 Methods

Sample Growth

1T-TaS₂ bulk single crystals were grown by chemical vapor transport, with iodine as the transport agent. Stoichiometric amounts of elemental Ta and S were sealed in a quartz tube. The tubes were held at a 950° C – 850° C temperature gradient for 240 h and then placed in ice water to stabilize the 1T phase. Samples were characterized by XRD, resistivity, and Raman (see Fig. 2).

Thermal quench

Bulk 1T-TaS₂ crystals were sealed in a 1" quartz tube filled with Ar gas. The 1T-TaS₂ samples were then annealed by warming them up to 420 K, below the polytype transition at 660 K, with an 8h hold. This was followed by either a fast quench in which the quartz tube is dropped in a reservoir of LN₂ or slow cooling at room temperature. In-situ quench was performed at the QM2 beamline of the CHESS synchrotron by alternating between hot gas and a LN₂ cryo-stream.

Estimate of the cooling rate

To provide an estimate of the cooling rate for our 1T-TaS₂ sample quenched within an Ar-filled quartz ampule shown in Fig. 22.4 a and Extended data, we solve the heat diffusion equation for a system with cylindrical symmetry under the assumption that 1T-TaS₂ is at all times thermalized with the Ar bath and that the outside surface of the quartz tube is thermalized with the bath. Thus, the limiting factor to thermalization is the heat diffusion from the hot Ar volume at the starting temperature ($\rho_{Ar} = 1.8 \text{ kg/m}^3$, $K_{Ar} = 0.0179 \text{ W/(m}\cdot\text{K)}$, $C_p^{Ar} = 400 \text{ Jkg}^{-1}\text{m}$) through the 1.1 mm thick quartz wall with the outer surface acting as the heat sink ($\rho_Q = 2650 \text{ kg/m}^3$, $K_Q = 1, C_p^Q = 700 \text{ Jkg}^{-1}\text{m}$)).

X-ray High Dynamic Range Reciprocal Space Mapping

Hard x-ray (20 keV) HDRM was performed at the QM2 beamline of Cornell High Energy Synchrotron Source (CHESS) using a Pilatus 6M area detector. The sample is mounted on a Kapton pin using GE varnish and rotated around three different axes by 360° . Data is collected at every 0.1° step with a frame rate of 0.1s. The data is reduced into a 3D stack, indexed, and projected into a 2D dataset using the beamline software.

In-house XRD measurements

In-house XRD measurements were performed on a Huber four-circle diffractometer in combination with a micro-focused Ag K_α x-ray source and a 256 x 256 pixel GaAs detector (pixel size 55 x 55 μm) situated 96 cm away from the center of rotation. Data was reduced using the same software as for the CHESS data.

STM/STS measurements

STM and STS measurements were performed on a RHK Technology PanScan Freedom closed-cycle STM. Samples for the STM/STS measurements were mounted on stainless steel post holders using conductive silver epoxy and quenched as previously described. After the quench, the samples were characterized by XRD and kept below $T = 370\text{K}$. The surface of a 1T-TaS₂ crystal was cleaved at room temperature and $\approx 10^{-10}$ mbar by carbon tape and a cleaving screw before being introduced to the STM stage and cooled to 10 K. All data presented here were taken at 10 K.

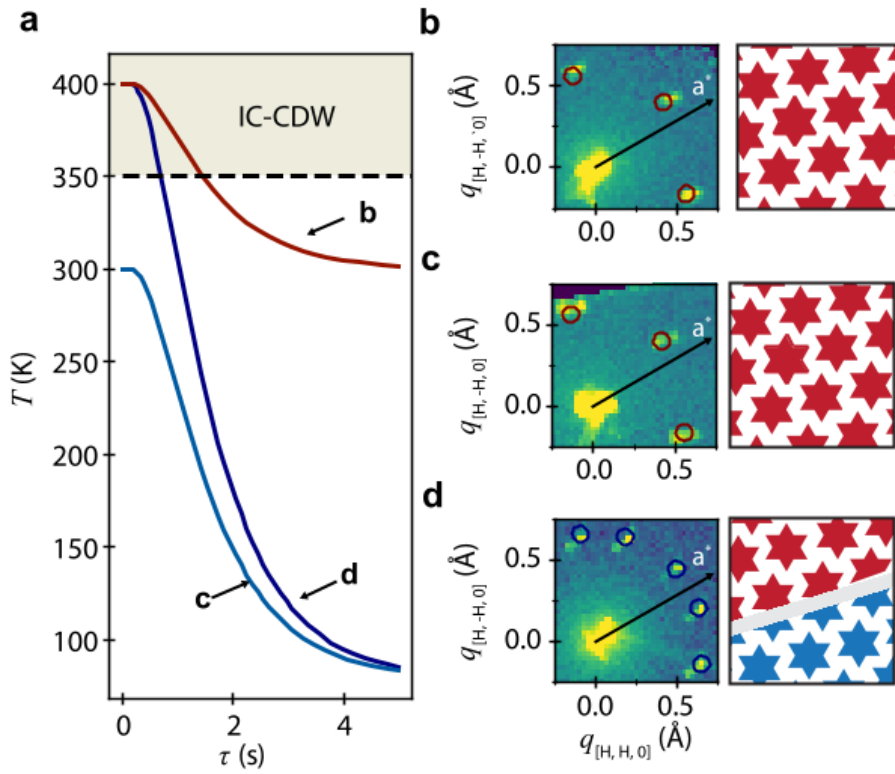
Resistivity

Resistivity measurements were performed using a Quantum Design Physical Properties Measurement System (PPMS). Samples were mounted on a DC resistivity puck and a standard four-probe method was used, with Au wires and Ag paste contacts.

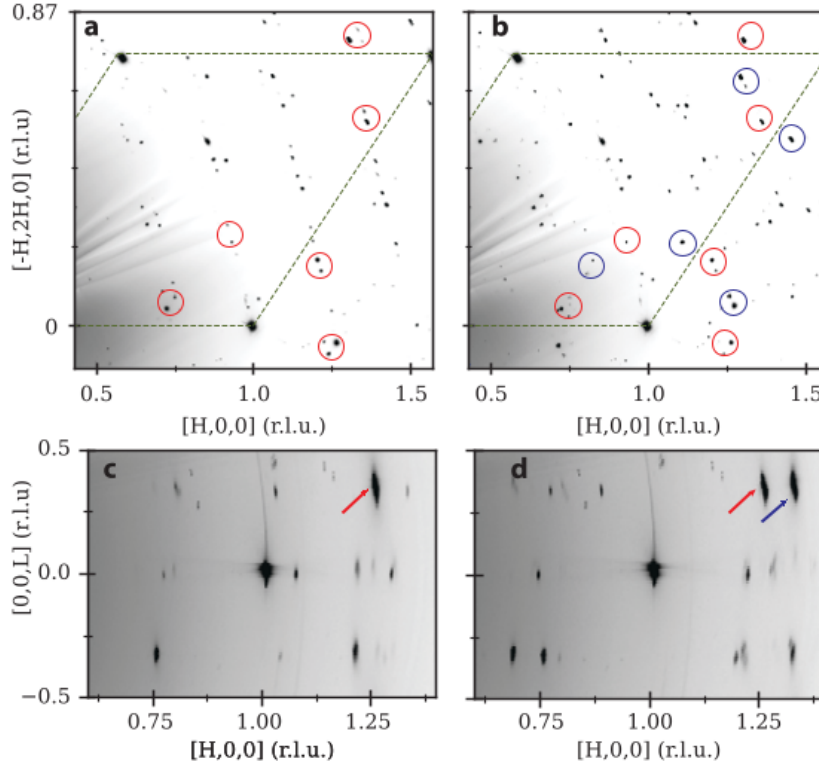
Raman Spectroscopy

Raman measurements of quenched and unquenched TaS₂ single crystals are performed at 5 K in a closed-cycle He cryostat. The samples are excited in a backscattering geometry with a 532 nm laser focused through a 0.6 NA objective lens with 40 $\times$ magnification. The laser power was measured to be 110 μW before the objective. The scattered light was collected through the same lens and directed to an imaging spectrograph with a liquid nitrogen-cooled charge-coupled device. Rejection of the Rayleigh scattered light is accomplished using three-volume Bragg gratings that allow measurement of Raman photons down to 10 cm^{-1} .

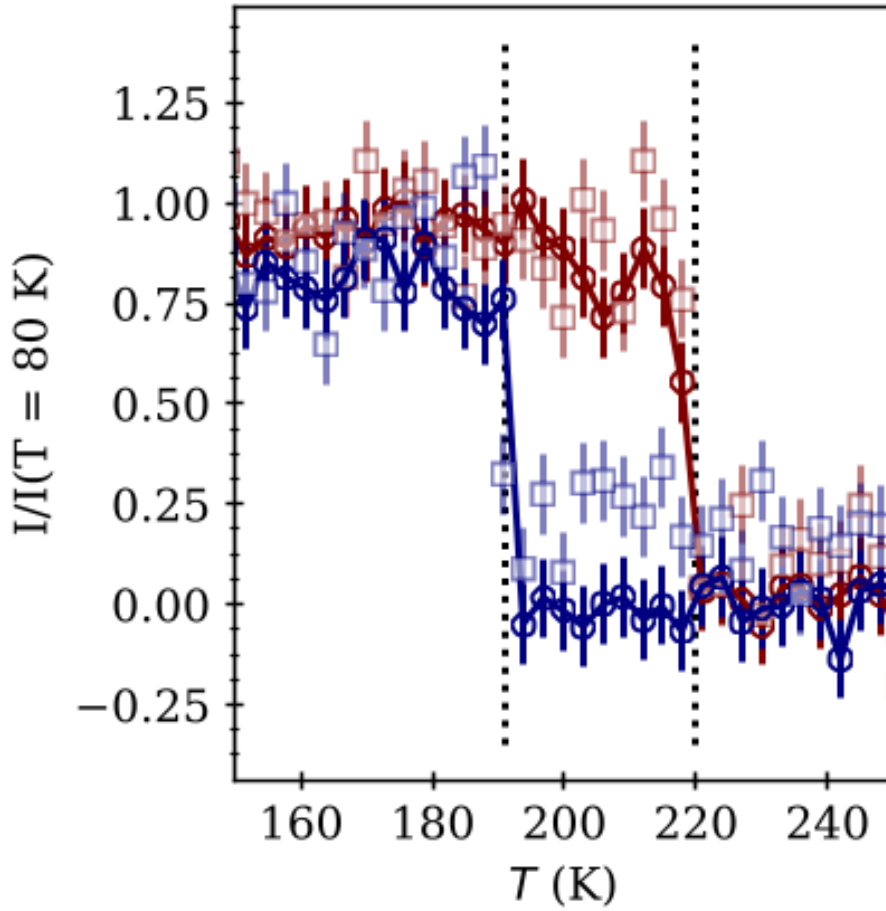
22.0.5 Extended Data



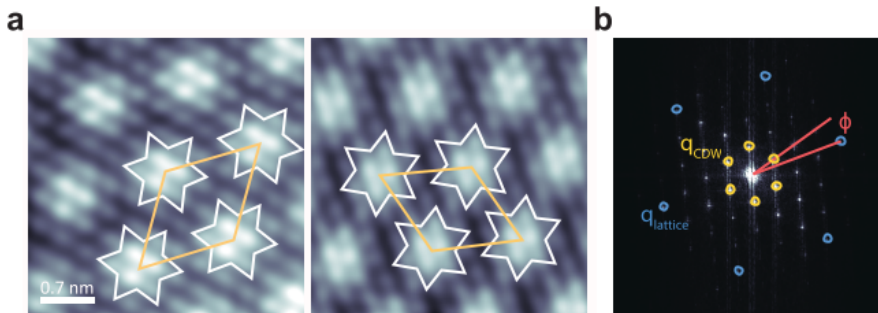
Extended Data 1: **a** Cooling rate simulations and reciprocal space maps and CDW state schematic **b-d** for three different scenarios: **b** slow cool from 400 K, **c** quench from 300 K and **d** quench from 400 K. Only the third case shown in **d** results in the emergence of the mixed CDW state.



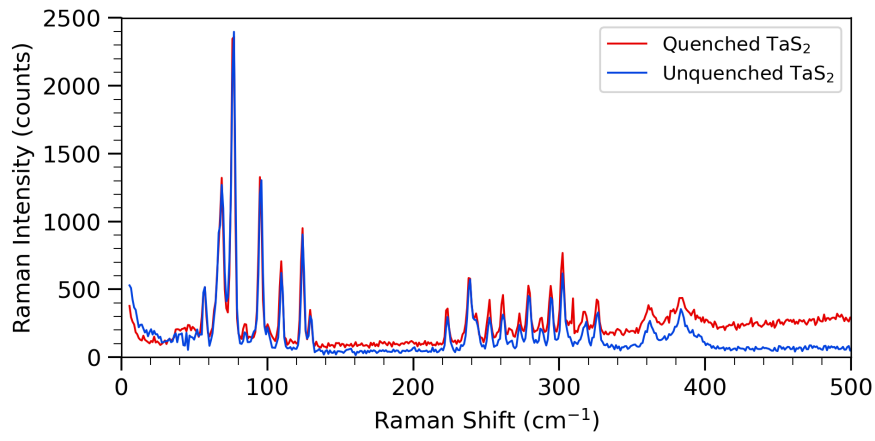
Extended Data 2: **a.** Reciprocal space maps parallel to the $[HK0]$ plane ($\delta L = .5$, $L = 0$) at $T = 300$ K for an as-grown sample. **b.** Reciprocal space maps parallel to the $[HK0]$ plane ($\delta L = .5$, $L = 0$) at $T = 300$ K after a quench. Red and blue markers highlight the original NC-CDW and the second set of satellite peaks that emerge after the quench, respectively. Green dashed lines highlight the a^* and b^* directions. **d** Reciprocal space map parallel to the $[H0L]$ plane for the as-grown sample ($\delta K = .15$, $K = 0$). **e** Reciprocal space map parallel to the $[H0L]$ plane for the quenched sample ($\delta K = .15$, $K = 0$). Red and blue arrows point to two sets of out-of-plane Bragg peaks corresponding to the NC-CDW. The L dependence and central value of these peaks are different than those seen in the mixed phase sample for the H- CDW phase.



Extended Data 3: Circular and square markers show the temperature dependence in cooling (blue) and warming (red) of two CDW Bragg peaks of opposite chirality in quenched samples of 1T-TaS₂



Extended Data 4: **a** STM data with atomic resolution in two domains with different chirality in Fig. 22.3b. **b** The high-intensity fundamental peaks (q_{lattice}) are highlighted in blue. The satellite peaks (q_{CDW} , yellow) are associated with the TH-CDW phase. The resolution of our STM measurements prevents us from resolving the difference in the magnitude and in-plane rotation of $|q|$ between the C-CDW and H-CDW.



Extended Data 5: Unpolarized Raman spectra in a quenched (red) and as-grown (blue) at $T = 5$ K.

Part VII

Experiments: Main Articles

23 Quantum jamming transition to a correlated electron glass in 1T – TaS₂ by Gerasimenko, Vaskivskiy, Litskevich, Ravnik, Vodeb, Diego, Kabanov, Mihailovic (2018)

Abstract

Distinct many-body states may be created under non-equilibrium conditions through different ordering paths, even when their constituents are subjected to the same fundamental interactions. (example?)

The phase-transition mechanism to such states remains poorly understood.

Here, we show that controlled optical or electromagnetic perturbations can lead to an amorphous metastable state of strongly correlated electrons in a quasi-two-dimensional dichalcogenide. (wasn't it known before?)

Scanning tunnelling microscopy reveals a hyperuniform pattern of localized charges, whereas multitip surface nanoscale conductivity measurements and tunnelling spectroscopy show an electronically gapless conducting state that is different from conventional Coulomb glasses and manybody localized systems.

The state is stable up to room temperature and shows no signs of either local charge order or phase separation (how is it?) .

The mechanism for its formation is attributed to a dynamical localization of electrons through mutual interactions.

Theoretical calculations confirm the correlations between localized charges to be crucial for the state's unusual stability.

23.0.1 Article

In the search for fundamentally new forms of quantum matter through non-equilibrium transitions ^{1–6}, other options may be available beyond standard Ginzburg-Landau transitions (and the Standard Model) or the currently popular topological transitions ⁷. Perhaps the most intriguing, and possibly the "deepest and most interesting unsolved problem in condensed matter theory" is the glass transition ⁸. However, in spite of significant studies by different types of excitation in very diverse systems that exhibit such transitions, profoundly new states have proved elusive. Most commonly in complex electronic materials, short-lived transient ordering of electrons is observed that rapidly reverts to the ground state ^{9,10}. Alternatively, metastable states may form, but these are usually closely related to nearby phases in the equilibrium phase diagram ^{2,11–16}. Among candidate systems that have multiple competing interactions and rapid electronic ordering ¹⁷, a material of recent interest is the layered dichalcogenide 1T- TaS₂ (Fig. 1a). In equilibrium this well-studied dichalcogenide has an extraordinarily rich phase diagram driven by lattice strain ¹⁸, Coulomb interactions ¹⁹, a Fermi surface instability ²⁰ and orbital ordering ²¹, and includes a hightemperature metallic state and various charge-density wave states, as well as superconductivity ²² and an unusual gapless quantum spin liquid-like ground state ²³.

Its phase diagram is extended by photoexcitation ¹³ and short-lived transient shifts of the electronic ordering vector have been reported under different conditions ²⁴.

Here we report a study of a dense metastable glassy electronic quantum state transition that is unrelated to any of the existing states of the equilibrium or non-equilibrium phase diagram of this or any other known quantum system.

It is formed by density-driven correlations of nonequilibrium electrons, which form a hyperuniform spatial charge density distribution ²⁵.

Hyperuniformity is an important category of non-equilibrium many-body ordering that leads to maximally random jammed packing ^{25,26}, a state with the highest achievable packing density ²⁵.

Such distributions were previously found in systems as diverse as the cosmic microwave background ²⁷(???) , cold (Bosonic) atoms ²⁸, chicken eyes ²⁹ (???) , fairy circles ³⁰ (???) and, theoretically so far, in spin-polarized free Fermions ³¹, but not observed experimentally in electronic states.

The commensurate (C) ground state of the system of 1 T – TaS₂ at 4.2 K from which we began our experiments is shown in the scanning tunnelling microscope (STM) image in Fig. 1c. Commonly, it is viewed either as a triple charge density wave ^{20,21} or a hexagonally packed Mott state of localized electrons-or polarons-subject to screened Coulomb interactions ^{19,22,23,32}. In the latter correlated state picture, polarons are formed by a central Ta atom with a localized electron, surrounded by 12 Ta atoms displaced towards it to form the shape of a hexagram that provides screening (Fig. 1c insets). Their characteristic signature appears in photoexcitation experiments as a peak in optical conductivity ³³. After exposure of a $d \approx 100\mu\text{m}$ diameter spot to a single 30fs, 400 or 800 nm (3 or 1.5 eV) laser pulse with fluence adjusted above a threshold value of $F \approx 3.5\text{ mJ cm}^{-2}$ (Methods, Supplementary Note 1 and Supplementary Figs. 1 and 2), the peak electronic temperature within a few hundred femtoseconds is estimated to be in excess of 4,000 K, whereas the lattice one exceeds 600 K after 15 ps (Supplementary Fig. 3). The STM image reveals a dramatic change caused by the photoexcitation (Fig. 1d,e). There is no sign of order, but the polarons now show an amorphous (A) arrangement that densely fills the entire surface. Remarkably, we saw no long-range density fluctuations, which is a signature of hyperuniformity ²⁶ rather than of randomness. A similar effect over an area $l^2 \approx 1 \times 1\mu\text{m}$ was observed when a 10 V pulse from an STM tip was passed through the sample (Methods). The amorphous structure was completely stable at 4.2 K during the scanning (Supplementary Fig. 4). Remarkably, under sequential STM scanning conditions at 77 K the system became perceptibly more amorphous with time, and showed no tendency of relaxation towards the C ground state. Measuring the polaron diffusion with consecutive scans revealed an anomalous diffusion exponent α with the mean square displacement $\sigma_d^2 \propto \Delta t^\alpha$ and $\alpha \simeq 0.6$. Such subdiffusion processes with $\alpha < 1$ are observed in glassy systems ³⁴ and commonly discussed in the context of non-ergodicity ³⁵. (A detailed analysis is

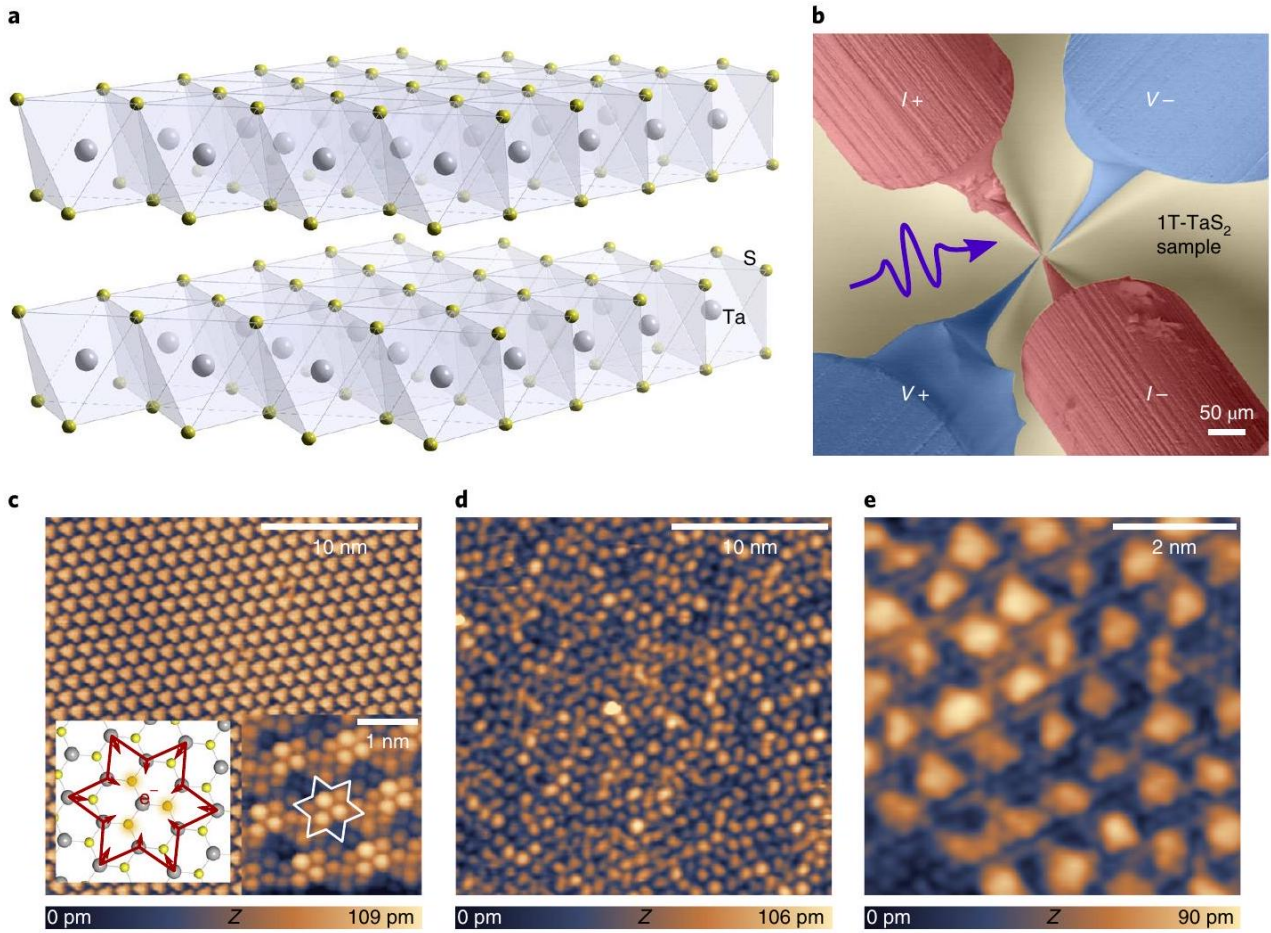


Fig. 1 | Structure, experiment and basic observation by STM of the initial and final states of polarons after excitation by a single laser pulse. a, Schematic view of two layers of a 1T-TaS crystal. The lines represent bonds. b, Four-tip ultrahigh vacuum low-temperature STM combined with ultrafast laser pulse excitation. The pseudocolour image is taken in situ from above with a scanning electron microscope. The tips coloured red and blue are used for current injection and voltage sensing, respectively, in the four-probe resistivity measurements.

c, The raw STM image of the C ground state exhibits a regular lattice of polarons. Left inset: a polaron schematic (only the top S layer is shown). Right inset: a (raw) atomic resolution STM image. A triangular pattern of S atoms on the surface around the central Ta atom is enhanced by the chosen tip bias voltage ($V_t = 100\text{ mV}$ for the right inset and -800 mV for main panel). Z is the apparent height measured by STM.

d, The raw STM image of the photoexcited state (A) formed after a single 30 fs pulse at 4.2 K shows an amorphous structure.

e, An atomic resolution image of the A state shows localized polarons superimposed on the atomic lattice.

presented in Supplementary Note 2.) The barrier for relaxation to the C state is thus clearly quite high, which is confirmed by the fact that the unperturbed state is stable for long periods (days) up to 200 K, and even at room temperature when pinned around imperfections. However, 3 V pulses from the STM tip eventually caused local patches of C order to appear (Supplementary Fig. 8). The fluence dependence of the spectral features of the collective mode

measured by coherent phonon spectroscopy reveals that the transformation was not limited to the surface layer, but was present up to a depth of at least 20 nm (Supplementary Note 1). This is confirmed by the tip-distance dependence of resistivity in multitip transport measurements described later.

Optimizing STM contrast and tip bias allows us to identify the relative positions of localized electrons and compare their polaronic pair distribution functions (PDFs) $g_{\text{pol}}^{(2)}(r)$, which give the average probability of finding two particles separated by distance r , in the A state with the C ground state (Fig. 2a-c). Two things became apparent: (1) the A state had a much smaller nearest-neighbour distance $d(1 \pm 0.05 \text{ nm})$ than the C state and (2) there was a notable absence of any peaks at $r > 3 \text{ nm}$, which implies an absence of long-range correlations beyond three nearest neighbours. A similar PDF analysis for the atomic pattern $g_{\text{at}}^{(2)}(r)$ (Fig. 2d,e) revealed that the smaller near-est-neighbour positions found in polaronic PDFs (Fig. 2b) coincide with the fifth atomic neighbour, which demonstrates that in the A state electrons predominately cause distortions on atomic sites, which correspond to nearest-neighbour polaron-polaron distances.

Clearly, separated peaks at large distances (Fig. 2e) signify that the underlying lattice is only locally distorted without perturbation of the long-range lattice order.

The simplest picture of the amorphous polaron state is that the local hexagram maintains its original shape whereas the longrange order of the hexagrams is lost. Figure 2e supports this picture, but the absence of atomic spots in the autocorrelation image (Supplementary Fig. 9) suggests that the local hexagram structure itself is not well-defined and not always centred at the Ta site, as it is in the C state.

Plotting the polaron number variance σ_N^2 , evaluated on different spatial scales R , as $\sigma_R^2 = (\sigma_N/(R/D))^2$ versus the normalized distance (R/D) , where D is the nearest-neighbour distance, we see a clear spatial decay, which is a signature of a hyperuniform distribution common in classic jammed systems²⁵. A fit (Fig. 2f) reveals a hyperuniformity exponent of $\beta = -0.60 \pm 0.03$. For comparison, random polaron packing would give $\beta = 0$ ($\sigma_R^2 = \text{constant}$) (Supplementary Method 1 gives a detailed analysis). We note that number density fluctuations in the A state are suppressed on length scales substantially larger than the estimated screening length of the electric field (Supplementary Fig. 12). Remarkably, the density of localized polarons in the A state is $\sim 23\%$ higher ($n_A = 0.98 \pm 0.02 \text{ nm}^{-2}$) than that in the hexagonally packed C ground state ($n_C = 0.80 \pm 0.02 \text{ nm}^{-2}$); a surprising fact, given that the hexagonal packing of charges in the C state is the densest possible packing of classic spheres in two dimensions (2D). The remarkable stability (to $> 200 \text{ K}$) and the absence

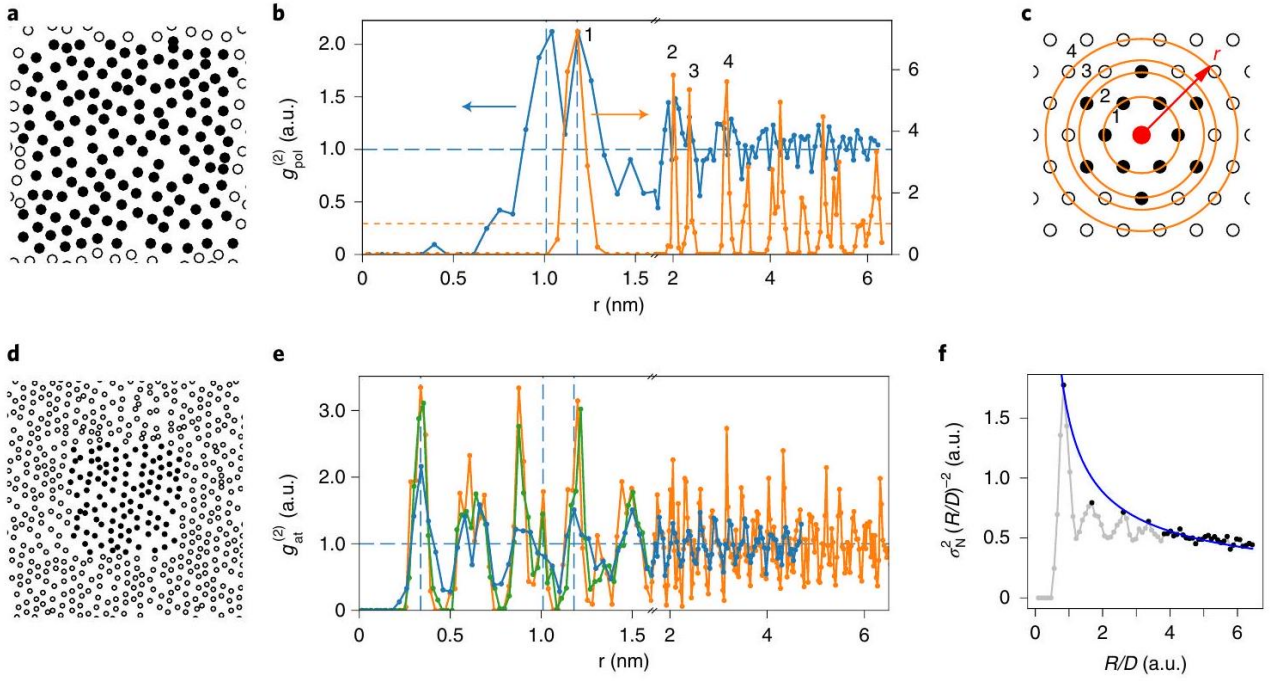


Fig. 2 | Distances in between polarons and atoms. **a**, A point pattern extracted from the experimental STM images of polarons in Fig. 1d (Methods). Filled black circles mark the particles over which the averaging was done in the calculation of the PDF. **b**, Polaron PDFs $g_{\text{pol}}^{(2)}(r)$ for the A (blue) and C (orange) states derived from **a**. Blue and orange dashed horizontal lines indicate the $g_{\text{pol}}^{(2)}(r) = 1$ levels (that is, lack of order-homogeneous particle distribution) for the A and C states. **c**, The peak assignments for the C state in terms of the nearest neighbours (coordination circles). **d**, A point pattern of atoms extracted from Fig. 1e. **e**, Atomic PDFs of the A (blue), C (orange) and simulated C (green) states. Blue dashed horizontal line indicate $g_{\text{at}}^{(2)}(r) = 1$ level. The PDF in the A state is distorted at 1 nm and 1.15 nm, which correspond to the nearest-neighbour polaron distances (blue vertical dashed lines). **f**, Radial dependence of the normalized polaron number variance $\sigma_N^2 = (\sigma_N/(R/D))^2$ (polaron density fluctuations). Here R and D are the observation window radius and characteristic polaron size. The blue line is a power law fit to σ_N^2 , which gives the hyperuniformity exponent $\beta = -0.6 \pm 0.03$ (Supplementary Method 1 gives details of the calculations and fit). a.u., arbitrary units.

of relaxation towards the C state implies that polarons are trapped in configurational space by strong mutual correlations and exhibit the kind of non-ergodicity that is expected for maximally correlated jammed states²⁶.

Investigating the electronic structure by scanning tunnelling spectroscopy reveals that the density of electronic states (DOS) derived from the logarithmic derivative of the conductance $\text{DOS} \propto (dI/dV)/(I/V)$ is convincingly gapless at all points on the surface (Fig. 3a-c) with a small V-shaped dip in the range $\pm 0.1\text{eV}$ from the Fermi energy (E_F) that can be interpreted as a signature of incipient localization by some fraction of the carriers³⁶, typical for interacting systems with disorder³⁷ (Fig. 3b shows the spot-to-spot variation of spectra). In contrast, the C state shows distinct sharp features commonly assigned to Hubbard bands^{19,38–40} and zero conductance within the gap from -0.1 V to $+0.15\text{ V}$ (Fig. 3a).

To ascertain the nature of charge transport with the evidently immobile charges in the A state we performed a four-STM-tip measurement with ohmic contacts, $\sim 2.5\mu\text{ m}$ apart (Fig. 1b and Supplementary Fig. 13). STM scans were first used to confirm the amorphous polaron structure after switching with a 30 mA pulse passed between a pair of tips (Supplementary

Method 2 gives details). The result of switching is unambiguous: the resistivity drops on $C \rightarrow A$ switching to $\rho \approx 18 \text{ m}\Omega \text{ cm}$, with a linear current-voltage characteristic (Fig. 3d). This is more than two orders of magnitude smaller than typical in-plane published values²² of the C state at 4 K or one order of magnitude smaller than the resistivity of crystals from the same growth batch⁴¹ at 20 K, as shown in Fig. 3d. The temperature dependence of resistivity by a four-probe measurement was found to be compatible with 3D variable range hopping (VRH) of the form $R_{\text{VRH}} \propto \exp(T/T_0)^\gamma$, with $\gamma \simeq -1/4$ (Fig. 3d and Supplementary Discussion 2). The 3D nature of transport is confirmed by the fact that the resistance between tips depends on the distance L between them and shows behaviour close to $R \approx 1/L$ expected for 3D (Supplementary Method 2). The implication is that the localized charges observed by STM are not responsible for transport—in fact, they do not move when a current is passed—but they are coupled to other carriers that show VRH-like transport.

Amorphous matter that is denser than the crystalline form is very rare in nature⁴², which leads to the intriguing question: what is the path that leads to such a new state in a system that already exhibits multiple and diverse orders and that does not lead to one of the existing ones? Emergent states of quantum matter may be created if—through many-body interactions—its constituents order before it reaches thermal equilibrium. The non-ergodic dynamics observed here suggest that the localization of a significant fraction of the available electrons takes place through mutual correlations.

If we consider the Coulomb repulsion as an analogue of hard-sphere interactions in classic systems, then above a certain critical density all the available space is filled by the localizing carriers and the electrons become immobilized as a result of mutual correlations following the classic density-driven jamming transition scenario. Thereafter, the band picture is no longer applicable, and we need to consider a coupled system of itinerant holes and jammed electrons, respectively, for which there is no obvious precedent. Note that the localized states occupy the same region of real space as the itinerant carriers, which can lead to quantum interference between the itinerant and localized states⁴³.

Conventional many-body electron localization may occur on a regular 2D lattice as a result of coupling to either slow spin²³ or lattice fluctuations^{44,45}, which leads to disorder and non-ergodic behaviour^{45,46}. However, so far such model discussions^{46,47} have led to single-system many-body localization with a gapped spectrum,

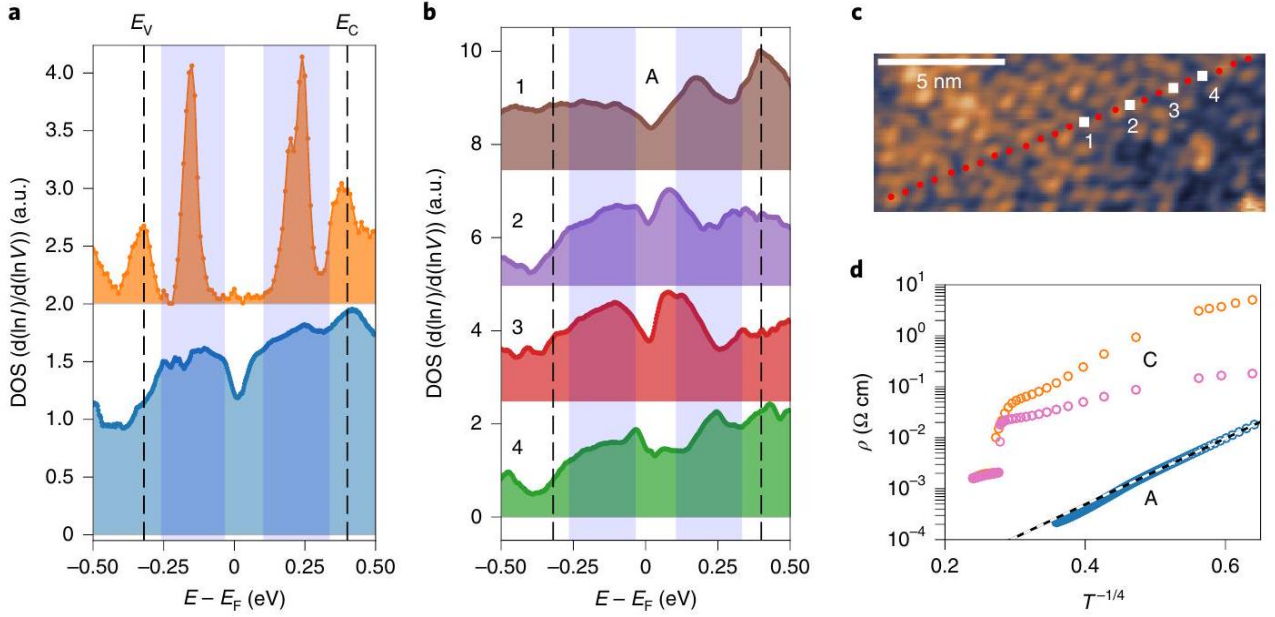


Fig. 3 | Electronic properties from tunnelling spectroscopy and transport measurements. **a**, Comparison of the DOS in the C (top) and A (bottom) states (the latter is averaged over 25 different points on the surface shown in **c**). The dashed lines indicate the C-state band edges, E_V and E_C , and the vertical grey regions indicate the position of the lower and upper Hubbard bands. The energy is shown with respect to E_F . **b**, Individual DOS curves measured at different points (white squares in **c**), which illustrate the variations of the DOS. **c**, Surface topography in the A state. Red dots indicate where the spectroscopy curves were measured for the average DOS in **a**. **d**, The four-tip resistivity in the C state and the A state measured with ohmic contacts. The C-state temperature (T) dependence is known to vary significantly from sample to sample, shown here for two extreme examples. In contrast, the T dependence of the A-state resistance is more consistent, with VRH $R \propto \exp(T/T_0)^\gamma$. The fits give $\gamma = -1/4$.

which is not compatible with gapless DOS and transport seen here. The stability of the correlation-localized electron subsystem, subject to Coulomb repulsion and lattice strain, can be investigated with the classic Hamiltonian $^{32}H = \sum_{i,j} V(i,j) (n_i - \bar{\nu}) (n_j - \bar{\nu})$. Here $V(i,j)$ is an exponentially screened Coulomb potential (provided by the itinerant electron background), $n_i = 1$ if the site is occupied and 0 otherwise, and $\bar{\nu}$ is the average polaron density. Model Monte Carlo simulations of H on a triangular lattice using the experimental density $\nu_A = 0.094$ per unit cell as a fixed input parameter gave a configurational minimum which compares remarkably well with the experiments (Fig. 4a,b), whereas a density that corresponds to the C state ($\frac{1}{13}$) leads to a hexagonally packed ordered state (Methods and Supplementary Discussion 3 give details). The minor differences in the local packing are probably related to the effects of the lattice that are not taken into account by the model, such as interaction via distortions and the fact that the polarons are not point charges but rather have a specific atomic arrangement that needs to be matched between the neighbours. Experimentally, our observation that relaxation proceeds in the direction of greater disorder (Supplementary Note 2) supports the implied notion that the A state is energetically favourable. The model also predicts a hyperuniform distribution of polarons—the PDFs (Fig. 4f) show quite good agreement with the STM data (Fig. 2b) and a comparable hyperuniformity exponent $\beta_{\text{theory}} = -0.87 \pm 0.04$ (Fig. 4g). Screened Coulomb interactions are thus apparently sufficient to obtain a hyperuniform polaron distribution even without considering spin or lattice disorder. However, as charge transport is limited by carrier diffusion within this model 32,48 , by itself it cannot explain the observed transport properties.

Although the localized carriers discussed by the polaron lattice gas model do not contribute to transport, coupled quasiparticles lead to transport that is similar to that in regular charge density waves. The major difference is that the A state is gapless, and hence the VRH behaviour and not a simple activated temperature dependence defined by a charge density wave gap. Such itinerant VRH/localized carrier duality has been observed, but not yet properly understood, in some other complex multiband systems, most notably cuprate superconductors⁴⁹.

Generically, self-assembled glasses may be thought to result from competing interactions with different ranges. The glass-like behaviour is predicted theoretically to arise as a result of the appearance of an exponentially large number of metastable states with different effective charge density⁵⁰. The undoped C ground state structure has an electron number density $\nu = \frac{1}{13}$ per 1T-TaS₂ elementary unit cell, but other electron-rich metastable structures with different $\nu = \frac{1}{4}, \frac{1}{7}, \frac{1}{9}, \frac{1}{12}, \frac{1}{13} \dots$ are possible; their primitive cells are shown in Fig. 4e. The observed average experimental density in the A state is $\nu = 0.094$. The effective charge q^* of each localized polaron is shown by a Voronoi cell construction shown in Fig. 4a,b for the experimental data and the model, respectively. It reveals a tiling of irregular polygons with no translational or rotational symmetry. Generally, $q^* \neq e/13$ so each electron is shared between different numbers of Ta atoms. By analysing the inter-polaron distances, we can assign polaron surroundings to the corresponding primitive cells (Fig. 4c,d), which shows a tessellation with tiles whose charge densities are between $e/9$ and $e/13$ per elementary unit cell. Significantly, there was no sign of phase separation or aggregation into any kind of regular structure, which confirms that the A structure is a local minimum of energy. Reaching this minimum requires dynamic localization that leads to a density-driven transition to the hyperuniform state.

The present experiments suggest a specific path of the quantum glass transition to a hyperuniform state of a system of thermalizing Fermions. In the present case, there are specific features of the Fermi surface that appear to be relevant, such as the dispersionless band close to the Fermi level²⁰ (Supplementary Fig. 16), which leads to localization and jamming of some proportion of the non-equilibrium electrons. However, we may expect to find more examples of an amorphous state in 2D fermionic systems on the basis of screened Coulomb interactions on square lattices, as in transition metal oxides, for example, where competing orders are very common.

Although we have discussed the problem in terms of the polaron picture, an alternative viewpoint (discussed in Supplementary Discussion 4) invokes a description of the observed charge density in terms of coherent superpositions of electrons in the bands near

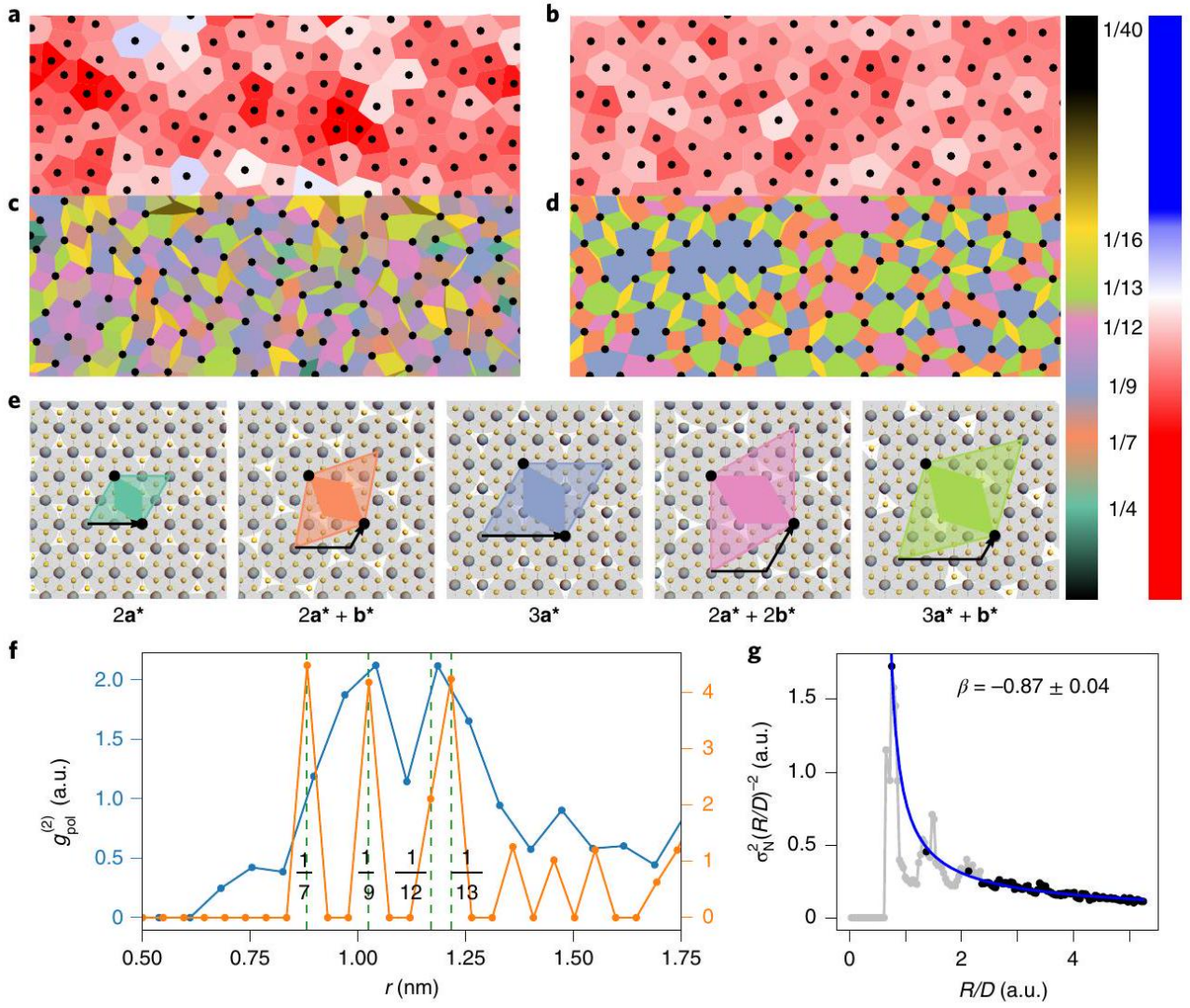


Fig. 4 | Tiling patterns formed by polarons in the A state, comparing experiment (**a, c**) and theory (**b, d**). **a, b**, The effective polaron charge for each Voronoi cell, which varies from $\frac{1}{7}$ to $\frac{1}{16}e^-$ per atomic unit cell (right vertical colour bar). **c, d**, Tiling based on the distances between the nearest neighbours in the pattern that corresponds to the characteristic superstructures on the triangular atomic lattice shown in the primitive cell (**e**). The fractions in the colour bars show the effective localized charge per atomic unit cell; the latter is defined by the basis vectors $\mathbf{a}^*$ and $\mathbf{b}^*$. **e**, Five consecutive commensurate superstructures, from left to right, $\frac{1}{4}$, $\frac{1}{7}$, $\frac{1}{9}$, $\frac{1}{12}$ and $\frac{1}{13}$ (grey circles) on the triangular atomic lattice and their primitive cells (coloured polygons). The black arrows show the respective atomic periods. **f**, Experimental (blue) and theoretical (orange) polaron PDFs. The dashed vertical lines show the positions of the peaks that correspond to specific superstructures (**e**). **g**, Normalized polaron number variance ($\sigma_N/(R/D))^2$ versus R/D from theory (grey curve) and power law fit (blue curve). The fitted value of the hyperuniformity exponent is $\beta_{\text{theory}} = -0.87 \pm 0.04$.

the Fermi level, akin to laser speckle³¹. However, without Coulomb interactions it is not clear how to explain the origin of metastability purely in terms of such a wave picture. We note that the demonstrated resistance switching by charge injection and room-temperature stability provides a new correlation-driven mechanism for an ultrafast all-electronic resistance-switching memory device.

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23.1 SM: Methods

Switching to the A state. Measurements were done with a customized Omicron Nanoprobe ultrahigh-vacuum low-temperature microscope with four independent STM scanners and equipped with the optical input for an ultrafast laser and scanning electron microscope located on top of the STM chamber (Fig. 1b)¹⁶. Optical switching was done at 4.2 K with a single 800 nm or 400 nm 30 fs pulse the latter obtained by a second harmonic generation from the 800 nm Ti:sapphire ultrafast laser and focused to a $100\mu\text{m}$ spot on the sample. The exposure was repeated several times with a 10 s interval. Electrical switching with an STM tip was done by approaching at a gap voltage of +10 V and a setpoint current of 200 nA. The tip was then retracted back and returned to its normal scanning conditions. The switching was done at a temperature of 4.2 K. Two/four-tip switching details are described in Supplementary Method 2. There is no qualitative difference between the resulting topography or electronic properties of the A state obtained by either optical or electrical switching, but in the former case much larger areas are switched, and the image appears flatter.

STM image analysis. To take into account the non-ideal scanner calibration, raw STM images were corrected for the atomic structure to match the ideal triangular lattice using the standard Fourier transform affine algorithm in SPIP software. Affine coefficients were several percent for all the images. The respective values varied within the error due to Fourier peak width and did not affect the results of the PDF analysis and the conclusions of the paper. Sample tilt was subtracted in all the images. Polaronic and atomic features in the STM images were detected using a maximum filter or Laplacian of Gaussian algorithm (Supplementary Fig. 17 gives details).

Monte Carlo simulations. Monte Carlo simulations of the Markov chain dynamics for the Hamiltonian $H = \sum_{i,j} V(i,j) (n_i - \bar{n})(n_j - \bar{n})$ on a triangular lattice were performed using the standard Metropolis algorithm⁵¹. The proposed successive state in the chain consists of setting $n_i = 0$ at an occupied site and $n_j = 1$ at a randomly selected unoccupied site⁵². The simulations were performed with a fixed number of charged particles on the lattice of the size of $L \times W$ ($L = 84, W = 78$) with periodic boundary conditions and with the lattice period a . The amorphous configuration was also confirmed as the number of particles varied within 5%. The interaction potential $V(i,j)$ in the simulations shown in the paper has a Yukawa form with the screening radius $r_s = 4.5a$ and was cut at distances larger than $24a$. Note that the screening length is larger than the polaron radius in the C state. Various screening radiuses ($1 \div 50a$) were checked to give the amorphous configuration. The annealing simulations were performed by decreasing the temperature from 10^{-2} to 10^{-3} with a step of 10^{-5} with 1.4×10^6 Monte Carlo steps at each temperature point. The temperature was measured in the units of $e^2/k_B\epsilon_0 a$, where e is the electron charge and ϵ_0 is the static dielectric constant of the material in the C state.

For rigorous confirmation that the A state is, indeed, an energetically favourable low-temperature polaron configuration, we also employed a parallel tempering Monte Carlo algorithm⁵³. Here M replicas are simulated in parallel using standard Monte Carlo procedures, where replica m is assigned a fixed temperature T_m . In our simulations we always used $M = 32$ replicas. With this relatively large number of replicas it was sufficient to distribute the temperatures in regular intervals ($T_m = T_1 + \frac{T_M - T_1}{M}m$). For simulations of a single replica we used the Metropolis algorithm as described above. This was done for ten Monte Carlo sweeps between two successive replica exchanges. The proposed exchange was between the nearest- and next-nearest-neighbour replicas. In a single equilibration simulation, a total of 1,000 replica exchanges was typically superfluous to achieve convergence.

23.1.1 SM Note 1: Signatures of the A state in the time-resolved optical reflectivity

We have performed three pulse destruction-pump-probe (D-P-Pr) measurements on 1T-TaS₂ at $T = 160$ K using the method previously reported¹ to monitor the coherent phonon behaviour upon switching to the A state. A low repetition rate (1 kHz) pulsed laser was used¹ to allow the sample cool down between the pulses. To minimally disturb the sample, P and Pr fluences were set to very low values (0.2 and 0.05 mJ/cm² respectively). D pulse fluence was varied to observe switching to different states. The D pulse arrives 50 ps before the P pulse, which allows us to measure the switched sample. Suppl. Fig. 2a,b shows P-Pr traces and their respective Fourier transform spectra for different fluences of D pulse. For low fluences practically no changes to the spectrum are observed. For fluences above 1 mJ/cm² the phonon frequency shifts from 2.36 to 2.22 THz, which can be seen as an increase of oscillations period in Suppl. Fig. 2a, and as a shift of the peak in Suppl. Fig. 2b. This corresponds to the switching from the C to the H (hidden) state (frequencies of C and H peaks are shown with vertical dashed lines), and is in agreement with previous measurements¹. Further fluence increase strongly damps oscillations (Suppl. Fig. 2a), which results in the H state peak becoming less and less prominent (Suppl. Fig. 2b). The area under the H state peak (the shaded part on Suppl. Fig. 2b) shows rapid decrease above certain fluence. We attribute this to switching of more and more layers of the crystal to the A state (the penetration depth at 800 nm is 20 ~ 30 nm at this temperature²). Due to amorphous nature of the A state, we expect destructive spatial interference of phonons and thus less pronounced phonon oscillations, which is clearly seen at highest used fluences.

23.1.2 SM Note 2: Stability of the A state at various temperatures. Anomalous diffusion.

The A state at 4.2 K is extremely stable without any visible signs of relaxation (change of polaron positions) within 10 hours of scanning at $V_g = -800$ mV, $I_t = 300$ pA (Suppl. Fig. 4a,b). At 77 K it becomes more malleable: from scan to scan polaron positions fluctuate less than the nearest neighbor distances (< 1 nm), but global pattern does not change with time (Suppl. Fig. 4c,d). Remarkably, even at 150 K during scanning (Suppl. Fig. 4e,f) there are changes in relaxation compared to 77 K. Interestingly, there is no polaron exchange between ordered and amorphous parts of the sample in the studied temperatures region (4.2 – 150 K) (Suppl. Fig. 4), signifying the qualitative difference between these states. This is an unusual situation from the perspective of the dynamics of phase transitions. In particular, an inhomogeneous mixture of two phases tends to evolve towards a formation and growth of domains with time because of diffusion and surface tension - the so-called Lifshitz-Allen-Cahn growth^{3,4}. Deviation from such behavior indicates that system does not relax thermally up to 150 K. Remarkably, azimuthal cross-sections of Fourier transform (FT) (Suppl. Fig. 5) of the initial and final images in the consecutive scans series at 77 K readily reveals that the FT weight in between the peaks (i.e. random part) increases towards the end of the series. This is equivalent to the system becoming effectively more random with time and suggests non-ergodic behavior. See Supplementary Discussion 1 below for the details of the A state in reciprocal space.

To investigate non-ergodic properties, we track changes in the polaron positions with time by comparing consecutive STM scans of the same area at 77 K. To cancel thermal drift effects, observation area was linked to three defect sites seen in every scan in the set. The polaron positions detected in five frames are shown in Suppl. Fig. 6a. Histogram in Suppl. Fig. 6b shows the distribution of polaron displacements with respect to the initial position at different times since the first frame. The histogram is averaged over all the directions and cut off above

the nearest neighbor distance. Variance as a function of time, plotted in Suppl. Fig. 6c, has a nonlinear form $\sigma_d^2 \propto t^\alpha$ with $\alpha \approx 0.6$ consistent with anomalous diffusion and being an evidence for non-ergodicity⁵. Detailed proof of non-ergodicity is generally difficult and would require an analysis of temporal correlation functions, which goes far beyond the scope of the present paper.

23.1.3 SM Discussion 1: The A state in reciprocal space

Reciprocal space analysis is a simple approach to the angular correlations in the particle positions, which can shed some light on the path from the C to the A state. Suppl. Fig. 7a shows the Fourier transform (FT) of the STM image of the C state. It consists of six sharp peaks, which form hexagonal unit cell of a regular triangular lattice of polarons. The unit cell is determined by 3 inequivalent vectors Q_C . They are rotated by 13.9° from the reciprocal atomic unit cell vectors (a^*, b^*), and has the length $Q_C/a^* = 0.277$, as follows from the commensurability condition $Q_C = \frac{1}{13}(3a^* + b^*)$. Together they form $\sqrt{13} \times \sqrt{13}$ star of David reconstruction, with the "3 + 1" atomic units periodicity of the polaron lattice⁶. In contrast, in the A state the Fourier density becomes circular with six-fold diffuse peaks on top. The latter is seen in more details in the azimuthal cross-section (Suppl. Fig. 7b): the A state has non-vanishing intensity at all angles; it is the largest in the atomic vector direction (a^*) and is the smallest in between. No prominent peak is observed at the Q_C direction. Diffuse angular FT intensity is consistent with loss of directional long-range order of polaronic lattice with respect to the atomic one. Suppl. Fig. 7c shows 2D projection of FT intensity in the A state on angular and radial axes with respect to the atomic lattice. The latter is well-defined as can be seen from the size of the respective peak. Fourier intensity from polarons is mostly spread into $\pm 13.9^\circ$ range around the atomic lattice direction. The simultaneous presence of both negative and positive deviations is not observed either in the C state (i.e. no double peak structure symmetrical to atomic direction) or any other state in the 1 T-TaS₂. The peak along a^* is clearly split, with at least two values Q' and Q'' identified (Suppl. Fig. 7d), consistent with the splitting observed in the polaronic PDF (Fig. 2b in the main text). It signifies the loss of the long-range translational order in the polaronic lattice. The split peaks are located at $Q'/a^* = 0.286$ and $Q''/a^* = 0.306$. The former is close to the Q_C ("3 + 1" period) by length, but the direction coincides with that of the atomic Bragg peak. Such a vector is known to appear in the equilibrium incommensurate charge density wave phase at high temperatures⁶. The second peak, Q'' , is not observed in any equilibrium state in 1 T-TaS₂ and most likely corresponds to the 3 atomic units distance between polarons seen in the polaronic PDF (Fig. 2b in the main text).

23.1.4 SM Method 1: Analysis of particle number fluctuations and hyperuniformity in the A state

To investigate the hidden order (hyperuniformity⁷) that might be present in the amorphous state created by an electric or ultrafast laser pulse, we perform a statistical analysis of the point pattern deduced from the coordinates of the centers of polarons (see Suppl. Fig. 10a). We are particularly interested in the variance in the number of points within the circular observation window of a radius R , $\sigma_N^2(R)$ ⁷. In the beginning, we separate the square image with side L with point pattern into the array of circles of radius R centered at the points of the pattern. To avoid edge effects, we restrict the number of points to those lying inside the square with the side $(L - 2R)$. Then, we count the number of points within each of the circles and build a histogram. Finally, we calculate the number variance, $\sigma_N^2 = \langle N^2 \rangle - \langle N \rangle^2$, where averaging is done over all circles. The procedure is then repeated for another R . In Suppl. Fig. 10b one

can clearly see that the width of number distribution increases with R , hence variance also increases (Suppl. Fig. 10c). For a 2D disordered point pattern variance is known to grow as fast as the area of the observation window, $\sigma_N^2(R) \propto R^2$. For a 2D periodic lattice it grows as a surface area instead, $\sigma_N^2(R) \propto R$. Intermediate behavior means that number fluctuations will decay on large scale and system will actually become long-range ordered on these scales. More strictly, quadratic term must become zero at $R \rightarrow \infty$. Such systems are called hyperuniform⁷.

The straightforward way to check whether the system is hyperuniform is to plot $\sigma_N^2(R)/R^2$ as a function of R . If it decays with R rather than being constant, then system is hyperuniform. The corresponding plot is shown in Suppl. Fig. 10d and clearly demonstrates normalized variance decay at large R .

The oscillations at small R correspond to short-range order present in the system, as seen in pair distribution function. The variance has a local maximum for radii lying in between the nearest neighbors. The exponent of decay can be extracted in two ways. One way is to fit the overall dependence. Another one is to choose only peak values in the oscillating part, which actually represent the degree of local disorder in the system. Both curves show power law decay, the respective exponents are extracted from the slope of the linear fit in double-logarithmic coordinates and are somewhat different: -0.34 (green) and -0.60 (blue). Similar values were obtained for another dataset. Structure factor $S(k) = 1 + \rho h(k)$ also shows decay $S(k) \rightarrow 0$ when $k \rightarrow 0$ (Suppl. Fig. 11b), as expected for the hyperuniform pattern. Here $h(k)$ is the Fourier transform of the generalized PDF, $g^{(2)}(r) - 1$.

It should be noted, that generally point patterns are analyzed for monodisperse systems⁸. In contrast, we are dealing with particles of different sizes and, more importantly, shapes. For polydisperse system, analysis of point pattern can give false negative⁹, which is not the case here.

The alternative approach in the polydisperse case is to analyze the variance of the local volume fraction⁸. However, this approach relies strongly on the way the volume fraction is calculated, and for real images reconstruction is necessary to estimate it correctly⁹. In the current case we do not perform such reconstruction and corresponding analysis, since jammed polaronic distortions on the discrete atomic lattice give volume fraction quite different from that for soft-spheres due to significant shape variation.

23.1.5 SM Method 2: Multi-tip experiment - in situ switching and characterizing the A state

A four-tip experiments were performed to switch part of the sample into the A state with a short electric pulse and measure the resistance of the new state. Resistance measurements were done in the standard four-probe configuration with tips positioned in a line. All the tips were made from chemically etched W wire and cleaned in situ at UHV conditions to strip the oxide layer and obtain high imaging resolution. Low aspect ratio tips were used for current leads for switching to avoid melting from high currents, high aspect ratio tips were used otherwise to achieve precise positioning (see Fig. 1b in main text). All the operations were done at 4.2 K base temperature, where the bulk C state resistance is high. Positioning was done using SEM (Suppl. Fig. 13b): the beam at 25 keV was focused on the sample and the image was taken with the backscattered electrons detector. Typical current values with the 100 μm aperture used were $\sim 1\text{nA}$. It was checked in advance that with such parameters SEM scanning leaves the A state intact.

To avoid sample damage, tips were approached in such a way that ballistic contact was established. High sample resistance was taken into account when choosing setpoint (30 mV and 100 nA were used as the reference). Tip-sample separation for the current leads was further adjusted to achieve proper linearity of the two-tip I-V curve and low resistance. In the present

case values of 10 kOhm for a tip separation of 2 – 5 μm were achieved.

Switching and measurements were done using a Keithley 6221 current source and 2182A nanovoltmeter (Suppl. Fig. 13a). In the typical STM measurement configuration, the sample is grounded, so that tips can be approached independently at their own potential (Suppl. Fig. 13a). The current source and voltmeter were used in the floating mode, with one of the current leads grounded and the sample ungrounded. Proper grounding was used to avoid transient pulsed during interconnections. Two and four-tip I-V curves were taken before and after the switching (Suppl. Fig. 13c,d). The switching was routinely done with a single 10 – 30 mA pulse of 30 ms duration. All four tips remained in contact with the surface even after switching. Resistance has dropped after the single pulse. To confirm that the switched state is indeed amorphous the surface around and in between the contacts were imaged at -800 mV and 100 pA. Resistivity was estimated using the tip geometry seen in SEM (Fig. 1b) by assuming finite penetration depth of current due to factor of 10 inter/intralayer resistance anisotropy in the C state, which gave $\rho_A \approx 18\text{mOhm} \cdot \text{cm}$ (after thermally cycling the sample to 60 K). In addition, resistivity in the A state was extracted by scaling the tip separation in the linear four-probe configuration¹⁰. Lower boundary obtained by setting the geometric factor $\equiv 1$ is $\rho_A \approx 3\text{mOhm} \cdot \text{cm}$ (Suppl. Fig. 13e).

The temperature dependence was measured with the help of the commercially available FTV sample holder. It has the sample stage resting on four thin posts providing weak thermal link to the cryostat. The stage has its own large-area meander Pt heater ($\sim 30\text{Ohm}$ at 4.2 K) and Si-diode thermometer connected with manganin wires to contact posts kept at the base temperature (Suppl. Fig. 13b). To avoid loosing the contact between the leads and the sample, the former were lowered additionally by 5 nm. To avoid large thermal drift, heating was limited to 60 K. Temperature was ramped at 0.3 K/min to allow for proper thermalisation. $R(T)$ curves were measured on cooling with a DC current of alternating polarity in a four-probe configuration.

23.1.6 SM Discussion 2: $R(T)$ in the A state

The insulating temperature dependence of resistance in the A state clearly does not follow the Arrhenius activation law, slowing down at low temperatures (Suppl. Fig. 14a). To estimate the type conductivity, we have analysed the function $F(T) = -d \ln R / d \ln T$, plotted as $\ln F$ vs $\ln T$ (Suppl. Fig. 14b). Such choice of axes allows to extract the exponent of T and distinguish between various regimes of hopping transport¹¹. The plot clearly shows $-1/4$ exponent at low temperatures, consistent with 3D Mott variable-range hopping¹¹. At higher temperatures, the exponent changes to ≈ -1 . Fitting the slope in latter temperature range on Arrhenius plot gives activation energy of ≈ 64 K.

In the limited temperature range we cannot clearly distinguish exponential and power-law behavior. The exponent in the latter case can be extracted by analysing the derivative of conductivity, $G(T) = d(1/R)/dT$ plotted on the double-logarithmic scale (Suppl. Fig. 14c). The slope is 0.92, which gives $\sim T^2$ behavior of conductivity. It can indeed stem from the V-shaped dip at the Fermi level observed in the density of states, given the mobility is temperature independent in this range. However, the latter is known to be strongly temperature dependent in the ground C state¹², which makes this interpretation less plausible. Further experimental investigations are necessary to clarify this issue.

23.1.7 SM Discussion 3: Details of the Monte Carlo modeling of the A and C states

As it was stated in the main text, the key difference between the models for the C and A states is the polaron density ν . Experimental results show that in the C state $\nu = 1/13$ and in the A state $\nu \approx 1/10.56$. In our simulations we fixed ν to the experimental values and were able to reproduce the experimentally observed polaron patterns for both cases. This was shown in the main text.

Lattice Coulomb gas model was explored in details for various values of ν by Vodeb et al.¹³. Magic densities were found at which a hexagonal polaron lattice is commensurate with the underlying atomic lattice ($1/3, 1/4, 1/7, 1/9, 1/12, 1/13, 1/16, 1/19, 1/21, \dots$). This explains the C state as a $1/13$ magic density case. Results from Karpov et al.¹⁴ show that if the polaron density is perturbed slightly from a magic density, a magic density lattice with domain walls emerges. However, the density of the A state is far from being only slightly perturbed. It lies approximately in the middle between the magic densities $1/9$ and $1/12$ ($\sim 15\%$ underdoped $1/9$ or $\sim 14\%$ overdoped $1/12$). Vodeb et al.¹³ show that the polaron lattices overlayed on top of a hexagonal atomic lattice at densities far from the magic densities cannot be hexagonal due to the frustration between the repulsive interaction and the atomic lattice. This results in a large near degeneracy of different long range ordered polaron arrangements which causes glassy features in the system and a glassy transition. In contrast, each magic density case exhibits a clear first order order-disorder crystallization transition. Therefore, there is a narrow range of densities around each magic density in which crystallization occurs (with domain walls). In between these narrow ranges one obtains a much wider range of densities where a glassy transition is present to an amorphous state.

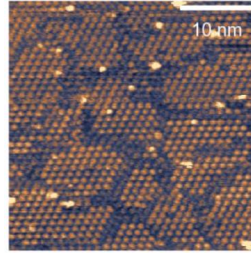
In order to rigorously confirm the fact that the model for C state indeed exhibits crystallization and that the model for A state shows an energetically favorable disordered polaronic pattern at low temperatures we performed MC simulations using the parallel tempering method. The parallel tempering method was employed in an even wider temperature range and confirms the presence of the A state down to temperatures as low as $k_B T = 0.001 V_0$, where $V_0 = e^2/\epsilon_0 a$, where e is the electron charge, ϵ_0 the static dielectric constant of the material and a the lattice constant. The acceptance ratio between nearest neighbor replicas $A_{i,i+1}$, defined as the ratio between accepted swaps and the total number of proposed swaps, can be used for detecting a phase transition in a system^{15–17}. Phase transitions are detected as pronounced suppressions of $A_{i,i+1}$ at the critical temperature. Suppl. Fig. 15 shows the dependence of $A_{i,i+1}$ versus temperature. It is clear that there is a first order phase transition in the case of $1/13$ or C state. Meanwhile, there is a glassy transition present in the case of $1/10.56$ or A state. There is a suppression of $A_{i,i+1}$ present at a lower temperature but it is not as pronounced as in the case of C state. We interpret the temperature at which the suppression is present as the temperature of the glassy transition, where the entropy of the many low lying energy states dominates the thermodynamics down to very low temperatures (as low as MC allows). It is clear that no ordering occurs in the case of A state based on our calculations.

It is unusual that the disordered A state is more energetically favorable than multiple phase separated ordered states. Pokrovsky and Uimin¹⁸ have shown for frustrated triangular lattices that multiple almost degenerate minima are present between $1/9$ and $1/12$ as well as other magic fillings, in consistency with the current conclusions. Interestingly, similar results stemming from frustration were also found on a square lattice^{19,20}.

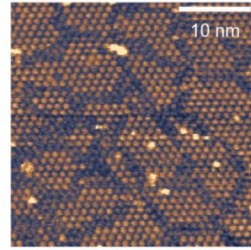
23.1.8 SM Discussion 4: Quantum interference between jammed electrons

CDWs are often considered as standing waves formed from counterpropagating electrons with opposite momenta²¹, so we may consider the A state as an interference between waves with pseudo-random wavevectors of similar magnitude. Such a distribution is known to lead to hyperuniform patterns, the well-known laser speckle pattern being a good example^{22,23}. For this to work, the de-Broglie wavelength between carriers λ_{dB} needs to exceed the interparticle distance. Initially, at ~ 4000 K, $\lambda_{dB} = \hbar/\sqrt{2mk_B T_e} \sim 0.1$ nm is too short for coherent interference on the 1 nm scale. Estimating the time-evolution of with a customary two-temperature model (Suppl. Fig. 3), after 20 – 30ps the electrons equilibrate with the lattice, and $T_e \sim T_L = 600 \sim 700$ K. At this point λ_{dB} exceeds the inter-particle distance ($\lambda_{dB} \gg 1$ nm), and electrons can interfere constructively to provide a hyperuniform fermionic speckle pattern^{23,24} in a similar way as the IC state can be considered as a quantum interference of nested electrons²¹. Within this quantum interference picture, the relaxation bottleneck in the region of the 'Fermi ridge' defines the wavevectors and energy of the participating electrons. The bottleneck thus provides a k-space analogue to jamming that localizes electrons in the Fermi ridge (FR), providing the necessary slow, long wavelength electrons with a wide distribution of k-vectors, but closely spaced in energy. A crucial property of the A state is metastability. Within the CDW picture, in order to achieve the observed metastability, e-h recombination needs to be suppressed such that the excess electron density is stabilized. This is not provided by the above scenario, which has the weakness that Coulomb interactions are neglected, so the picture is incomplete as such.

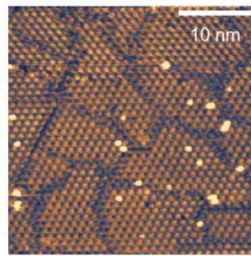
$$F \approx 1.1 \text{ mJ/cm}^2$$

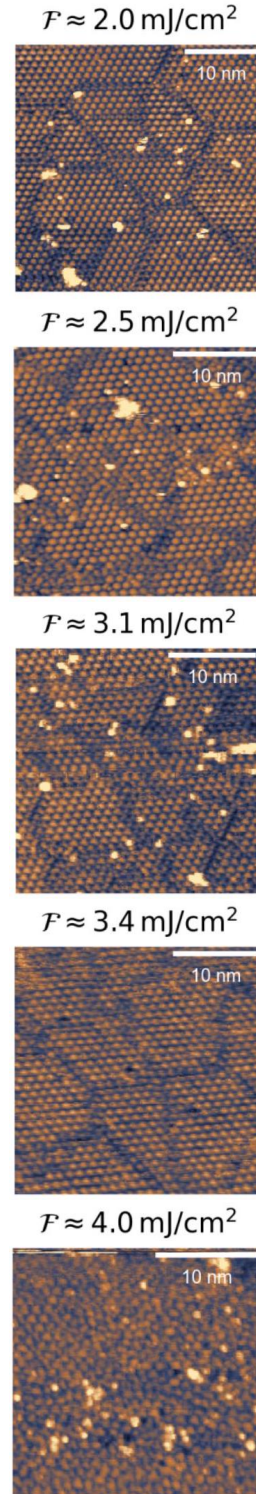


$$F \approx 1.5 \text{ mJ/cm}^2$$



$$F \approx 1.7 \text{ mJ/cm}^2$$

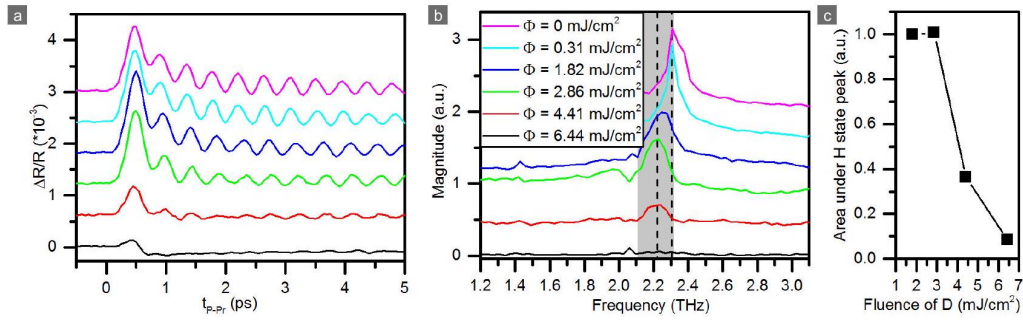




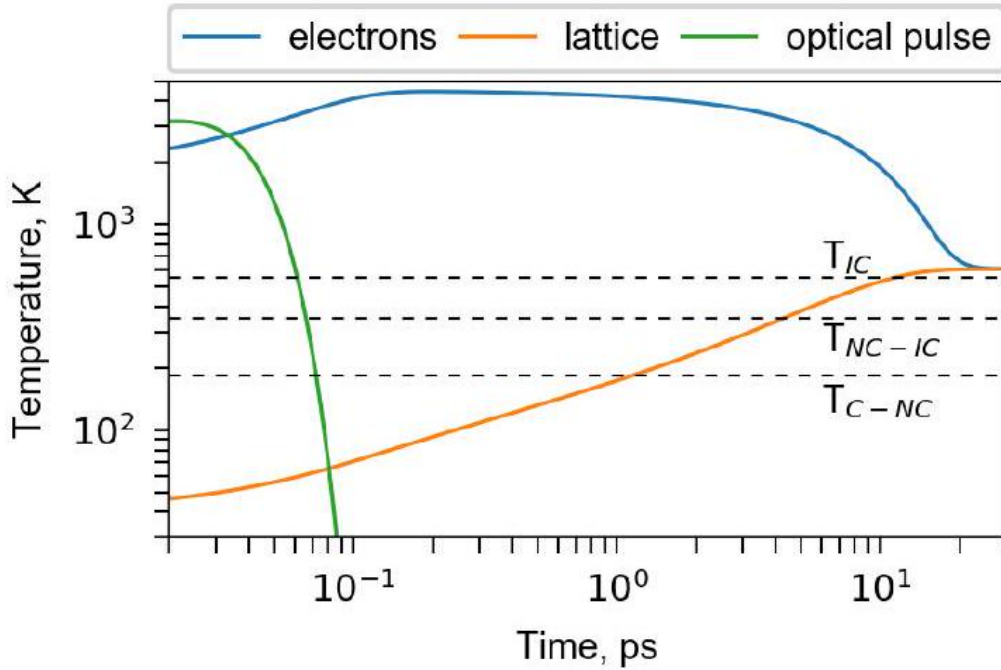
Supplementary Figure 1: Evolution of the polaronic patterns with fluence: set of STM images taken at $T = 6$ K at increasing optical fluence, $\mathcal{F}$, in the range $1 \sim 4$ mJ/cm². The threshold switching to the A state is clearly seen on crossing the threshold of $\gtrsim 3.5$ mJ/cm². Below the threshold, the domain textured "hidden" (H) state is observed. The density of domain walls is not correlated with the fluence in the H state. These data conclusively shows the A and H states to be distinct, and negates the notion of a continuous transformation between them. Comparison of electronic properties is provided below in Suppl. Fig. 18.

To avoid ambiguity in experimental conditions, the switching was done with a single optical (800 nm) pulse with the peak fluence above the threshold, and the whole dataset was measured within the area exposed to a laser spot. The gaussian spatial profile of the fluence in the spot was characterized outside and inside the UHV STM chamber. Scanning electron microscope

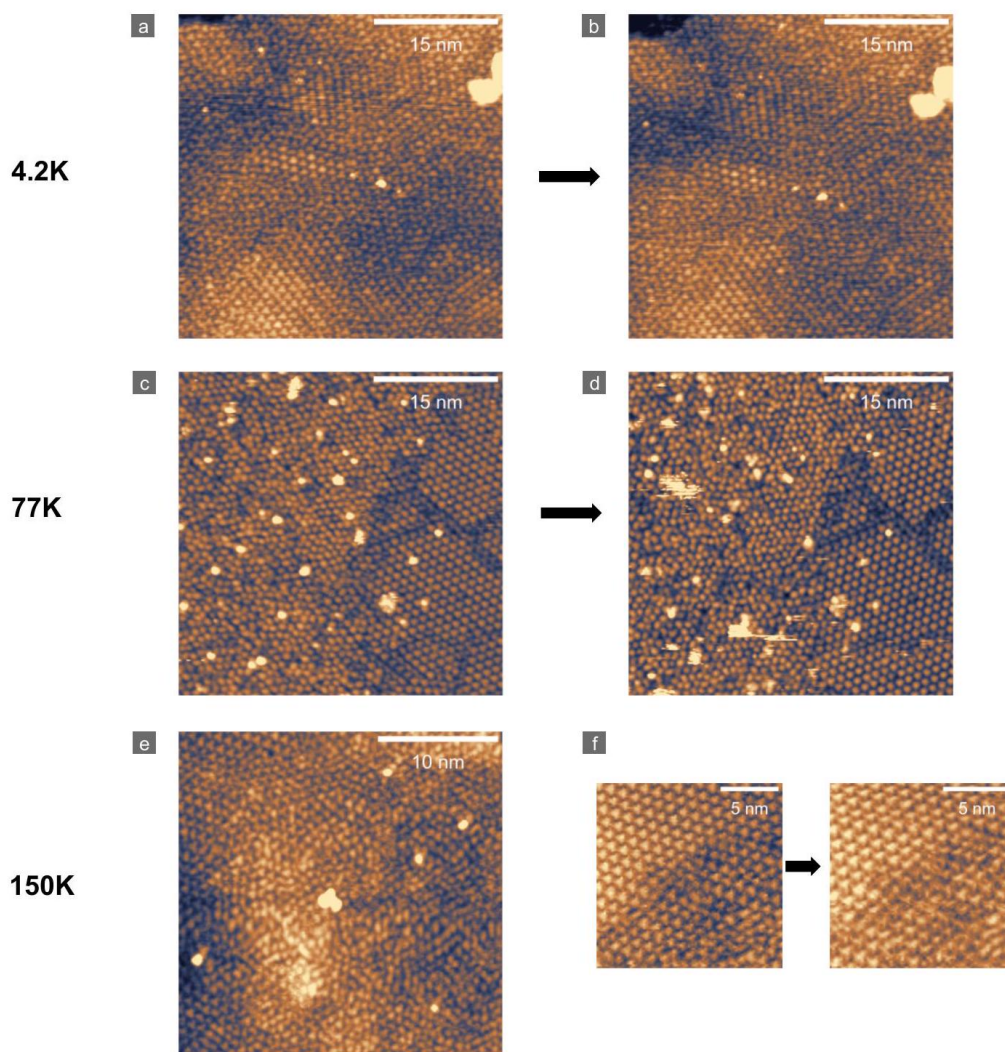
was used for the precise in situ STM tip positioning within the spot.



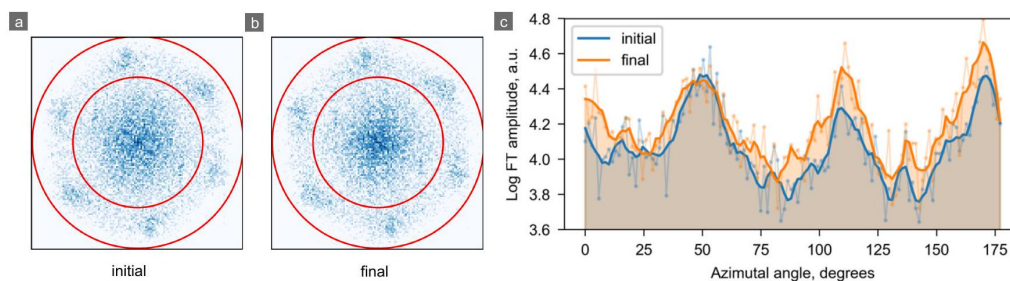
Supplementary Figure 2: Three-pulse optical pump-probe reflectivity measurements to detect the A state: **a**, **b**, time traces of the normalized transient reflectivity (a) and their Fourier transform (b) for a set of switching pulse (D) fluences in a range of 0 – 6.44 mJ/cm². **c**, normalized FT spectral weight in the frequency range of the H peak in FT (b) as a function of fluence.



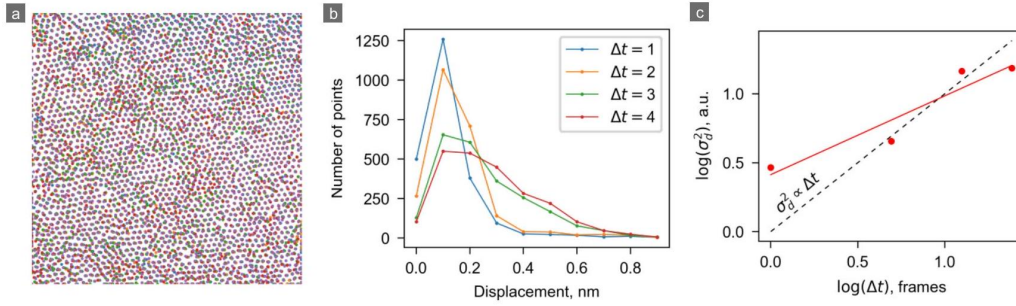
Supplementary Figure 3: Estimation of the electron and lattice heating by a single ultrafast pulse with the two-temperature model: Time dependence of the electron and lattice temperatures calculated within the two-temperature model for 1T-TaS₂^{2,26} for the optical pulse fluence of 4.25 mJ/cm² applied at $T = 10$ K. The fluence is slightly above the threshold for the optical switching to the A state, as can be seen from Suppl. Fig. 2. Dashed horizontal lines show equilibrium transition temperatures in 1T-TaS₂ upon heating. C– commensurate, NC– nearly commensurate, IC– incommensurate charge density wave states. Triclinic phase to NC is a crossover rather than a transition, so it is not shown explicitly. Optical pulse shape is shown with the green line, amplitude is plotted in arbitrary units.



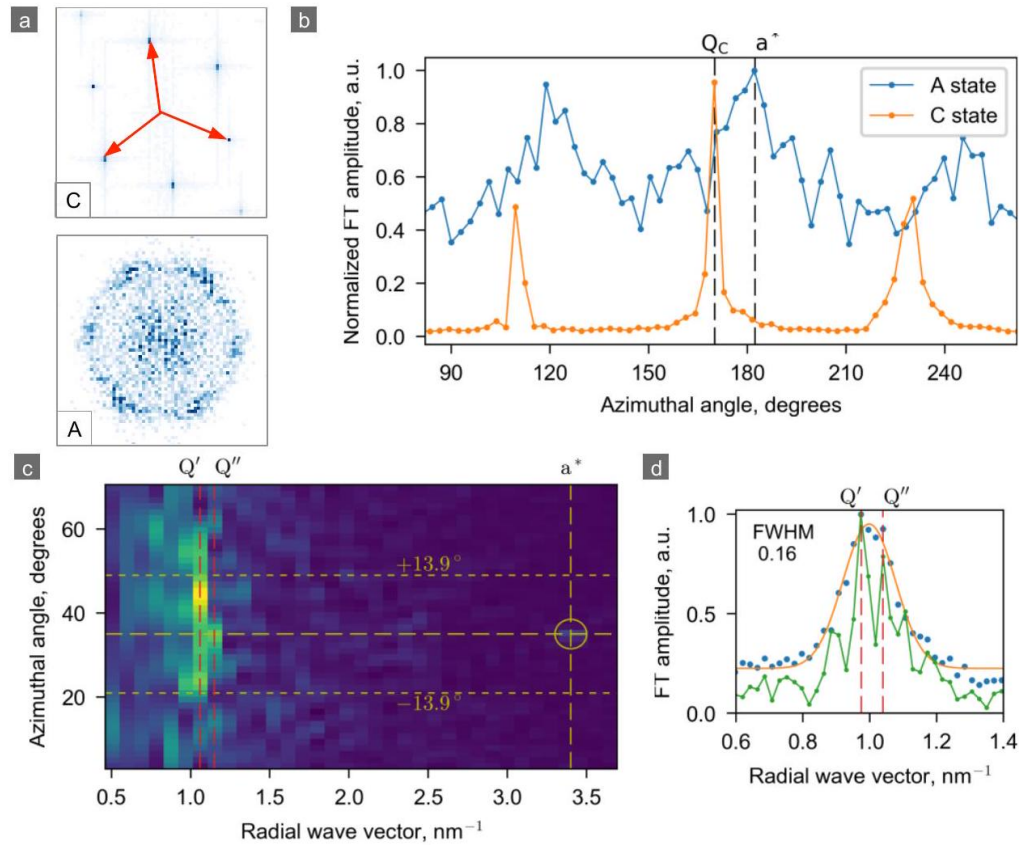
Supplementary Figure 4: Stability of the **A** state at various temperatures: stability of the **A** state at various temperatures: a-b, 4.2 K , 10 hours scanning; c-d, 77 K, 2.5 hours; e-f, 150 K - single large scale image (e) and series (f), 1.5 hours. Nonlinearities in the panel (f) are due to large thermal drift.



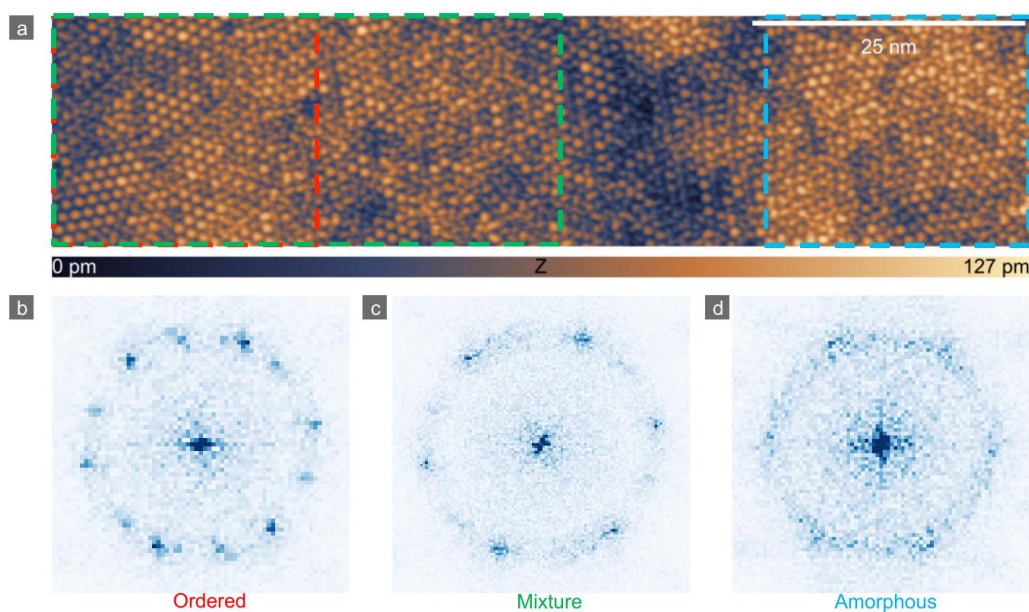
Supplementary Figure 5: Evolution of the **A** state image Fourier transform with time: azimuthal cross-sections of the FT (see also Suppl. Fig. 7b for conventions) of the **A** state in the initial and final images in the consecutive series (2.5 hours) taken at 77 K .



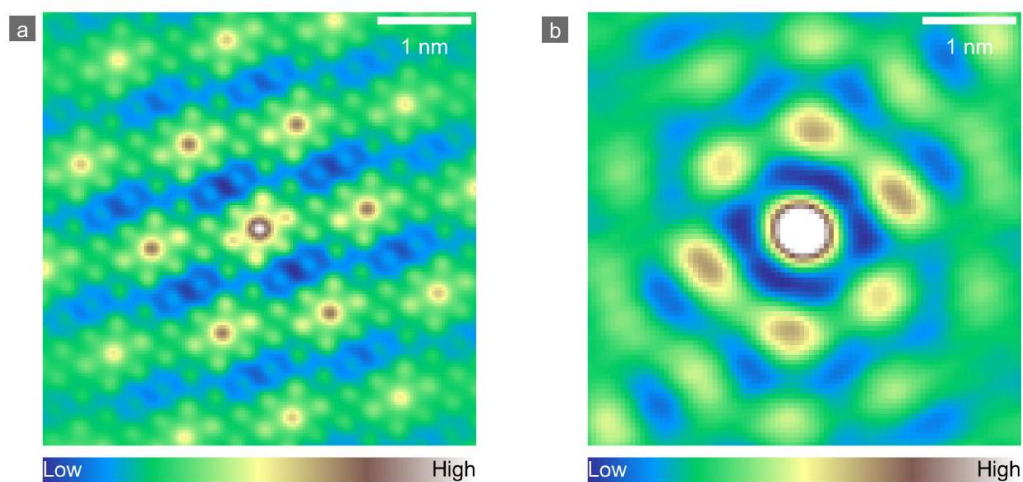
Supplementary Figure 6: Anomalous polaron diffusion in A state at **77 K**: a, polaronic point patterns for five consecutive scans (blue, orange, green, red, purple) overlaid on top of each other; b, histogram showing the distribution of jumps in polaron positions with respect to the initial ones in the first scan; c, double-logarithmic plot of the variance of the distribution of jumps (in b) as a function of time showing $\sigma^2 \propto (\Delta t)^{0.6}$ dependence; black dotted line shows the slope expected for the conventional diffusion $\sigma^2 \propto \Delta t$



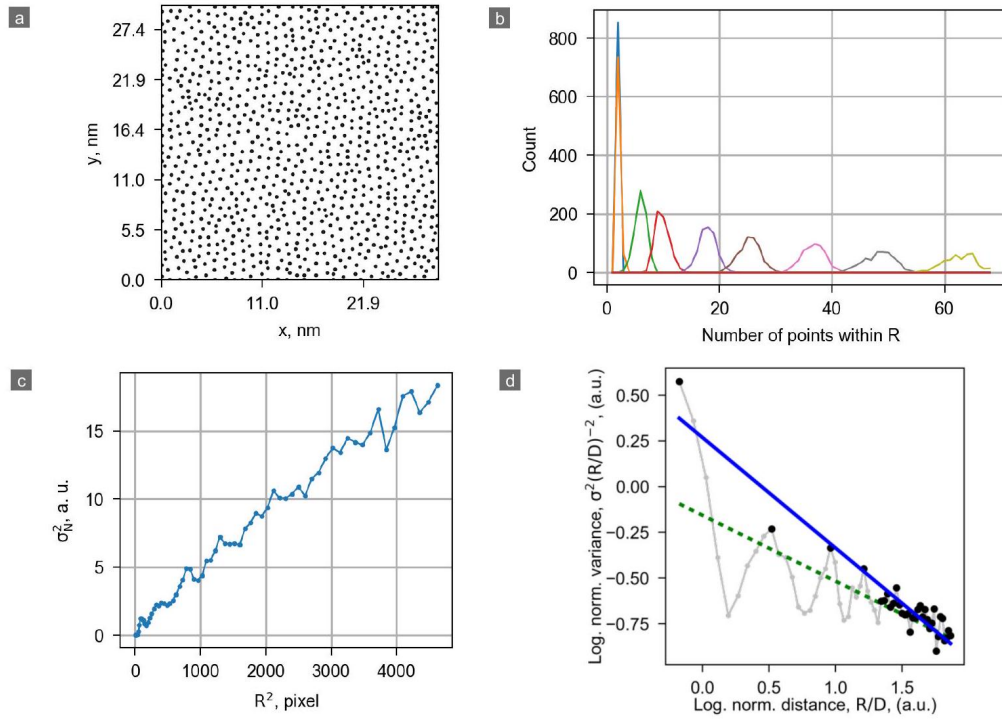
Supplementary Figure 7: Reciprocal space analysis of the A state: a, 2D Fourier transforms of STM topographic data in Fig. 1c,d in the main text. b, 180 degrees azimuthal cross-section of FTs in (a) averaged over 10-pixel ring centered at CDW peaks. c, Radial cross-section of the FT of atomically-resolved STM image of the A state (Fig. 1e in the main text) shows the distribution of polaron positions with respect to the atomic lattice a^* (the corresponding peak is marked with the yellow circle). Polaron peak groups are marked with Q' and Q'' . The lines at $\pm 13.9^\circ$ show the expected C state angles. d, 35-degree average (blue dots) of the one of the radial cross-section curves (green) from high reciprocal resolution FT. Orange curve shows Gaussian fit of the averaged data with the spread of wave vectors length about 16% (compared to resolution of $\sim 2\%$). Peaks are located at $Q'/a^* = 0.286$ and $Q''/a^* = 0.306$.



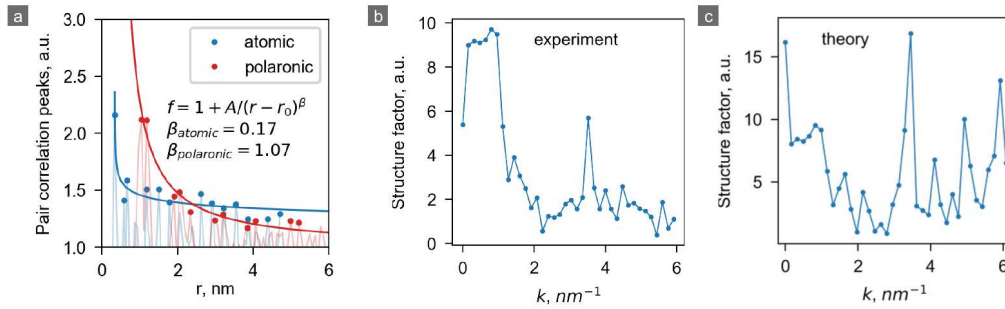
Supplementary Figure 8: Pulse-induced relaxation from A to C states: a, STM image of the A state after a small voltage pulse (3 V ; measured current $\sim 30 - 60\text{nA}$) was applied on the left side. Red, green and blue squares show relaxed (ordered), mixed and amorphous parts respectively. The relaxation can be understood as local injection of charge with smaller concentration than the one present during the creation of the A state. The direction of relaxation is thus towards the C state with $1/13$ reconstructions (smaller polaron density) rather than $1/12$ or $1/9$ (larger polaron density). b-d, Fourier transforms of the ordered, mixed and amorphous parts shown by squares in (a).



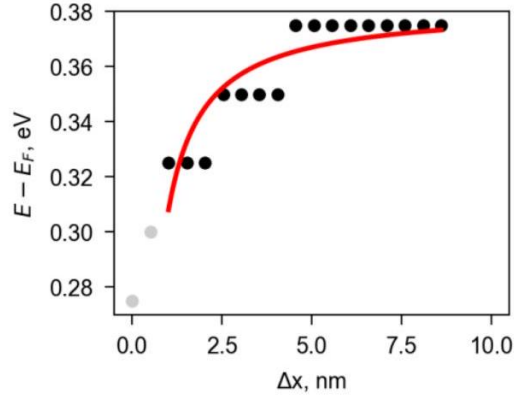
Supplementary Figure 9: Autocorrelation of the atomically resolved images of the C and A states: a, C state, hexagram reconstruction characteristic of sulfur atoms is seen; b, A state, no universal reconstruction pattern is found, emphasizing multiple polaron shapes, rather than the single hexagram pattern.



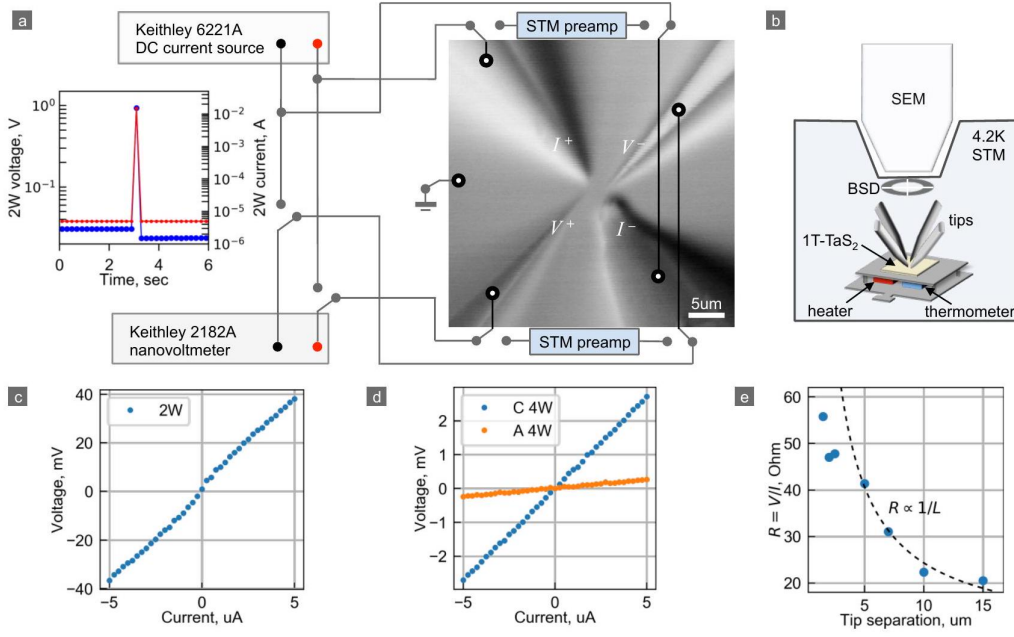
Supplementary Figure 10: Analysis of polaronic pattern for hyperuniformity: **a**, point pattern derived from detected polaron centers. **b**, histograms showing the number of points within the circular observation window of radius R (increases from blue to yellow curve). **c**, variance (the width of histograms in (b)) as a function of window radius R . **d**, double-logarithmic plot of the variance normalized by area of observation window as a function of its radius (gray curve). Solid blue and dashed green curves show power law decay fit of peak only (black) and all experimental points respectively.



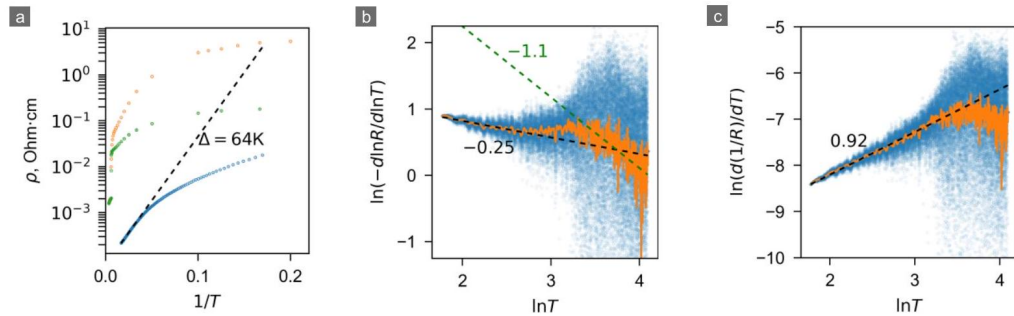
Supplementary Figure 11: Properties of the polaronic and atomic patterns: **a**, power law fits of atomic and polaronic pair correlation peaks (dots), full PDF is shown by semi-transparent solid lines. Based on the decay rate, we can ascribe polaronic distribution to short-range ordered, while the atomic one - to quasi-long-range ordered. **b**, structure factor of the experimental polaronic pattern clearly shows decay for $k \rightarrow 0$, as expected in case of hyperuniformity. **c**, structure factor of the theoretical (MC) polaronic pattern also decays for $k \rightarrow 0$. Large value $S(k = 0)$ is due to PDF average being different from 1, which is related to the finite size of the image in MC simulations.



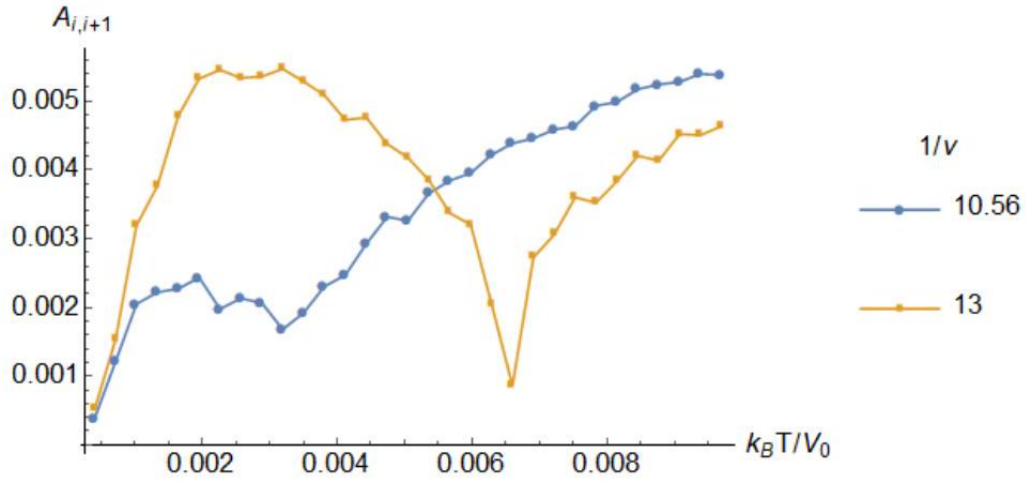
Supplementary Figure 12: Estimation of the screening length: the data points show band edge bending as a function of distance caused by an isolated domain wall in the C state (numerical data is adapted from the tunneling spectra in Fig. 1d in Ref. ²⁷). $\Delta x = 0$ corresponds to the domain wall center, black (gray) dots correspond to the outside (inside) the domain wall. 1T-TaS₂, as a layered 2D system, is expected to be screened on the scales larger than the thickness of the stack ²⁸ ($\sim 10\text{nm}$ in this case). The fit (red) with Debye screening $\exp(-\Delta x/a)/\Delta x$ outside the wall gives screening length $a \sim 1.7 \text{ nm}$ in the C state. The conductivity in the A state is almost two orders of magnitude higher than in the C state, hence the screening length will be even smaller.



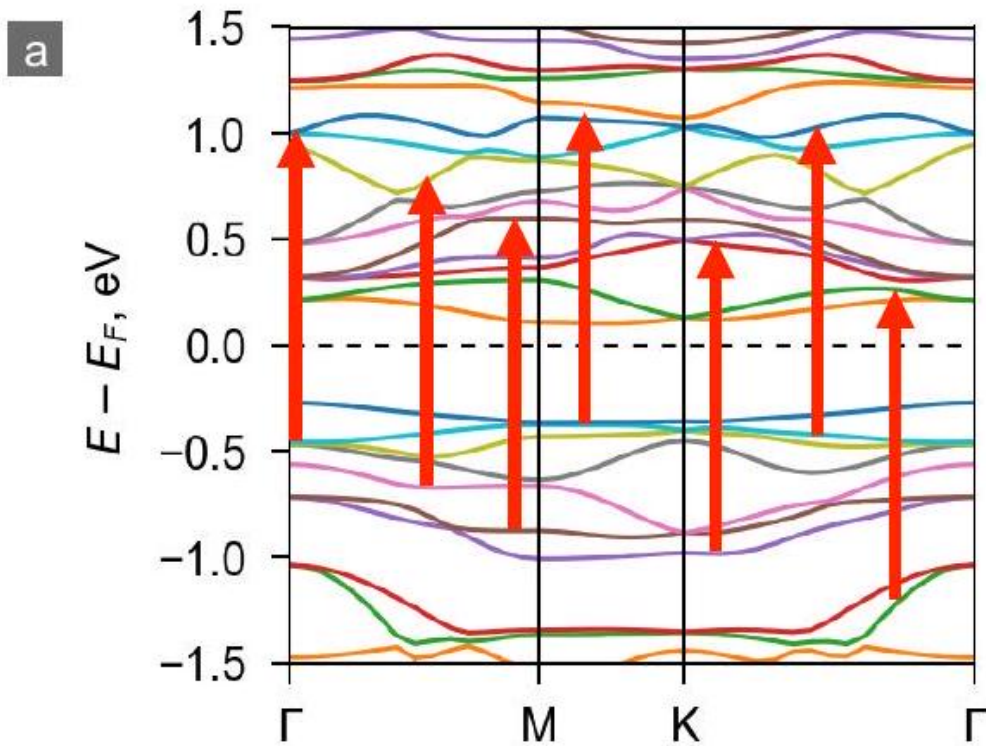
Supplementary Figure 13: The multi-tip experiment - in situ switching and characterizing the **A** state: a, schematic circuit diagram for switching and 2-probe (2W) or 4-probe (4W) resistance measurements. SEM image shows tips configuration used for switching. Plot on the left shows time trace of 2W current and voltage upon switching (thermal EMF subtracted). b, schematic view of the system: SEM - scanning electron microscope, BSD - backscattered electrons detector. c, I-V curve between two current leads before switching (C state). d, four probe I-V curve before (C state) and after switching (A state); resistance values: $R_C = 542\text{Ohm}$ and $R_A = 500\text{Ohm}$. e, scaling of the four probe resistance with tip separation in the A state is consistent with $R \propto 1/L$ (black dashed line) 3D transport. Lower bound for resistivity $\rho_A \approx 3\text{mOhm} \cdot \text{cm}$ can be extracted, if geometric factor is set $\equiv 1$.

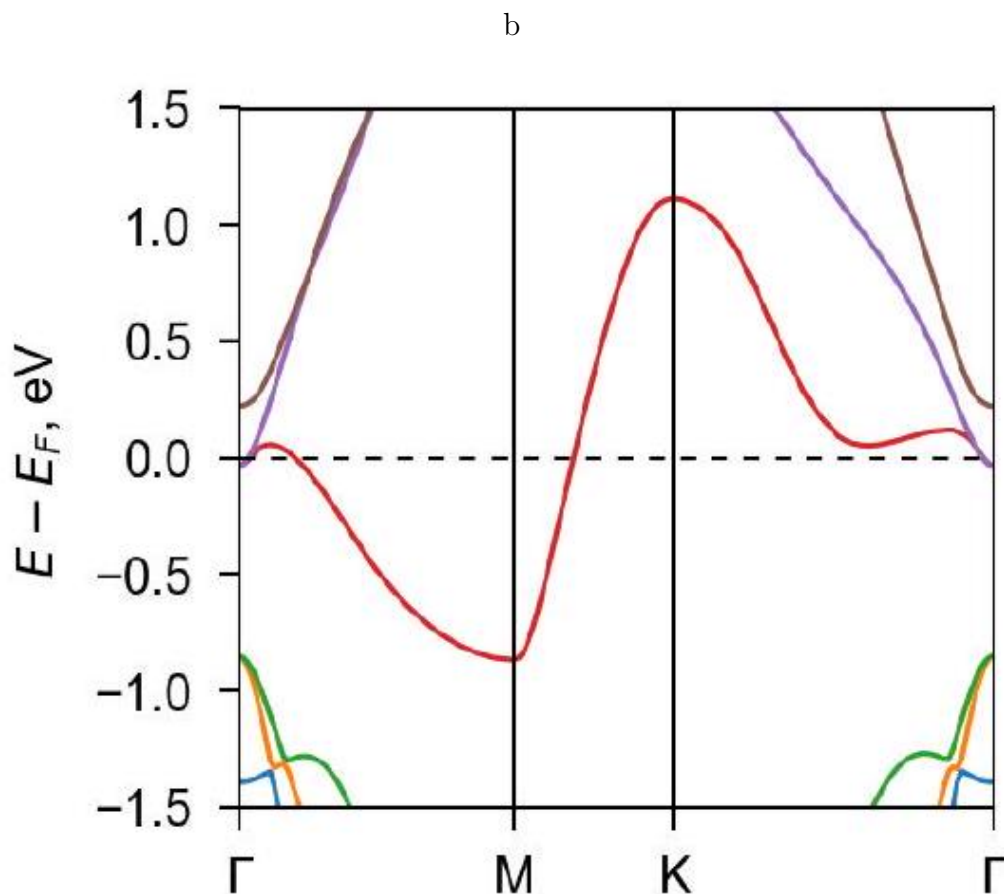


Supplementary Figure 14: $R(T)$ in the A state: a, Arrhenius plot of the temperature dependencies of resistivity in the A (blue) and C states (orange, green - different samples). High-temperature part can be fit (dashed black line) to an activation law. b, double-logarithmic plot of the logarithmic derivative of $R(T)$ used for estimating possible T -exponent in the hopping transport: pale blue dots are raw data, orange curve - smoothed data, black and green dashed lines - linear fits of the low and high-temperature parts respectively. c, double-logarithmic plot of the derivative of conductance $1/R(T)$ used for estimating possible power-law behavior: pale blue dots are raw data, orange curve - smoothed data, black dashed line - linear fit of the low-temperature part.

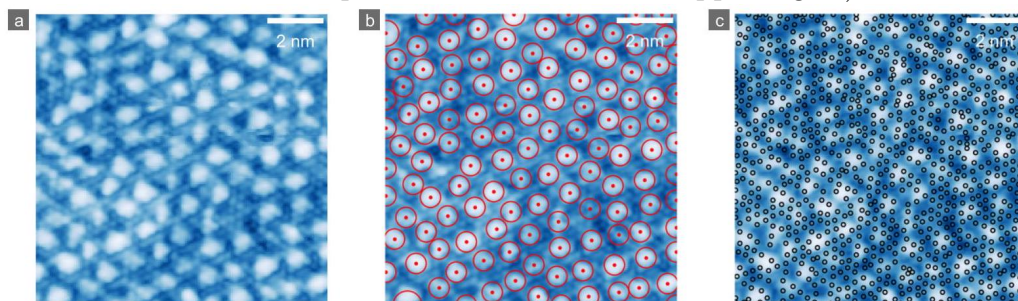


Supplementary Figure 15: Acceptance ratio $A_{i,i+1}$ dependence versus dimensionless temperature $k_B T / V_0$: The legend on the right of the image shows the corresponding filling of the system ν . In the case $1/\nu = 13$ it is clear from the pronounced suppression of $A_{i,i+1}$ at $k_B T = 0.007V_0$ that there is a first order phase transition present. The suppression of $A_{i,i+1}$ at the filling $1/\nu = 10.56$ is much less pronounced and broadened out, which is the consequence of the glass transition present in this case.



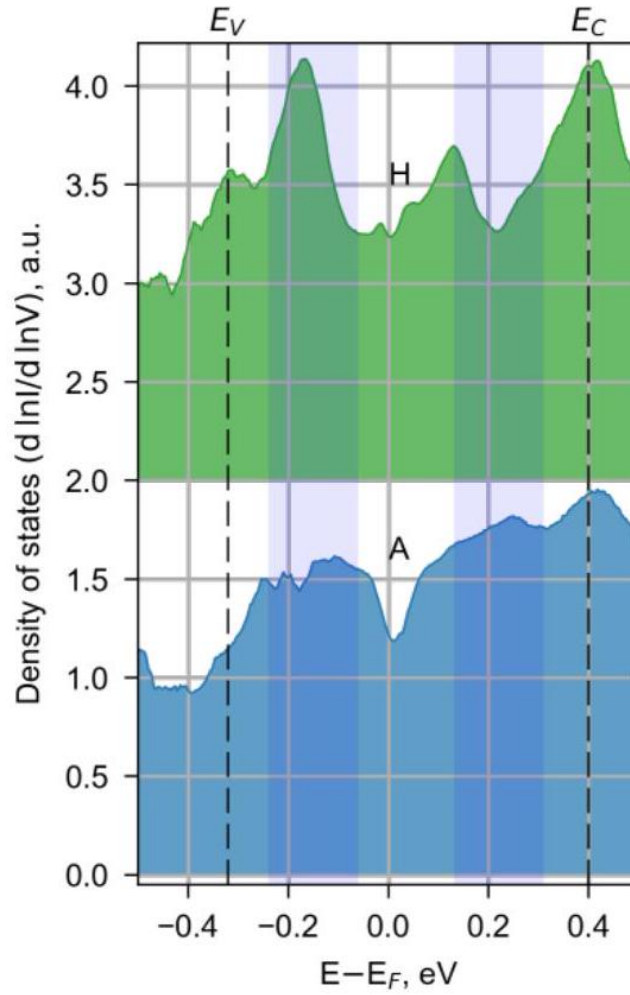


Supplementary Figure 16: Schematic of optical transitions within the initial **C** state bands and the resulting high-temperature band structure after photoexcitation: a, low-temperature **C** state below $T = 190$ K calculated by LDA for a single TaS₂ layer (Jernej Mravlje, private communication). The arrows show possible photoexcitation transitions at 1.5 eV (800 nm) photon energy. The low- T band structure has multiple bands due to Brillouin zone folding caused by the $\sqrt{13} \times \sqrt{13}$ unit cell reconstruction in the **C** state. This provides multiple excitation paths for a large set of energies, rather than a single dominant transition. b, The high-temperature metallic state band structure above $T_{IC} = 550$ K after photoexcitation with 3.5 mJ/cm² pulses. is dominated by a single band crossing Fermi level, with a 'Fermi ridge' along the $K - \Gamma$ direction. (The estimated electron temperatures are shown in Suppl. Fig. 3)



Supplementary Figure 17: Atomic and polaronic features detection in STM images: a, atomically-resolved image of the A-state; b, the same image (a) with detected polaron centers, marked with red dots, and red circles of various radii reflecting Gaussian width for each polaronic feature found by the LoG algorithm²⁹; c, the same image (a) with detected atoms black circles of almost the same radii found by the LoG algorithm. Detection fails at the centers of polarons, as the protracting orbitals smear out topographic features of the top layer S atoms. The parameters used for atomic (polaronic) detection are: maximum Gaussian width = 1 (7)

pixels, minimum Gaussian width = 0 (5) pixels; overlap threshold for neighboring Gaussians = 1%. Image size is 203 pixels.



Supplementary Figure 18: Comparison of the A state with the photoinduced "hidden" state in 1T-TaS₂: The C state can be switched with a single shot laser pulse of the fluence $\sim 0.8 - 3 \text{ mJ/cm}^2$ into a long-range ordered domain textured phase²⁵ called "hidden" state² (see also Suppl. Fig. 1). Here we compare the spatially averaged spectra in the A and hidden states taken on the same sample and with the same tip. Dashed lines and shaded lines show the position of CDW and Hubbard band in the C state respectively. Absence of the CDW peaks and explicit Hubbard bands clearly show that the A state is qualitatively different from the hidden state. This result, along with the threshold switching to the A state, allows one to dismiss the notion that one can smoothly vary the fluence to increase the domain wall density in the hidden state to obtain the A state.

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²⁹

http://scikit-image.org/docs/dev/api/skimimage.feature.html#skimimage.feature.blob_log

24 Chiral domain dynamics and transient interferences of mirrored superlattices in nonequilibrium electronic crystals by Ravnik, Vaskivskyi, Vodeb, Diego, Venturini, Gerasimenko, Kabanov, Kranjec, Mihailovic (2023)

(maybe this article is just about experiments, that yes, there are domain reconfiguration, so on? i'll read later)

Abstract

Mirror symmetry plays a major role in determining the properties of matter and is of particular interest in condensed many-body systems undergoing symmetry breaking transitions under non-equilibrium conditions. Typically, in the aftermath of such transitions, one of the two possible broken symmetry states is emergent. However, synthetic systems and those formed under non-equilibrium conditions may exhibit metastable states comprising of both left (L) and right (R) handed symmetry. Here we explore the formation of chiral charge-density wave (CDW) domains after a laser quench in 1T-TaS with scanning tunneling microscopy. Typically, we observed transient domains of both chiralities, separated spatially from each other by domain walls with different structure. In addition, we observe transient density of states modulations consistent with interference of *L* and *R*-handed charge density waves within the surface monolayer.

Theoretical modeling of the intertwined domain structures using a classical charged lattice gas model reproduces the experimental domain wall structures. The superposition (S) state cannot be understood classically within the correlated electron model but is found to be consistent with interferences of *L* and *R*-handed charge-density waves within domains, confined by surrounding domain walls, vividly revealing an interference of Fermi electrons with opposite chirality, which is not a result of inter-layer interference, but due to the interaction between electrons within a single layer, confined by domain wall boundaries.

24.1 Article

24.1.1 Introduction

The hexagonal atomic lattice, which is common in layered 2D materials, supports commensurate (C) electronic superlattice ordering with various sizes of unit cell. Experimentally, the size of the superlattice unit cell has been observed in the range between 3 to 16 lattice constants, and values in between, which are allowed by the geometrical cosine rule ¹. Some of these superlattices break crystal mirror symmetry, which occurs when the superlattice ordering vector is not aligned with a symmetry axis of the atomic lattice. Such superlattices can exist in two possible chiralities, and we can transform one into the other by a mirroring operation over a high symmetry axis of the atomic lattice. If we write the superlattice unit vector as a combination of the in-plane atomic unit cell vectors $\mathbf{a}$ and $\mathbf{b}$ as $n\mathbf{a} + m\mathbf{b}$, then this condition is satisfied when $n \neq m$ and $n, m > 0$. Examples of such superlattices are described by unit cells

such as $\sqrt{7} \times \sqrt{7}$, $\sqrt{13} \times \sqrt{13}$ and $\sqrt{21} \times \sqrt{21}$. The $\sqrt{13} \times \sqrt{13}$ superlattice is commonly found in nature¹, and appears in various materials, including 1T-TaS₂, 2Hb-TaS₂, 1T-TaSe₂ and 2Hb-TaSe₂². As a special case, also the $\sqrt{7} \times \sqrt{7}$ superstructure has been observed in doped surface layers of TaS₂³. Energetically, the L and R-handed superlattices are equivalent⁴. A mixture of the two would result in domain walls between them, which is energetically costly^{5,6} and thus coexisting mirrored domains are experimentally rarely found under equilibrium conditions. The presence of mirrored domains was nevertheless observed in the scattering experiments⁷, but it was not investigated in detail until recently^{8–10}. The scattering experiments are in this case limiting, as they simultaneously probe many layers as well as a relatively large area within each layer, and thus give little or no information on the microscopic ordering, making it unclear whether the L and R domains exist within a single layer or across many layers. Recently Ohta et al. investigated stacking of L and R domains in Nb substituted 1T-TaSe₂, reporting different electronic states due to the different stackings¹¹.

In non-equilibrium systems, however, various metastable states may be observable. It was recently shown by Zong et al. that applying an ultrafast laser pulse to a thin flake of 1T-TaS₂ leads to the appearance of the symmetrically equivalent CDW diffraction peaks which were attributed to the mirrored superlattice orientations¹², whereby the probability of switching increases with increasing the laser fluence. After the excitation, both diffracted peaks were present in regions of the size of $1.1\mu\text{m}$. Due to the experimental limitations, it was not clear whether this is an interlayer or an intralayer effect, and how the domains order and interact. In addition to mixed L and R superlattice states, an intriguing possibility exists in quantum systems. Considering that L and R configurational states are energetically degenerate, a superposition (S) of the L and R state is also possible. While CDWs are commonly described as classical objects, in which superpositions can occur, properties such as CDW tunneling reveal their quantum nature^{13–15}. In the quantum description, the CDW can be thought of in terms of a standing wave, arising from an interference of counter-propagating electrons with wavevector k_{CDW} . However, interference of CDWs with different in-plane chiralities within a single layer without proximity of adjacent layers has to our knowledge not been observed until now.

Using scanning tunneling microscopy, we investigate the microscopic structure of the mirror domains in the surface layer of 1T-TaS₂ created by laser excitation in the low-temperature C state. The STM images show the local density of states (LDOS), which in the quasiparticle approximation is given by: $\rho_{QP}(E, \mathbf{r}) \propto \sum_k |\psi_k(\mathbf{r})|^2 \delta(E - \varepsilon(\mathbf{k}))$, where $\varepsilon(\mathbf{k})$ is the energy of the electrons with different wavevector $\mathbf{k}$ that interfere locally at position $\mathbf{r}$, allowing us to measure interferences of CDWs. Such quasiparticle interferences surrounding an impurity were previously observed in cuprate superconductors¹¹, and for confined electron trajectories in transition metal dichalcogenide heterostructures¹². The observations by STM are classical, but the observed quasiparticle interference phenomenon is treated by solving the Schrödinger equation for counterpropagating quasiparticles. Since the observed order parameter does not have any out-of-plane component (STM scans are 2D and surface sensitive), we primarily consider the system as two-dimensional, where CDWs tilted L and R with respect to an in-plane crystal axis are considered two different chiralities.

1T-TaS₂ is a quasi-two-dimensional transition metal dichalcogenide, where tantalum atoms are sandwiched between two layers of Sulphur atoms (Fig. 1a). The layers are stacked together in the z -direction to form a highly anisotropic quasi-two-dimensional crystal. At temperatures above 550 K, the material is in a metallic state.

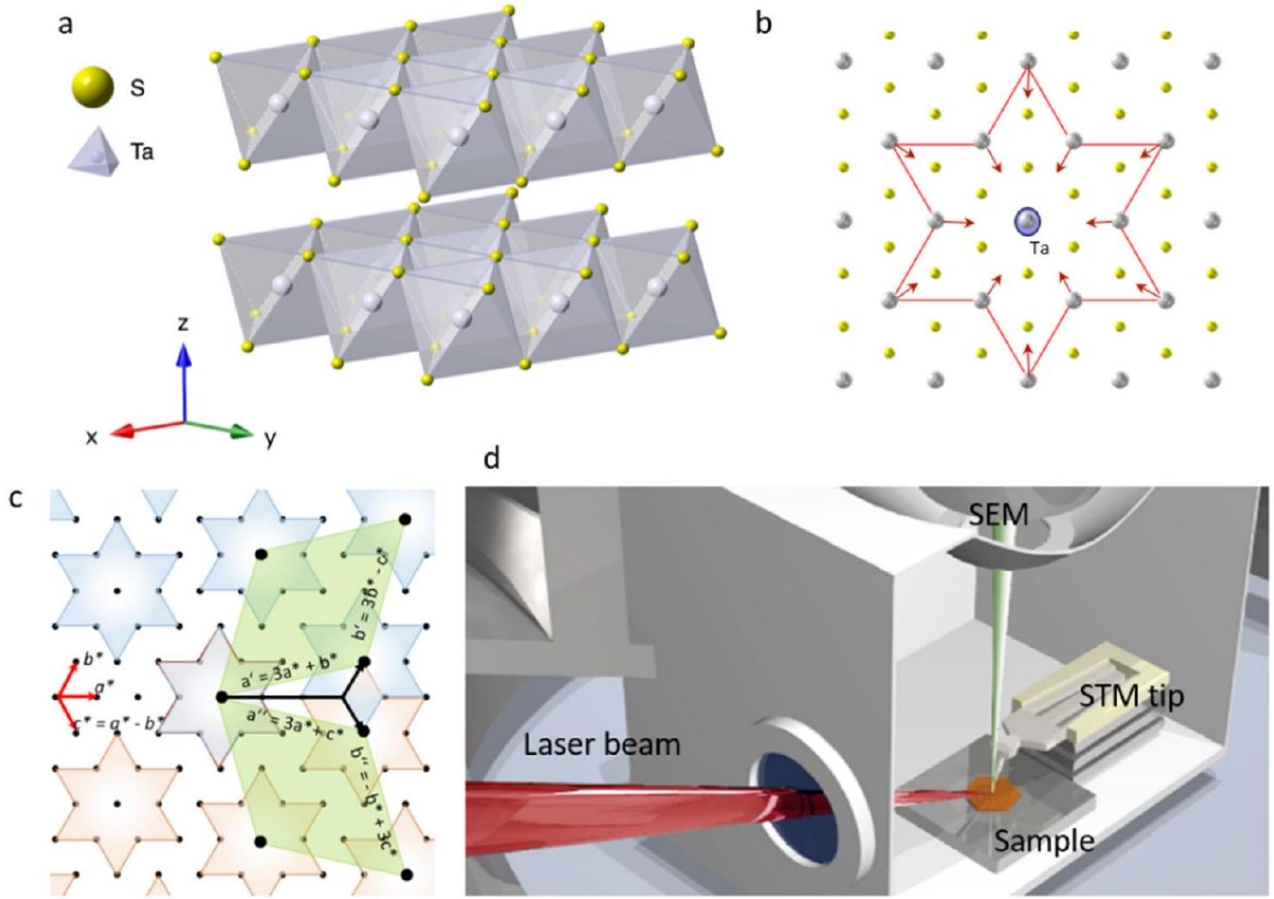


Figure 1. (a) Crystal structure of 1T-TaS₂. (b) A schematic representation of the polaron structure formed within the $\sqrt{13} \times \sqrt{13}$ superlattice. (c) The commensurate $\sqrt{13} \times \sqrt{13}$ superlattice can take two different orientations, rotated by $\pm 13.9^\circ$ with respect to the atomic lattice. (d) A schematic diagram of the experimental setup.

Below 550 K an incommensurate (IC) charge density wave appears, whose modulation vectors are aligned with the lattice direction, thus keeping the in-plane mirror symmetry intact, and breaking only translational lattice symmetry¹⁶. A mirror symmetry breaking transition to a nearly commensurate (NC) CDW state occurs at 350 K, where the direction of the charge modulation is misaligned with the lattice by $+11^\circ$ or -11° , as observed in diffraction or STM experiments^{2,17}. Below 180 K, the CDW becomes commensurate (C) and insulating¹⁸. Here, the angle between the $\sqrt{13} \times \sqrt{13}$ superlattice direction and the crystal lattice direction is about $\theta_S = 13.9$ degrees as defined by the geometry of electron ordering on a triangular lattice⁴. The superlattice unit cell is formed with 13 atoms, where twelve of the atoms move towards the thirteenth central atom to form a David-star-like cluster, as shown in Fig. 1b. In order for these clusters to cover the whole plane, two different tiling configurations are possible with angles at $\pm 13.9^\circ$ with respect to the atomic lattice (Fig. 1c). It was recently shown that we can use optical or electrical pulses to induce a metallic hidden (H) state^{19–22}. STM studies of the surface show that the uniform CDW pattern is broken into smaller domains. The domains and domain walls are metastable at low temperatures, which allows us to investigate their non-periodic microscopic order by STM^{21,22}. The H state formation is macroscopically a very reproducible phenomenon, as shown by electrical and optical experiments^{19,23,24}, but the microscopic domain distribution appears to be different after each switching attempt²⁴, which is in line with the probabilistic nature of the appearance of the mirror domains at higher temperatures¹². X-ray and electron diffraction experiments^{25,26} show that interlayer stacking

plays a role in ordering within the H state, but do not reveal any domain structure. STM observations on the other hand reveal that long-range order of the surface layers is broken in the H state. With STM we only probe the top layer and thus observe only the ordering along the h and k axis (parallel to the layers), while it is not possible to probe the out-of-plane dimension and thus hard to reach conclusions about the bulk. An important thing to note is that in three dimensions, the CDW state can have 4 possible orientations, as in addition to the symmetry within the $h - k$ plane, we must also consider the mirroring over the $h - k$ plane, thus negating the l component of the CDW. Since the observed order parameter does not have any out-of-plane component, we can distinguish only the difference within the $h - k$ plane, while the symmetric orderings with respect to the l direction appear identical. In this sense we consider the system as two-dimensional, justifying the use of the term chirality to describe L and R domains.

Apart from finding a rich variety of domain walls between L and R domains, that are not observed in equilibrium crystals, we also observe metastable domains where the local density of states shows complex flower-shaped spatial patterns, in which twofold symmetry axis is restored. We show that the symmetry and observed patterns can be understood in terms of superpositions of L and R states. We successfully model the domain walls using a charged lattice gas (CLG) model, while the complex interference patterns are modelled in terms of superpositions of L and R CDWs.

24.1.2 Experimental results

To induce the formation of mirrored domains, we perform a laser quench using a single or multiple 50 fs nearinfrared (800 nm) laser pulses to drive the sample inside the STM chamber out of equilibrium (Fig. 1d). After destroying the CDW order, the system spontaneously reverts back towards equilibrium, initially forming L and R domains in equal probability until symmetry is spontaneously broken, resulting thereafter in the prevalence of one type of domain. Here we investigate metastable states which form in this process, whose lifetime is sufficiently long to be observable by STM. (More details on the photoexcitation are given in the "Methods" section). The illuminated area ($\sim 200 \times 100 \mu\text{m}$ spot size) is large compared to the microscopic structures under investigation with the STM, so the illumination of the observed surface can be considered to be uniform. The sample is mounted on a cold finger in contact with either the liquid helium ($\sim 4\text{ K}$) or liquid nitrogen ($\sim 77\text{ K}$) bath. In both cases, the photoinduced domain states are stable on a timescale of minutes, but at 77 K significantly more relaxation is observed ²⁴. The switching laser fluence of about $3 - 5\text{ mJ/cm}^2$ is sufficient to form a number of such domains, which are sometimes intermixed with regions of an amorphous electronic phase ^{24,27}. The mirrored domains appear either alone, or in groups. Unfortunately, it is hard to estimate their density from present STM experiments, because relatively small areas are probed. A typical boundary between two different domains is shown in a large area image in Fig. 2a, while an atomically resolved image of a similar domain wall is shown in Fig. 2b. While the domain walls between domains of the same in-plane chirality usually tend to be straight with occasional kinks, as seen with STM ^{20-22,28} in large area scans, and-as we shall see later-also in model simulations ^{1,29}, the domain walls between L and R domains tend to be ragged, and their width is not easily defined. We have found that similar, mirrored domains can also be induced by a current pulse from the STM tip, but this method of excitation is not very uniform, and the result is local and not very reproducible.

Apart from neighboring L and R-handed domains, we also observe domains containing characteristic 'flowershaped' interference patterns (Fig. 2d, e), which appear both at 4 K as well as 77 K . Compared with single-chirality domains, such interference patterns are quite

rarely observed. The observed regions were typically $\sim 10 \times 10$ nm in lateral size and may be bounded by domain walls. Remarkably, the modulation amplitude of the LDOS (i.e., image contrast) in such patterns is approximately the same as for single L -or R -oriented domains. A fast Fourier transform (FFT) analysis of the interference region (of Fig. 2d) is shown in Fig. 2f. After eliminating scanning artefacts, an analysis of the intensities shows that the total intensity of the *L* and *R* components shown in Fig. 2f have intensities with ratio $\sim 2/3$. (The detailed analysis is given in the Supplementary Information). Distortions of shape may arise at the edges of such domains, due to the presence of DWs, and defects or imperfections. The interfering domains can also appear in the process of relaxation (see example in Fig. 2c, d). The interference patterns are observed to form spontaneously, and/or decay into L or R order on a timescale of minutes or less, which prevents more detailed investigations of electronic structure by scanning tunnelling spectroscopy.

Given that the observed LDOS pattern is an interference of L and R CDWs, an interesting question is how the S state modulation arises: is the LDOS modulation predominantly within the first layer, whereby the second

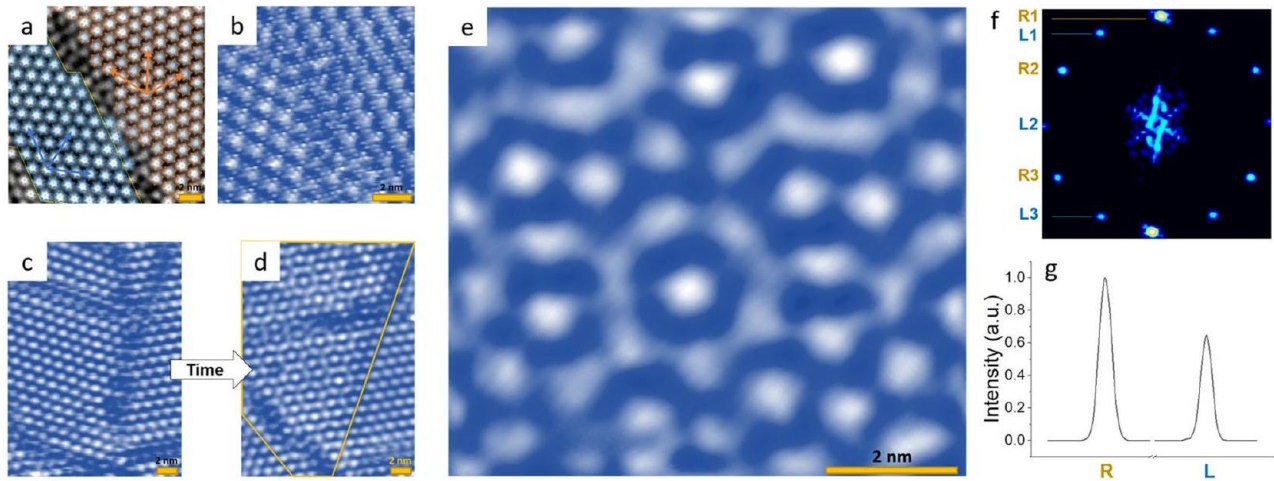


Figure 2. STM images of mirrored and interfering domains. (a) The photoinduced state with domains of L and R chirality ($V = -0.8$ V, $I = 1$ nA). An atomic lattice fit was used to accurately locate the domains and the David stars of different colors were drawn to mark the L and R superlattices. (b) An atomically resolved domain wall between domains with different chiralities. (c,d) The transformation of the CDW multiple-chirality domain structure to domains of interfering CDWs. The images are taken at 10 – min intervals. (e) an enlarged image of the CDW interference patterns ($V = -0.8$ V, $I = 0.4$ nA). The scale bar is 2 nm in each case. (f) A FFT of the section bounded by the yellow line shown in (d). (g) The total intensities in the L and R FFT peaks after correction of scanning artefacts.

layer possibly plays a subtle role, or are we observing a new state with two coupled fully hybridized layers? The role of the second layer is clarified by two additional steady-state experiments: (i) In equilibrium samples without domains (or domain walls) the S pattern is conspicuously absent when the first and second layers have opposite chirality. (The chirality of the second layer is observed by direct STM imaging through small purpose-made holes in the top layer-see Supplementary Information for details). (ii) An S state is observed after excitation of the selenide compound, 4Hb – TaSe₂. Here the top layer has the same 1T- TaS₂, but the second layer has a 1 H polytype structure, so its S pattern cannot be the result of interference between the first two layers. (see Supplementary Information for details). Altogether, the evidence clearly implies that the S pattern is primarily the result of CDW

interference within the top layer.

A number of factors can influence the ratio of amplitudes of the L and R components in the S pattern within the top layer. In particular, the in-plane boundary conditions surrounding a domain are likely to play an important role in determining the phase and amplitude of each of the two CDW components within the domain. The stability of the domain structure itself is topologically protected²², so the domain walls appear as an externally defined texture which imposes lateral boundary conditions for the CDW formation within the domain. We note that the domain structure itself is not independent of interlayer CDW stacking^{25,30}, so the S pattern is indirectly linked with the inter-layer stacking. Indeed, recent calculations show that an underlying periodic potential from the layer below plays a very important role in determining the orientation of quasiparticle interference patterns in confined 1T- TaS₂ nanostructures³¹. On the other hand, the absence of an S pattern in a sample without domains confirms that in-plane domain walls are essential for the S state to be observed.

In metastable states which contain domains (irrespective of how they are created), the domain walls of the second layer are faintly discernible, yet the CDW pattern within the top layer domains does not show any significant change of the LDOS modulation due to the phase-shifted layer underneath²⁰. In case of the mosaic or hidden state, the domain walls in different layers are never reported to be in register directly above each other, which is consistent with the fact that DWs repel each other^{1,29}. Finally, if the observed interference was a purely interlayer effect, it would very likely be seen every time we see a domain that is surrounded by domains of different chirality. An exception would occur if the domain in the top layer was in perfect register with a domain of the same size and orientation in the layer below, which is highly unlikely because of Coulomb repulsion. We will discuss the significance of this further in the Discussion.

24.1.3 Emergent domain structures within a correlated electron model

In order to obtain insight into ordering of the mirrored domains, we first compare the measurements to the results of Monte-Carlo calculations of sparsely filled, screened, correlated electrons within a charge lattice gas (CLG) model on a hexagonal lattice¹ in the Wigner crystal limit. The use of this model is justified by its success in describing the phase diagram of the material, particularly the commensurate phases at different fillings, the domain structure, and particularly, the presence of an amorphous phase^{1,21,22,24}. The filling $f = 1/13$ for the $\sqrt{13} \times \sqrt{13}$ superlattice in the C state. We start the simulation with polarons at random positions and perform Monte Carlo simulations of their discrete movements while lowering the temperature, eventually locking them in the lowest energy configuration at zero temperature. During cooling, ordered domains start appearing on the underlying atomic lattice. For a filling of exactly $1/13$ they eventually merge to a single domain, while for fillings that slightly deviate from this value, we obtain multiple domain states¹. Figure 3a shows an example of

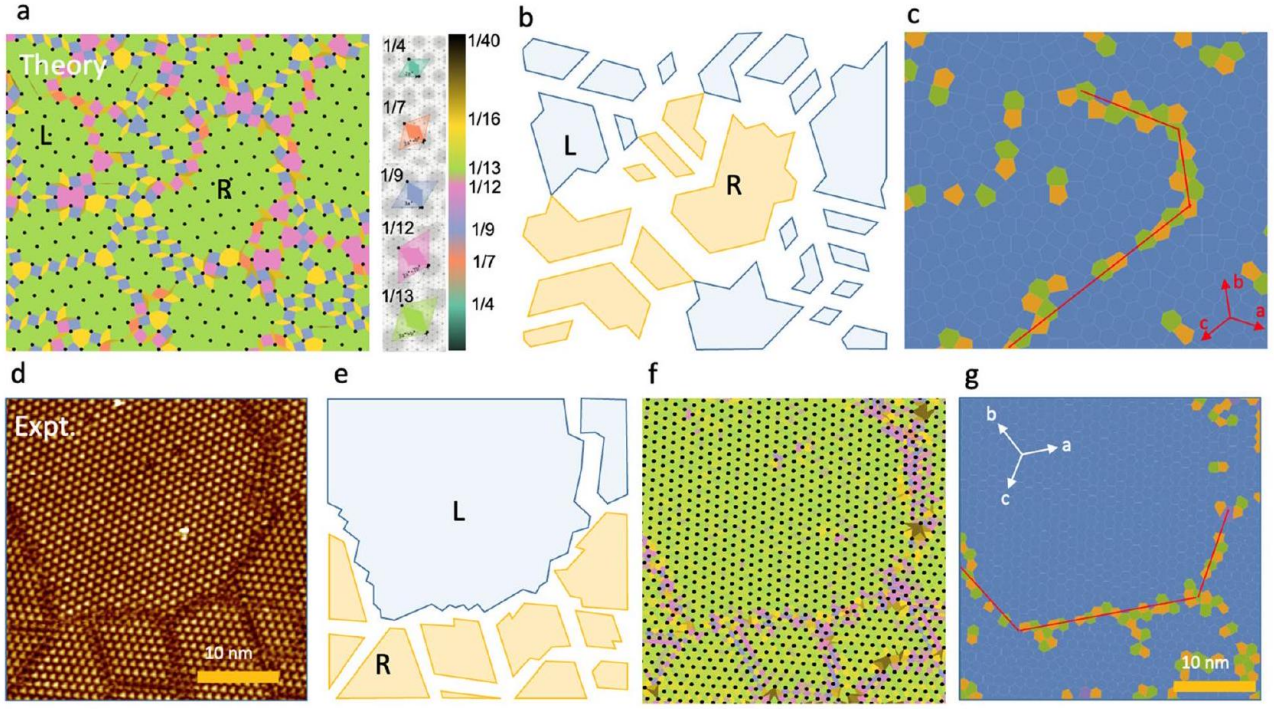


Figure 3. Comparison of the Monte Carlo model of the photoinduced state (**a – c**) with the STM measurements ($V_{\text{tip}} = -0.8$ V, $I = 1$ nA) (**d – g**). (a) Monte Carlo model calculation result, where the distances between neighboring polarons are shown with different colors. (b) A schematic showing the L and R domains. (c) The same data represented in the form of a Voronoi lattice, where yellow, blue and green represent $n = 5, 6$, and 7 -sided n -gons respectively where n is the number of sides of an n -gon. (d-g) Experimental images: (d) shows an original STM image, while (e-g) show the experimental data using the same representation as for the MC calculation in the first row. The red lines in (**c, g**) indicate the atomic lattice vector directions.

the simulated end-state with both domain orientations present. The black dots in Fig. 3a represent the polaron positions. Initially (at short times in the MC simulation), L and R domains appear in equal proportion, as there is no external symmetry breaking in the model (Fig. 3b). For very short annealing times, the crystal is frozen in the multi-chirality configuration. With increasing MC annealing time, the probability of finding mirrored domains in the simulation drops, showing that the presence of the mirrored domains is energetically more costly due to the relatively thick and ragged domain walls (see the Supplementary Information). The model calculation results can be directly compared to the experimental image shown in Fig. 3d-f.

Our experiments show that domains with different chiralities can be reached through processes in which the relaxation path goes through an intermediate state with restored mirror symmetry (Fig. 2c, d). When relaxing back to the $\sqrt{13} \times \sqrt{13}$ commensurate CDW state, the charge density wave may choose to form a domain with a chirality, that is not necessarily the same as the chirality of the surrounding CDW. This relaxation path may be aided by the high energy cost of L/R domain walls in the mixed state, as suggested by the MC calculations.

Colored tiling performed with diamond shapes (see legend in Fig. 3a), connecting neighboring polarons highlights the deviations from the $\sqrt{13} \times \sqrt{13}$ structure (Fig. 3c) ^{1,27}. The most commonly observed color (light green) corresponds to the superlattice unit cell of the commensurate CDW. In the model, the domains are homogeneously green, while in the experimental image occasional deviations are seen due to measurement errors. In the domain walls

the polarons can be either more closely or more sparsely packed, which is evident from the coloring.

To examine more closely the ordering within the domain walls we determine the number of nearest neighbors of each polaron by constructing a Voronoi diagram (Fig. 3c, g). Within domains, the polarons form a hexagonal superlattice, where each polaron has six nearest neighbors and its Voronoi cell is a hexagon. Adding straight domain walls between domains with the same chirality is effectively the same as stretching the lattice in one direction, which linearly deforms the hexagonal Voronoi cells. In this case, the number of nearest neighbors for each particle is conserved. On the other hand, when we look at the domain wall between two domains with different superlattice directions, we cannot simply represent it as a linear deformation of the lattice. Between L and R domains, additional particles are needed between domains, which manifests itself as a combination of pentagons and heptagons in the Voronoi diagram. In Fig. 3c, g, we show the Voronoi diagram of the model and a similar experimental image respectively. We color the n -gons yellow, blue and green for $n = 5, 6$ and 7 respectively. Both of the images are predominantly blue (covered by hexagons), with the large majority of the hexagons coming from within domains. Domain walls between domains of the same type are also predominantly formed of hexagons, where pentagons and heptagons still appear at the domain wall crossings (which cannot be represented simply as a linear deformation of the lattice). In domains with different superlattice directions,

the domain walls are predominantly formed of non-hexagons. For clarity, the chirality of the domains is highlighted in Fig. 3b, e with semi-transparent blue and orange shapes, where we can clearly see that pentagons and heptagons clearly highlight the boundaries between the mirroring domains. We note that this is somewhat less clear in the experimental image, due to the errors in fitting the polaron positions. The heptagon can be explained as a consequence of an additional infinite 60° wedge of material squeezed into the lattice and the pentagon as a removal of a 60° wedge³², both of which thus deform the lattice. A pentagon-heptagon (H-P) pair therefore adds a wedge and removes another wedge, leaving the material with an additional semi-infinite stripe of unit cells³². H – P pairs in the domain wall crossings between domains of the same type thus add a nonzero-thickness stripe of material, which is the domain wall itself. A H-P pair is topologically equivalent to a crystal dislocation on a hexagonal lattice. In this sense, both free standing pentagons and heptagons, as well as their pairs are topologically protected. On the other hand, the domain walls between domains of different directions are composed of a series of such H-P pairs. In analogy to graphene, a series of such pairs leads to a nonzero angle between the neighboring lattices³², which is equivalent to the case that we discuss here. Additionally, since the H – P pairs highlight the domain walls very well, we can use them as a guide to determine the domain wall directions. In Fig. 3c, g, we draw additional red lines that are aligned with the lattice direction as a guide to the eye. We can see that the mirror domain walls roughly align with the lattice direction. A further detailed discussion about domain wall directions can be found in the Supplementary Information.

24.1.4 Discussion

While the mixed L/R domain state can be described by the CLG model quite well, to describe the observed interference, we need to go beyond the strongly correlated classical polaron model. While Fermi surface (FS) nesting is considered to be rarely responsible for CDW formation in 2-dimensional materials, 1T-TaS₂ FS nesting was suggested to contribute to the CDW instability¹⁶. Irrespective of the extent of such nesting, we may consider a picture of the CDW, in which FS electrons form interference patterns of L and R-handed superstructures. The H state is metallic, and the system has a Fermi surface, so we may discuss the system behavior in terms of the quasiparticle picture. Starting from a Schrödinger equation description

of the CDW¹⁴, with degenerate L and R solutions for the broken symmetry ground state, a linear combination of states describes the superposition. This is true irrespective of the detailed interaction Hamiltonian, but requires the assumption that the state can be described by a Schrödinger Hamiltonian¹⁴. The L and R CDWs can thus be described in terms of the sum of one-directional CDWs: $A^m(\vec{r}) = \text{Re} \left(\sum_d e^{ik_d^m \vec{r}} \right)$, where the sum over $d \in \{1, 2, 3\}$ represents the three symmetry directions of the L and RCDW. $m \in \{L, R, 0\}$ is the wavevector index, representing the R and L superlattices, and the atomic lattice respectively. k_d^m are the three reciprocal in-plane wavevectors for the two possible chiralities of the superlattice, k_d^L and k_d^R are the wavevectors for the positive and negative rotation angle of the superlattice with respect to the atomic lattice, and k_d^0 is the atomic lattice wavevector.

The observed interference of the L and R CDWs (Fig. 4a) is described by $A^{\text{int}}(\vec{r}) = aA^L(\vec{r}) + bA^R(\vec{r})$, with L and R amplitudes $a = b$ is shown in Fig. 4b. We show the single chirality and double superlattices superimposed on the atomic lattice in Fig. 4c, d respectively. The calculated $A^{\text{int}}(\vec{r})$ matches very well to the STM measurements for $\theta_{L,R} \pm 13^\circ$. Note that this angle is not equal to the geometric $\sqrt{13} \times \sqrt{13}$ superlattice angle $\theta_S = 13.9^\circ$, where the pattern is different (see Fig. 4d) (interference plots for different $\theta_{L,R}$ are shown in the Supplementary Information). This discrepancy of $\sim 0.9^\circ$ between θ_S and $\theta_{L,R}$ is quite significant, and implies that the system is frustrated with respect to the ideal superlattice structure. We may attribute this frustration to the fact that the FS nesting wavevectors θ_N are not aligned with $\theta_{L,R}$ ¹⁶: In the high-temperature IC state, the CDW is aligned with the lattice ($\theta_{IC} = 0$), which is approximately aligned with the FS nesting wavevectors. In the NC phase, the CDW rotates to $\theta_{NC} \simeq 12 \pm 1^\circ$, and eventually to 13.9° in the C phase. In the superposition (S) phase, the CDW angles $\theta_{L,R}$ are thus in between the C phase and the NC phase.

It is interesting to consider the role of the atomic displacements in the superposition state. In this material, a Kohn anomaly is observed, associated with the IC transition, indicating that $e-p$ coupling is strong near the IC wavevector $0.284\mathbf{q}_a$, where $\mathbf{q}_a = 2\pi/\mathbf{a}$ is the reciprocal lattice vector along the $\mathbf{a}$ crystal lattice direction^{33,34}, implying that the periodic lattice displacements are closely following the electronic order. We can apply a simple tight binding model in order to consider the atomic displacements in response to the charge density in the superposition state (see Supplementary Information for details of the calculation). The predicted single chirality displacements are shown in Fig. 4c. Note that the displacements of the outer 6 atoms are in neutral positions, and are not displaced, which is not the commonly presented description of the polaronic lattice deformations (Fig. 1b). For the interference of L and R CDWs, the resulting atomic displacements correspond to the vector sum of the displacements arising from the L and R CDWs, as shown in Fig. 4d. Unfortunately, considering the state is metastable, and is mesoscopically embedded within the mixed chirality domains, the atomic displacements may be difficult to measure experimentally.

A conceptual free energy diagram is shown in Fig. 4e, indicating the cascade of transitions from the mixed state (M), with L and R domains spatially separated by domain walls, to the $L+R$ superposition state (S) which decays to the H state (either L or R), and eventually to a L or R commensurate ground state (C). The barrier energy separating these states is primarily determined by the non-equilibrium local boundary conditions, imposed by the domain walls. The periodic potential of both the lattice, and CDW ordering in the layer below is also likely to influence the stacking energy. It is difficult to define a single order parameter for the overall free energy diagram, and the free energy should be understood to be a multidimensional, time-varying orderparameter landscape, which depends on the instantaneous domain configuration. Unfortunately, this cannot be easily represented by a single- or two-dimensional dimensional plot, but one may simply imagine that a different

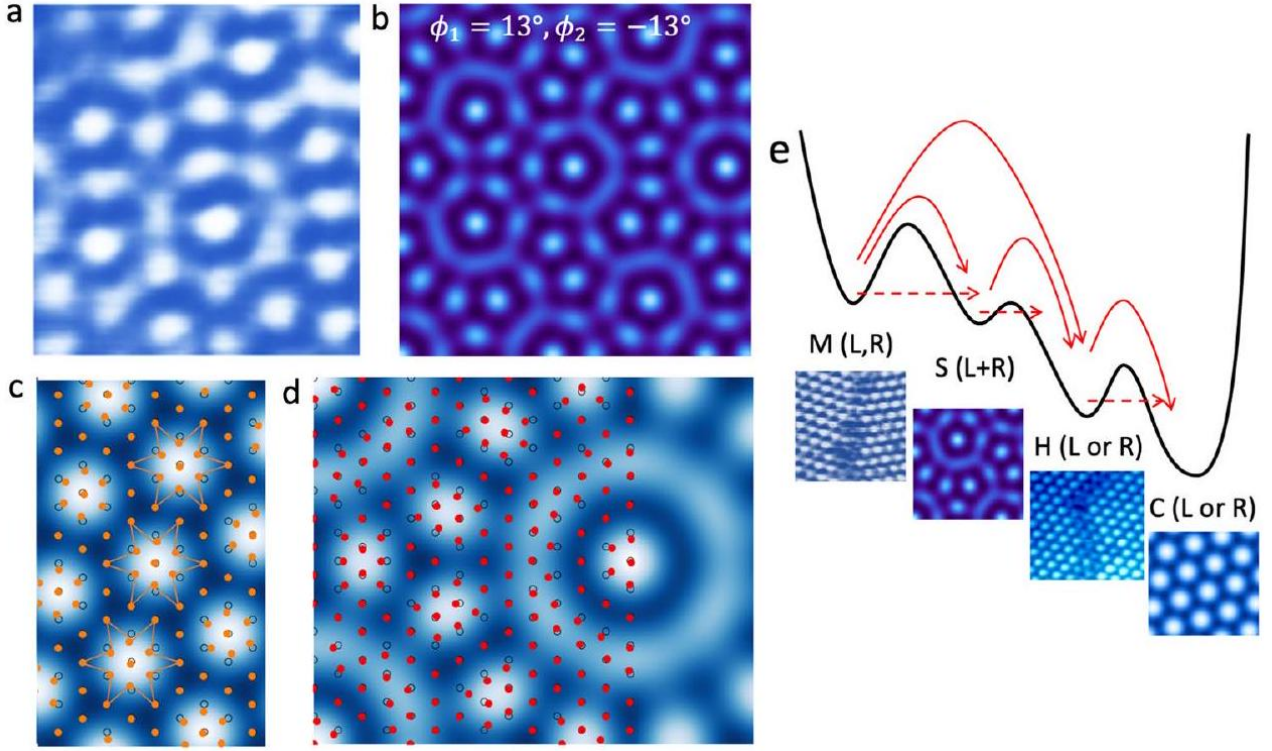


Figure 4. Modelling of the CDW interferences and lattice displacements. (a) An experimental STM interference pattern ($V_{\text{tip}} = -0.8 \text{ V}$, 0.4 nA). (b) The patterns obtained as the superposition of L and R -handed CDWs with $\pm 13^\circ$ L and R CDWs. (c) The atomic displacements for one chirality within the simple tight-binding model. (d) Monte Carlo simulations of the movement of atoms (colored dots) from their initial positions (black circles) with a double CDW potential with $\pm 13.9^\circ$, corresponding to ideal L and R commensurate structures of the $\sqrt{13} \times \sqrt{13}$ superlattice. (e) A free energy diagram showing the relaxation of the mixed state (M) via the superposition state (S) to the hidden (H) state and eventually to the single-domain C state. Relaxation can proceed by various thermally activated processes (solid arrows) or tunneling (dashed arrows).

order parameter is relevant for each of the transitions represented in the single-dimensional free energy diagram shown in Fig. 4e, and the free energy curve changes as the domain structure evolves with time. A more elaborate band structure calculation of the interfering CDW phase may help in revealing the origin of its metastability for particular cases, particularly when the interactions between TaS_2 layers are considered.

It is worth discussing the significance of the presently reported intra-layer interference in the context of commonly observed multi-layer interferences (Moiré patterns), such as previously observed on the surface layer of Nb -substituted 1T-TaSe₂ by Ohta et al.⁸. In the latter case the observed modulation arises from the interaction of the two topmost layers with different 2D chiralities. In the present case, we have argued in the results section that the layer below is not directly responsible for the L + R interference, and is fundamentally different from such inter-layer Moiré patterns. The observation of an intra-layer interference appears as a manifestation of the quantum behavior of the CDW for electrons confined within a domain created during the quench process. We note that a related effect of intra-layer quantum interference arising from in-plane electron confinement within triangular heterostructures was recently reported, although only irregular interference patterns were observed²⁸. In principle, the L + R interference effect within domains is possible for all CDW superlattices that have broken in-plane mirror symmetry with respect to the crystal lattice (e.g. $\sqrt{7} \times \sqrt{7}$ or $\sqrt{21} \times \sqrt{21}$)¹, but to our knowledge, this

is the first time it has been observed experimentally.

24.1.5 Conclusions

We conclude that transient non-trivial metastable CDW interferences and novel orders that are not known under equilibrium conditions can be observed under non-equilibrium conditions. The new metastable interference state-irrespective of whether it is described in terms of a correlated electron model, a periodic lattice distortion arising from electron-phonon coupling, or a superposition of Fermi electrons with wavevectors of opposite chirality-highlights the wave/particle duality of metastable systems close to localization. Within the correlated electron model, the mixed L/R phase is clearly seen as a natural consequence of the non-equilibrium nature of the system. A density functional theory calculation might further reveal the origin of the metastability of the observed states on the microscopic level²⁸, but the boundary conditions imposed by domain walls that are deemed essential for an accurate representation of the observed superstructures, impose unrealistic demands on such calculations at present. While full inter-layer hybridization is apparently ruled out on experimental grounds, inter-layer interactions might aid in stabilizing the superposition state, here observed experimentally as a transient state for the first time. Finally, we note that boundary conditions are clearly an important factor that can be manipulated in order to create new states of matter on the mesoscopic scale under non-equilibrium conditions.

24.1.6 Methods

Sample preparation

We grow the 1 T – TaS₂ crystals by chemical transport method using iodine as a transport agent. The average dimensions of the samples are $2 \times 2 \times 0.1$ mm. The samples are glued to the STM sample holder with UHVcompatible silver paste and cleaved under UHV.

STM measurements and optical switching

For the STM measurements we use a UHV LT Nanoprobe (Scienta Omicron) with optical access through obliquely angled side windows. For the photoexcitation, we use a 100kHz, 800 nm laser system, with 50 fs pulses. The number of pulses was selected using an acousto-optic modulator. The laser beam is guided into the STM chamber using an automatic stabilizing system with a positioning precision of $< 5 \mu\text{m}$. The laser beam profile was carefully determined externally with a CCD camera. A scanning electron microscope mounted above the STM allowed for precise tip positioning. The center position of the laser beam was determined from the perimeter defined by the border between the equilibrium and switched states. The peak fluence on the sample is kept between 3 and 5 mJ/cm². The tip voltage was adjusted for maximum spatial modulation of the LDOS (typically -0.8 V w.r.t. the sample) enabling fast scanning of metastable domains. The tip currents were kept below 1 nA to avoid influencing the dynamics as much as possible. The usual time between the optical excitation and the STM scanning varies between minutes to hours, mainly depending on the time needed to find a suitable area that exhibits interferences.

Charge lattice gas model

The model of classical chiral domains is based on the charged lattice gas (CLG) Hamiltonian $H = \sum_{i,j} V(i,j)n_i n_j$ where n_i is the occupational number of a polaron at site i with values either 0 or 1 and $V(i,j) = V_0 \exp(-r_{ij}/r_s)/r_{ij}$ is the Yukawa potential that describes the screening. $V_0 = e^2/\epsilon_0 a$ in CGS units and $r_{ij} = |r_i - r_j|$, where r_i is the dimensionless position of the i -th

polaron and r_s is the dimensionless screening radius. The dimensions are normalized, so that the value 1 for both $|r_i|$ and r_s corresponds to one lattice constant a . The value of $r_s \rightarrow \infty$ (see Ref. ²⁷ for details) in the Wigner crystal limit. e and ϵ_0 are the electron charge and static dielectric constant of the material respectively. Polarons can only occupy the sites of the underlying triangular lattice. The ratio of polarons in the system divided by the total number of lattice sites is expressed as the filling f . The Monte-Carlo method used to simulate the model was described previously ¹, where we studied the phase diagram of such a system at fixed values of f and optimized r_s . The CLG interpretation of polarons assumes a system of interacting phonons and repulsive electrons that is canonically transformed into a system of interacting small polarons in the strong electron-phonon coupling limit. We neglect spin effects, assume a screened Coulomb interaction, and assume that the hopping of polarons $\tilde{t} \ll V_0$, which is justified by the static nature of observed charges and set to zero in this model.

Periodic lattice distortion model

We use the Lennard-Jones equation $V(r) = 4\epsilon \left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6 \right]$ to model the potential energy between the atoms. To normalize the model, we set $\sigma = 2^{-\frac{1}{6}}$ so that the neighboring two particles are in equilibrium, when they are at the distance of $r = 1$ and $\epsilon = 1$ so the depth of the potential is $V_{\min} = -1$. We introduce the CDW as an outside potential energy in form of the cosine wave with the depth of U . The particles are positioned on a perfect hexagonal lattice and their movement is simulated using a Monte-Carlo simulation. The calculations give qualitatively the same result for U ranging from 0.1 to > 100 .

24.1.7 Supporting information

We glue a bulk 1T-TaS₂ sample to the STM holder and insert it into the STM. We cleave the sample in an ultrahigh vacuum to ensure a clean, non-contaminated surface. We use a UHV LT Nanoprobe (Scienta Omicron) device with optical windows, through which we introduce laser pulses for photoexcitation. We use a 100kHz, 800 nm laser system, which produces 50 fs pulses. We use a single pulse or multiple pulses to photoexcite the sample, where the number of pulses ranges to as much as 10^6 pulses (corresponding to a 10 -second exposure of the sample to the 10 kHz pulse train). The exposure time is controlled with an acousto-optic modulator. The effects of using a large number of pulses and higher fluences lead to many more interesting phenomena, which are out of the scope of this paper and are already well described in [1]. The laser spot size is very large ($\sim 200 \times 100 \mu\text{m}$) compared to the typical STM scan size (up to and rarely above $\sim 50 \times 50 \text{ nm}$) and the microscopic structures under investigation. Due to the large difference in sizes (an STM scan is about 3 orders of magnitude smaller than the size of the beam), we can consider the observed surface to be uniformly excited, even though the beam has a Gaussian profile. The center position of the laser beam was determined from the perimeter defined by the border between the equilibrium and switched states and the local laser fluence at the point of measurement was recalculated given the distance from the center of the beam (for more details see reference [1]). We mostly see the mirrored domains at fluences of $3 - 5 \text{ mJ/cm}^2$, sometimes intermixed with regions of an amorphous electronic phase [1,2], but they do appear also at lower and higher fluences. The fluences between $3 - 5 \text{ mJ/cm}^2$ are a good choice, as they are high enough to create domain states, with a high possibility to observe domains of different chiralities, but not high enough to damage the sample.

The measurements were performed at either $\sim 4 \text{ K}$ or $\sim 77 \text{ K}$ (cooled by liquid helium or liquid nitrogen respectively). The lifetime of the photoinduced domain states at such temperatures is long enough to assume that the states are static and perform reliable measurements, regardless of whether we have only one orientation of domains or mirrored domains. In some

cases, occasional changes in the domain structures are seen, which do not affect the measurement performance. Measuring a typical image takes between one minute and 10 minutes, while the domain structure usually stays largely unchanged on the timescale of hours or even days, thus changes in the domain structure are very rarely seen between two consecutive scans. At 77 K the domain relaxation is a bit more pronounced than at 4 K and it mostly happens at the outskirts of the beam [1]. Conversely, we cannot claim this for the interfering domains. We have in most cases seen the interference pattern change (appear or disappear) between two consecutive scans (a few minutes) or even as an abrupt change during a scan, both at 77 K as well as at 4 K. The examples are described in detail in the following sections.

The tip voltage was adjusted for maximum spatial modulation of the LDOS (typically -0.8 V w.r.t. the sample) enabling fast scanning of metastable domains. The tip currents were kept below 1 nA to avoid influencing the dynamics as much as possible.

Scan of a large area, where domains of different chiralities are observed

Here we present a scan of a larger area with domains of different chiralities. Note that most of the domains are of one chirality, while there are three very large and a few smaller domains of the opposite chirality.

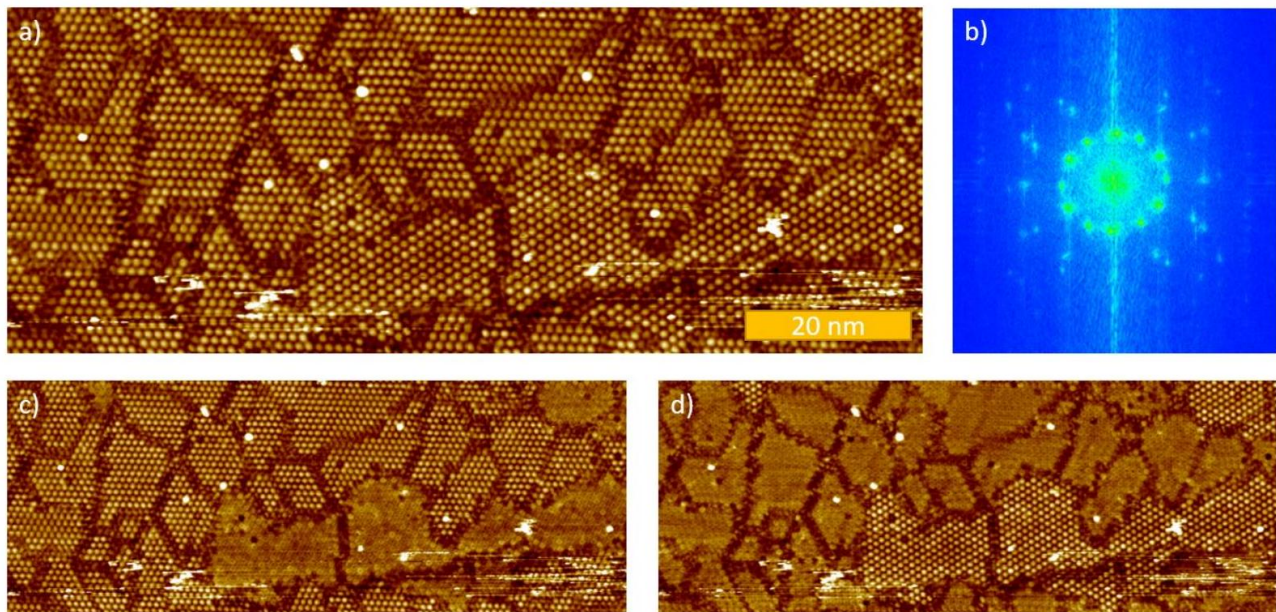


Figure S1. a) A larger area ($110 \times 40 \text{ nm}$), where domains of both chiralities were observed. b) Fourier transform of a). We can clearly see the 12 large main (inner) peaks (6 of them belong to each chirality). The outer, weaker peaks are higherorder peaks. c) and d) show the same as a), but with one chirality of the domains masked out, for easier interpretation of a).

Relaxation of domains

Both at 4 K and at 77 K we observe very little spontaneous relaxation of the photoinduced states on the timescale of STM measurements. In most cases, we see movements of individual atoms, but very rarely we see full domains collapse. Since the measurement itself perturbs the sample, a detailed analysis would be needed to estimate what portion of relaxation is caused by the STM tip and what portion of the relaxation happens spontaneously. We have left the STM device scanning the same area for over six hours. We show the changes in Fig. S2.

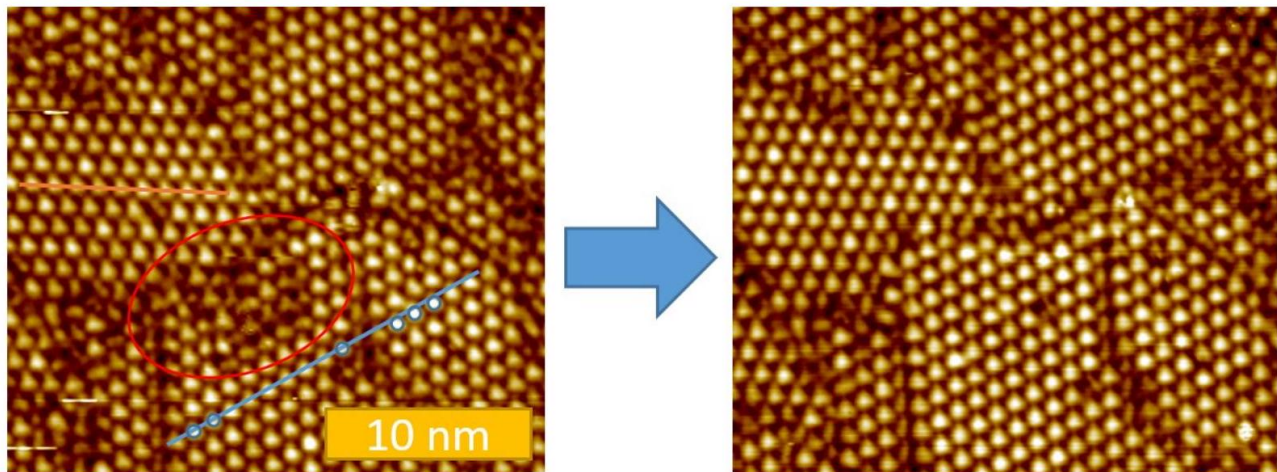


Figure S2. Relaxation of the domain over a period of six hours. We can see some rearrangement of the domains, but on a larger scale not much is changed. The red ellipse highlights the region with the most prominent changes. Blue and orange lines are guides to the eye for the orientation of the domains. Blue circles show the approximate positions of the peaks of CDW within the domains and aligning them to the blue line highlights the change of the CDW phase between the two domains of the same chirality.

Additionally, we have tried to induce relaxation by applying voltage pulses at the borders between the domains of different chiralities. The process strongly depends on the quality of the tip and is in cases of bad tip quality not very reproducible. The threshold voltages for inducing electronic changes in the sample and damaging the sample are sometimes very close and thus extreme caution is needed. Typically, we find that voltage pulses of about 1 V are enough to induce some changes to the electronic states. In Fig. S3 we show the process of relaxation of a chiral domain, using a series of 1 V pulses triggered at the approximately same position on the sample every time. In total, we have applied around ten voltage pulses, but we show only the two cases where an actual change was observed. Since the rearranging of the domains does not happen every time a pulse is applied, one has to be patient and not increase voltage too much, as this can lead to partial removal of the top layer(s) and the creation of holes in the sample.

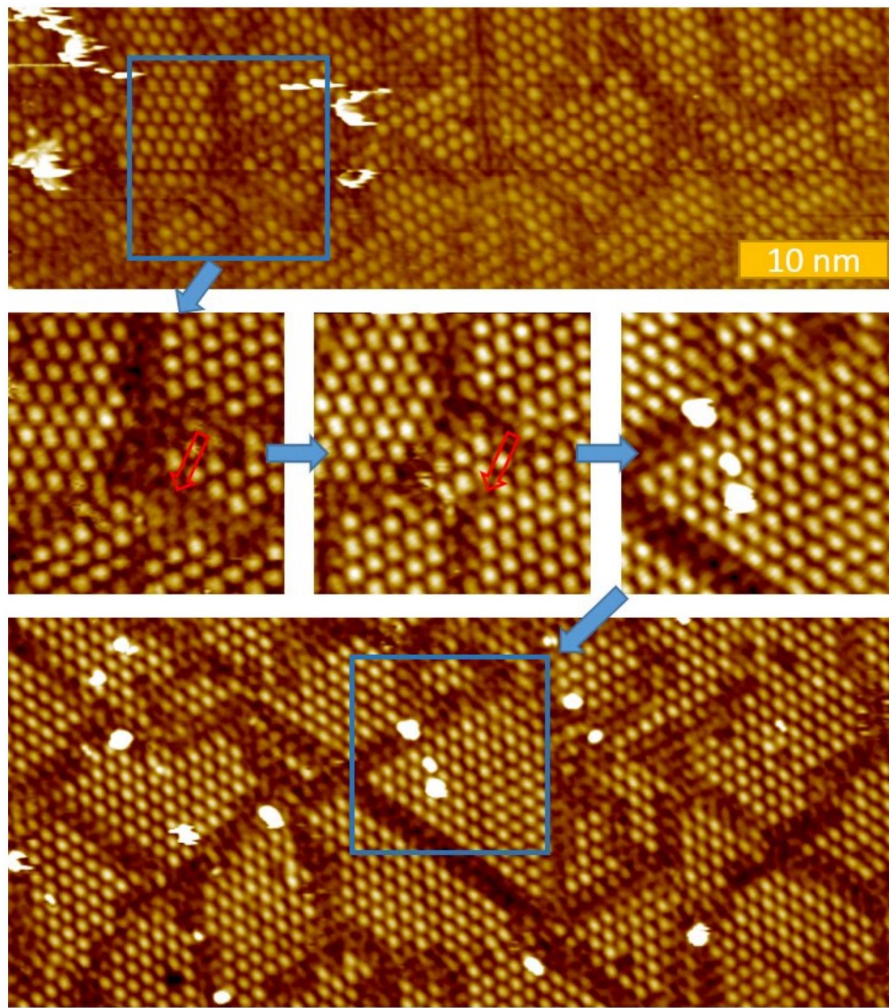


Figure S3. Relaxation of the domains after applying voltage pulses. Top: the larger area around the observed area before any pulses were applied, middle: the small observed area before and after applying voltage pulses, and bottom: extended area after the pulses were applied. The blue arrows are denoting the time sequence in which the images were taken, and the blue rectangles show the position of the small area within the larger area. The red arrows denote the approximate positions of the voltage pulses.

The detailed transition between the domains of different chirality through a domain with interfering chiralities

Here we show a relaxation process from the domains of different chiralities, through a domain with interfering chiralities to the domain state with only one chirality present in Fig. S4 a), b) and c). We

perform Fourier filtering on the domain with the chirality interference (filtered images in d) and f) are both taken from the image b)), which remarkably shows the remains of the domain structure that we observed before the transition and the hints of the domain structure after the domain structure. Thus the filtered data in d) resembles the domains in a) and the filtered data in f) resembles the domains in c). The time between the images is below 10 minutes for a) and b) and tens of minutes between b) and c).

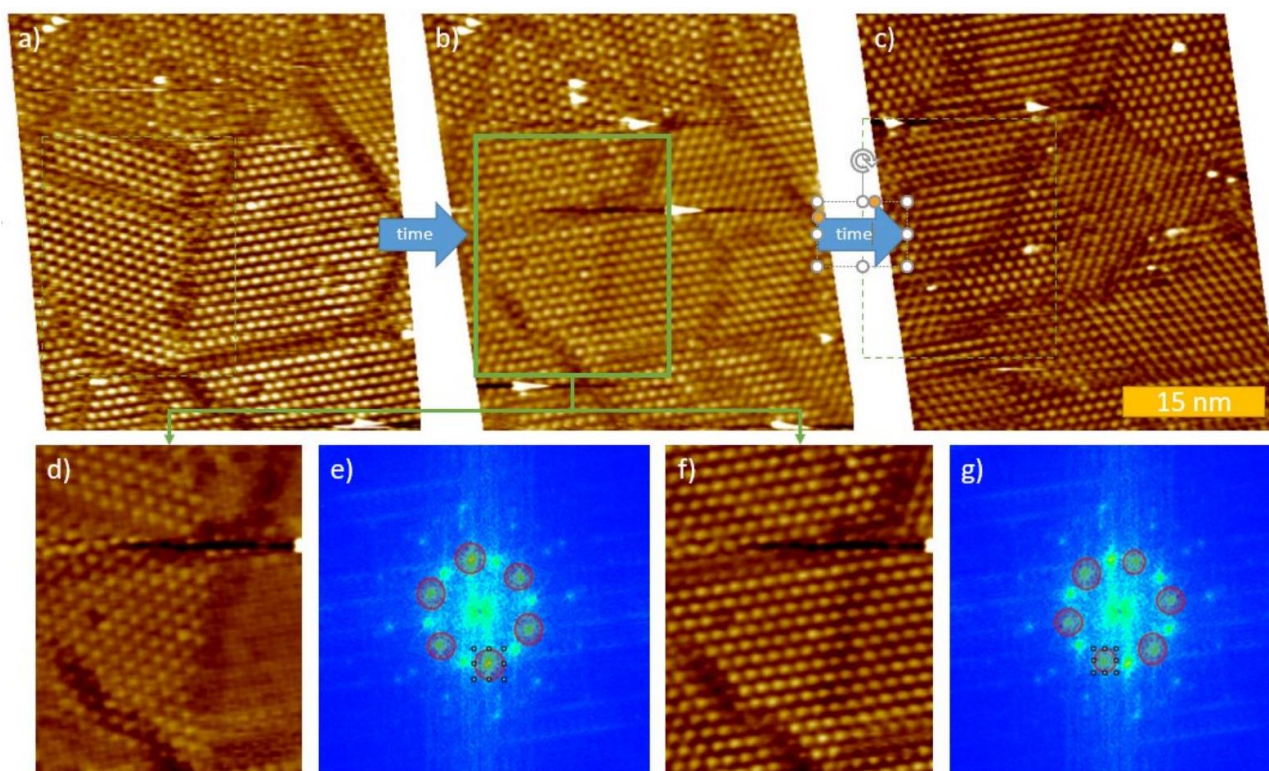


Figure S4. The relaxation of domains of different chiralities through a domain with interfering chiralities. a), b) and c) show approximately the same region at three different times. In a) we can see domains of different chiralities in the left and right parts of the image. In b), the chirality from the right side of the image propagates into the domain on the left, and we see a domain with the interfering chirality. c) shows the same region when the interfering domain relaxes to only one chirality. d) and f) show the zoom-in to the green rectangle from b) with an applied Fourier filter to only see the contribution of one of the chiralities. e) and f) show their respective Fourier transforms with filtered frequencies marked with red circles.

Fourier analysis of interfering chiralities

In order to perform the Fourier analysis, careful consideration of all the scanning data is required. For most of the data, only the Z-scans (height maps) are considered, since the STM is operating in the constant current mode. Taking into account the fact, that this mode highly depends on the sensitivity and speed of the feedback loop as well as on the tip movement speed, the real-life image which is obtained is in a quasi-constant-current mode. Taking into account both the height and current data for each of the STM scans, we can highly improve the analysis.

The 4 raw scans considered for the analysis are presented in Fig. S5. The top-row panels show Z(height)-scans up (**a**– forward/right, **e**– backward/left) and down (**i**, **m** respectively). The next row shows the I(current)-scans obtained as a result of low feedback speed. The last row represents 2D-FFTs of the corresponding scans (in each pair: left for H and right for I). All the data is presented as measured without any filtering or corrections.

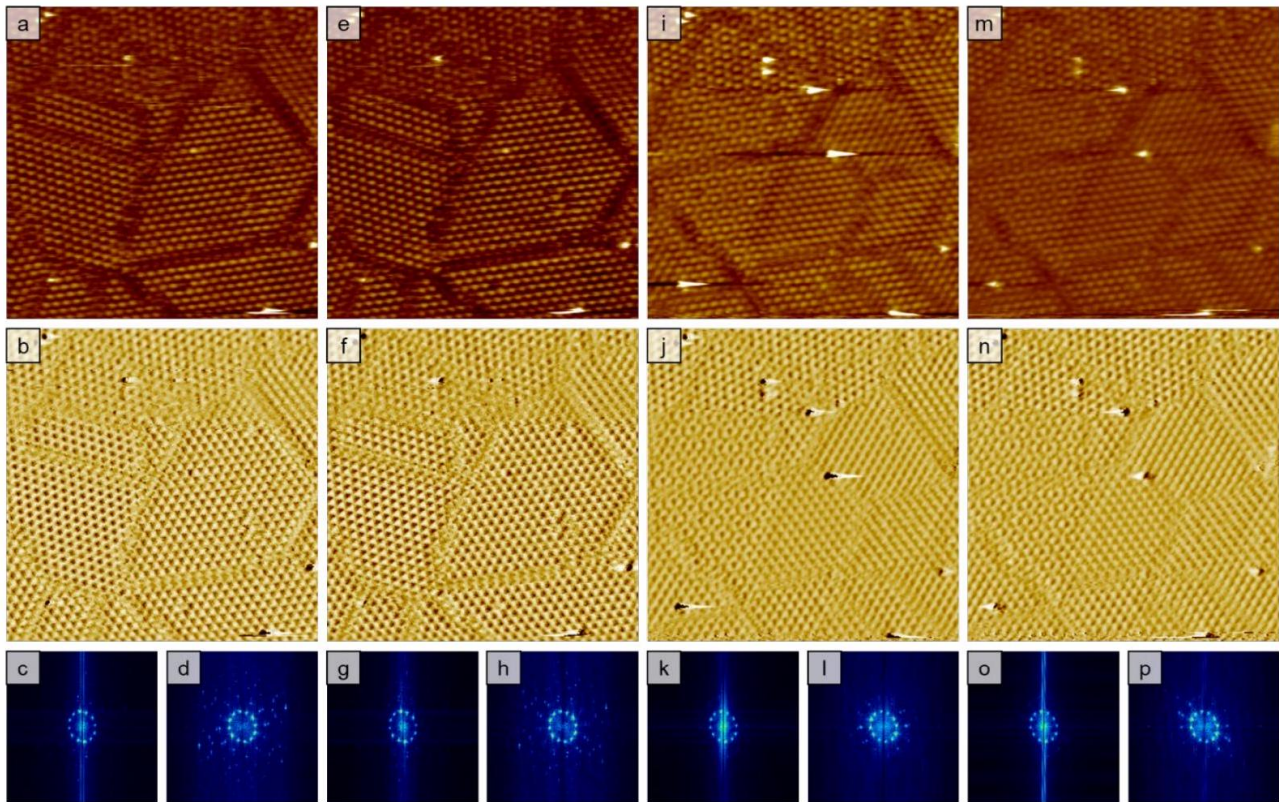


Figure S5. The original STM scans during which the interference was observed. a-d) up-forward. e-h) up-backwards. i-l) down-forward. m – p) down-backwards. Panels a, e, i, and m present Z (height) images in the constant-current (feedback) mode of STM. Panels b, f, j and n present I (current) images as a result of low feedback speed during the scans. Panels c, g, k, o present 2D-FFT for height and d, h, l, p - 2D-FFT for current images in the corresponding scans.

To examine the effect of feedback, the first scan in the series (Fig. S6a) before the interference appearance is considered. For the 2D-FFT calculation and quantitative analysis of both L and R chiralities, the same number of polarons in a single group with a similar symmetry is considered (marked in green areas). Figs. S6b,c show the 2D-FFTs for the height and current map respectively. As seen from the panels, there is a defined direction (vertical), along which the intensity of the FFT peaks is enhanced/suppressed. The same effect is easily seen in the bottom row of Fig. S5 - this is the result of the line-rastering noise.

Panel d of Fig. S6 presents the cross-sections of each FFT peak. Their peak values are presented in panel e together with the sum of Z and I FFT peaks. As can be seen in the figure, the total sensitivity of

the tip during the scan is direction-dependent but does not have any sharp features which are presented in Z -only or I -only data. This can be considered as the effect of tip shape. Fig. S6f shows the comparison of the FFT analysis performed for scans forward (Fig. S5a,b) and backward (Fig. S5e,f). Since the data is similar, our data can be considered regardless of the scan direction along the fast (X) axis.

Fig. S6g marks 4 different areas with R-only chirality of polarons on the scan down (Fig. S5m,n). Area 4 contains the other 3 areas. It can be considered the most precise since it covers the largest part of the original scan. Fig. S6h represents the results of FFT analysis for the areas marked in panel g. The reason for the different behaviour of area (3) is unknown but can be connected to bad statistics in different directions because of highly-elongated AOI.

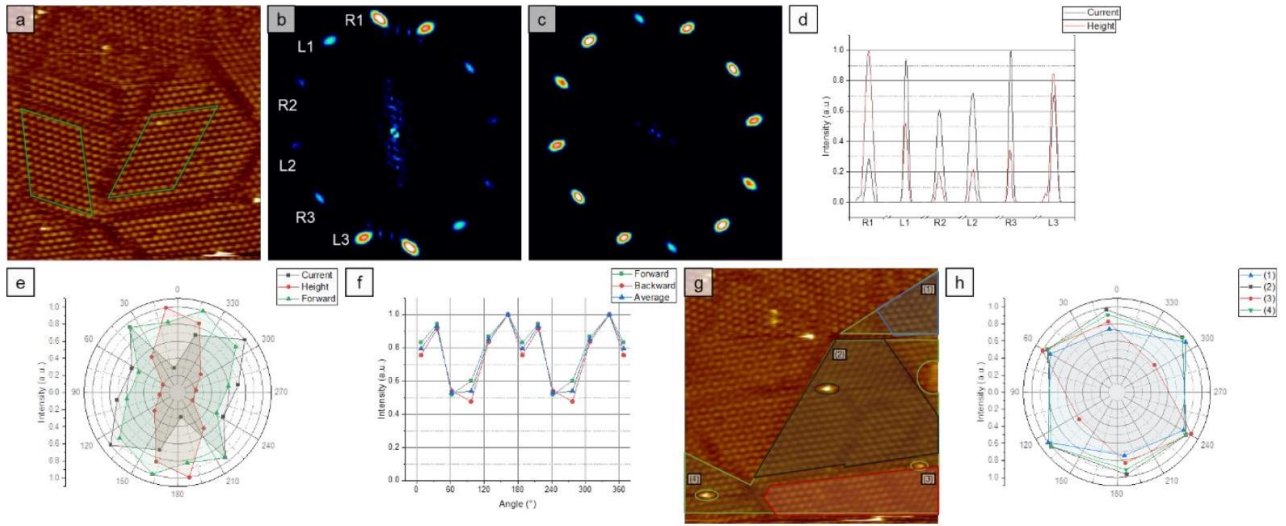


Figure S6. a) Z-scan of the sample before interference appears as in Fig. S5a with marked areas for quantitative 2D-FFT analysis containing the same amount of polarons with the same symmetry. b) 2D-FFT of areas marked in panel a with peaks labelled. c) 2D-FFT of the same areas in the I-scan as in Fig. S5b. d) Quantitative comparison of R and L FFT peaks in both Z and I-scans. e) Quantitative analysis of R and L FFT peaks considering the spatial directions. The green plot represents the sum of Z and I-scans. f) Comparison of FFT analysis for scans forward (Fig. S5a,b) and backward (Fig. S5e,f) and their average. g) Z-scan of the area with interference observed as in Fig. S5m with different parts of R-only chirality marked for analysis. h) Comparison of FFT analysis for areas marked in panel g. Both Z and I-scans are considered in each curve.

Fig. S7a,b show the interference area considered in the analysis as well as the R-only chirality for comparison (the same as Fig. S6g,h (4)) on height and current-maps respectively. The corresponding 2D-FFTs are shown in Fig. S7c,d. As can be seen from the FFT analysis (Fig. S7e), the intensity of all the L peaks is lower in comparison to all the R peaks. Also, peak $R3$ has the same feature, as one in Fig. S6 h(4) which is almost twice less intense as compared to the other two R-peaks, marking elliptical asymmetry of the CDW intensity observed in this area.

One can perform an ellipse-to-circle correction on the resulted interference curve as shown in Fig. S7f (purple) to the peaks $L2$, $R3$ and $L3$ if considering the following axes of the ellipse: $a = \text{average}(R1, R2)$; $b = R3$, as well as the radius of circle $r = a$.

If we consider the total part of L chirality as $L = L1 + L2 + L3$ and R chirality as $R = R1 + R2 + R3$, for the FFT peaks with radial cross-sections as shown in Fig. SY3g, the result of $L \approx 0.648R$ is obtained. Fig. S7h shows the sum of cross-sections from panel g.

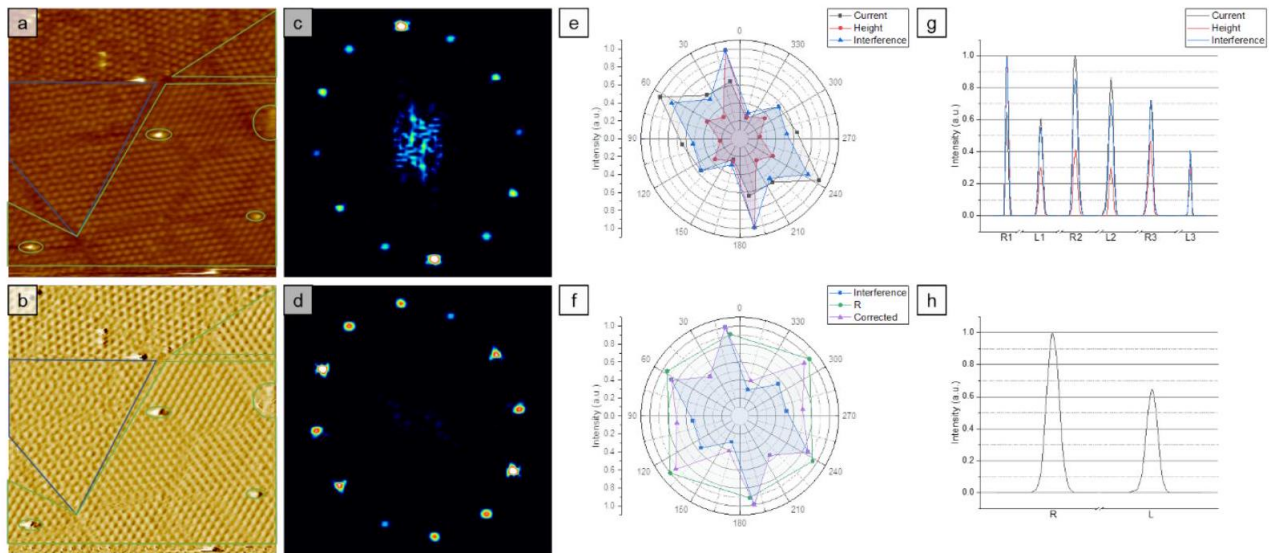


Figure S7. a,b) Z and I-scans with the interference area marked as well as R-only chirality. Both panels as in Fig. SY1m,n. c,d) 2D-FFT for the interference area in Z and I-scans. e) FFT analysis of the interference image. f) Comparison of the interference FFT with the FFT of R-only chirality. The corrected curve presents an ellipse-to-circle correction performed on the interference plot with R3 (129.6° and 309.6°) peak corrected to an average value of R1 and R2. g) Radial cross-sections of each FFT peak for Z, I-scans and their sum. h) Sum of cross-sections for all R and L peaks after correction for the FFT peak-to-centre distance due to image drift during the scan. The peak of the **L**-curve is **64.8**.

One more piece of evidence of the similar intensities of the two chiralities in the interference pattern can be seen in the domain walls (DWs), visible in the STM scan. The area of interest marked in Fig. S7a,b. contains two DWs - a straight one corresponding to the R chirality and aligned to the R CDW in all other parts of the image (a "stronger" DW); and another straight DW which was observed before (Fig. S5a,e), aligned to the L chirality (a "weaker" DW). Considering the exact same position of this DW as on the previous scans, as well as the absence of any bottom-layer DW effects visible in other parts on the same scan at these conditions, we can attribute this "weaker" DW to the top layer the same way as the "stronger" one.

Appearance of the interfering CDW domain during a single scan

In one case, we were able to witness the switching to the domain with the interfering chiralities during a single STM scan. The scan was taken from the bottom to the top. As we can see, it starts with great atomic resolution of a single domain (it is unclear that this is a domain, since there are no visible domain walls, as the scanning area is too small and just covers a single domain). At approximately one third of the scan, the image changes abruptly: we lose the resolution and the pattern changes significantly. We do not know the exact cause, but a plausible explanation is that the single atom at the end of the tip either dropped or moved. This clearly explains the loss of resolution. During tip reshaping, a short current/voltage spike may have been triggered that induced the change in the sample. This explains why the top part of the image has a different symmetry than the bottom part.

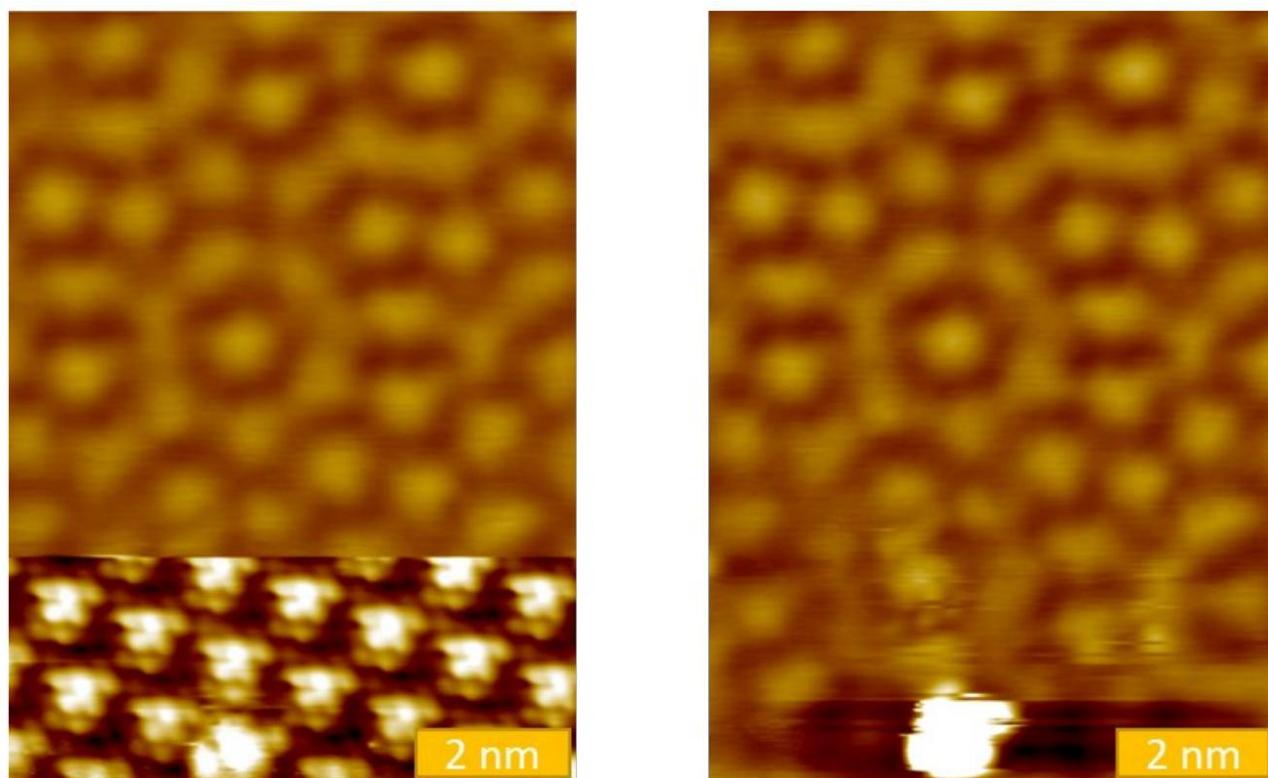


Figure S8. a) STM image of the H state domain (scanning upwards), which abruptly changed to the domain of two interfering CDWs and b) image of the same region taken on the scan down.

A similar process to the one shown in Fig. S8 could have happened also in Fig. S4a. Fig. S4a was scanned on the way up (bottom of the image is taken earlier) and it seems the appearance of the top quarter of the image (where interfering chiralities are present) is a bit different. Since we did not scan this part of the sample before and since the contrast is not very obvious, we cannot claim with confidence when exactly the transition happened, but it is likely that it also happened during the scan.

Influence of the bottom layers on the top layer

To exclude the possibility of interference between electron orders of different chirality in the top two layers, we must look at some examples, where the top and bottom layer CDW are not the same, but we observe no interference effect. The first argument against a multilayer effect is interlayer stacking. It was shown that polarons do not very likely sit directly above polarons in the bottom layer [3,4]. It

was shown previously that in the domain state, the domain walls are shifted, so that the polarons are not aligned between the different domains [5,6]. The polarons from the top and bottom layers would be vertically aligned only if also the domain walls are perfectly aligned, which was shown not to be the case [5]. If - as observed experimentally [4,5] - the domains are shifted with respect to each other, the vertical stacking of polarons varies significantly.

Another argument is that if the interlayer interference was a strong effect, we should see the polarons in the microscope image appearing differently across the image, but they seem to be mostly unperturbed by the layer underneath. In Fig. S8 we present the same argument for the interlayer interference between mirrored superlattices. Here we see that the top layer is partly transformed to the 1 H polytype, which has no charge modulation above 75 K (the image was taken at 80 K) and thus appears very flat in STM, and is 'semi-transparent',

revealing the charge modulation below. We can clearly see that the superlattice in the layer below has a different direction than in the layer above. Thus, unless there is no domain wall in perfect register with the border between 1H and 1T polytypes (which is very unlikely), there is no interference between the domains of different chirality. Furthermore, if such interlayer interference was strong, it should very likely be observed every time a mirrored domain appears, assuming there is not an identical domain under it, which is again very unlikely.

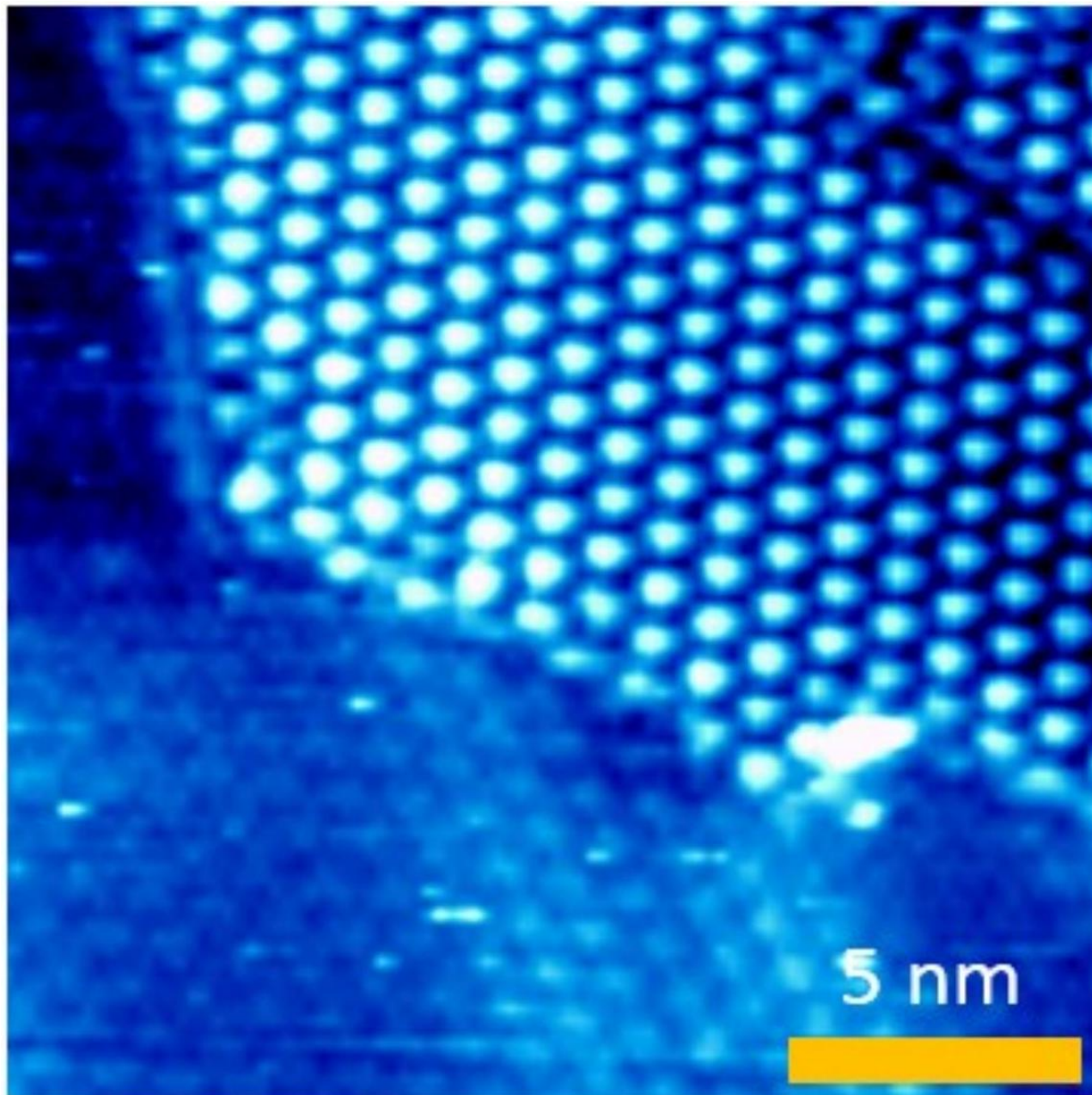


Figure S9. STM image of the **H** state, where the domains from the bottom layer are also seen. b) partly transformed top layer to the "transparent" **1H** polytype. We can see that the CDW modulation in the bottom layer is mirrored with respect to the top layer. In both cases we see no interlayer interference effect.

In order to check for the possibility of similar chirality interference patterns as a result of interaction between the CDW in the top and the second layers of the same 1T polytype, additional STM experiments were performed. During the experiments, the top layer of the material was conditioned in a way to create small (up to 5 nm laterally) single-layer defects (voids in the atomic structure) to be able to directly scan the second layer (Fig. S10a,c). The two CDW lattices (one for L and one for R chirality) were carefully assigned to every domain in the top layer to have the best fit on large-area images. The visible parts of the second

layer were fit to the same lattices with no adjustments except for the lateral position. The abovementioned CDW lattices of the second layer were extended towards the expected areas of overlap with the opposite chirality in the top material layer (Fig. S10b,d). The performed analysis has shown, that no chirality interference is observed in the top layer of 1T-TaS₂ even when the second layer has an opposite CDW chirality.

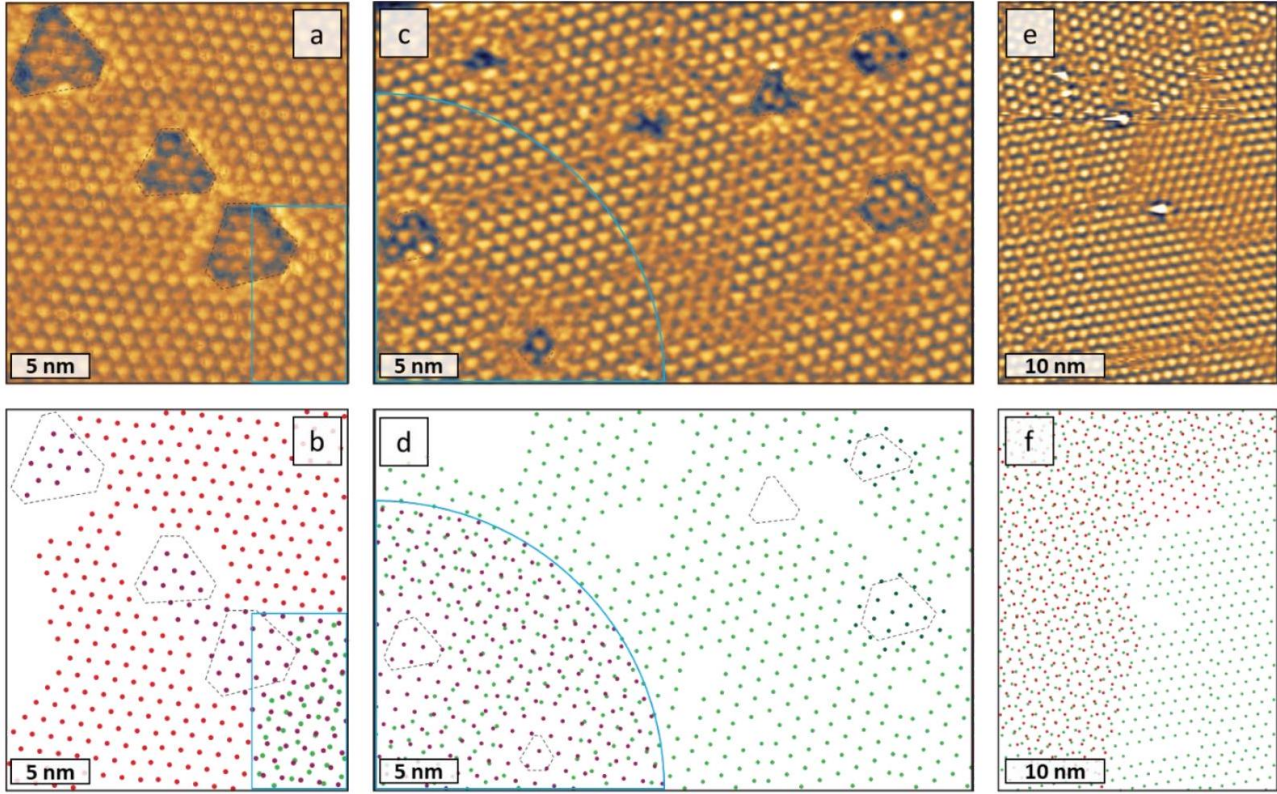


Figure S10. Chiral CDW domains of **1T – TaS₂** observed with STM in the top layer(s). CDW lattices are marked for domains of *L* (lime) / *R* (red) chiralities in the top and *L* (green) / *R* (violet) chiralities in the second layer. Blue solid lines are marking expected areas of chirality interference (overlap) between layers, gray dashed lines are marking single-layer defects for easy referencing.

a, c) 1T- TaS₂ layers with both (panel a) / single (c) chiralities in the top layer and single (a) / both (c) chiralities in the second layer. No interference pattern is observed.

b, d) CDW lattices fit the experimental data and marking areas of chirality overlap for panels a, c.

e, f) Observed chirality interference pattern and its fit to the CDW domains, partially visible in the top layer.

Interference pattern in 4Hb – TaS₂

We performed measurements also on 4Hb-TaSe₂ where 1T and 1H layers are alternating. A transition from an incommensurate to a commensurate $\sqrt{13} \times \sqrt{13}$ charge density wave for 1 T layers occurs at around 410 K [7]. This is the same superlattice modulation as in the commensurate state of 1 T – TaS₂. In 1H layers, the CDW transition to a $\sim 3 \times 3$ CDW appears at around 75 K. The measurements on the 4Hb – TaSe₂ were made at 77 K, where we expect 1 T layers to be in the commensurate CDW phase and 1H layers in the normal phase, just above the phase transition.

Figure S11 a) shows a step between layers with a line scan profile. The top layer is in the 1 T phase with a $\sqrt{13} \times \sqrt{13}$ CDW modulation, while the bottom 1 H layer has only very weak modulation with a similar periodicity, arising from the 1 T layer below the 1 H. While scanning the top 1 T layer we applied several high-voltage pulses (6 V, 5 ms) with the STM tip. We observe an interference pattern 30 nm away from the position where the pulses were applied as shown in Figure S11 b). The interference pattern is stable even after scanning for 4 hours. After moving around different areas, the tip hit an impurity particle on the surface and produced an electrical pulse on the surface. After this, the interference pattern is lost (see Figure S11 c). This is consistent with the observed change in the interference pattern reported in Figure S8 on 1T-TaS.

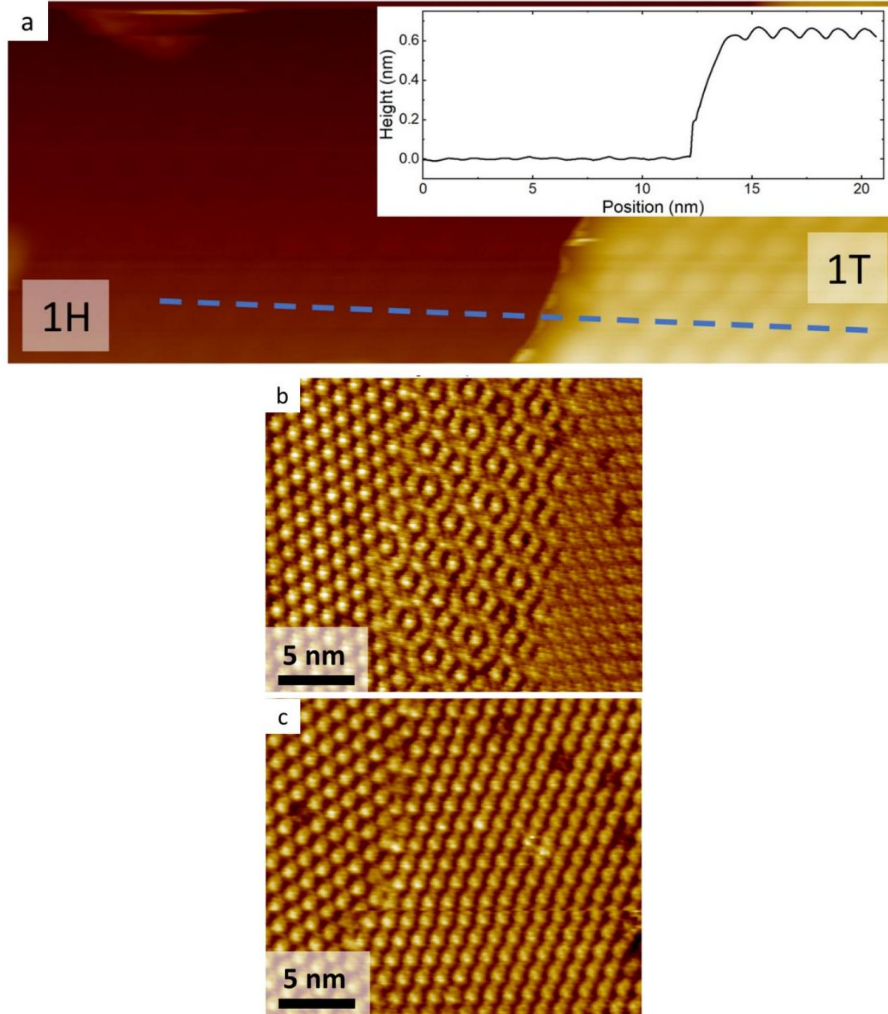


Figure S11. a) Step between layers of the **4Hb – TaSe₂** : the top layer is **1T** with the $\sqrt{13} \times \sqrt{13}$ CDW modulation (right part of the image), while the bottom **1H** layer does not exhibit significant modulation (left part of the image). Inset shows a line profile across the step between layers. b) Interference pattern observed on the 1T top layer after several strong electrical pulses from the tip were applied around 30 nm away. c) Interference pattern is lost after scanning over a piece of dirt that produced an unintended electrical pulse. The scanning area of b) and c) are the same.

The structure of domain walls separating domains of different chirality

Between two mirrored domains, the geometry does not allow a simple straight domain wall. In this case, we can nevertheless expect that the domain wall would take the closest approximation to a straight line, in order to minimize its length and thus its energy [8]. In Fig. S12 we show a few conceptual drawings of domain walls, where we attempt to find domain

walls with higher symmetry for one or both domains, while keeping the domain wall straight. We can see that in order to keep the boundary of one domain straight, the other domain must asymmetrically adapt to keep the domain wall of a certain average width (Fig. S12a). Such a domain wall is periodic, and the pattern repeats every 13 superlattice sites. Between the two extreme points, where one domain boundary is perfectly straight and the other one adapts and vice versa, we can create an infinite number of different domain walls, which are distorted on both sides. At the midpoint, there is a number of symmetric domain walls, where domains have symmetrically distorted edges. An important thing to notice is the period on which the two domains overlap, which can be described by a linear combination of $13a^*$ and $13b^*$. Thus, there are lattice positions which correspond to both superlattices and having such polarons in the domain wall may potentially lower the overall energy of the domain wall and further stabilize it. With this in mind, we can try to construct a few such periodic and symmetric domain walls, which are shown in Fig. S12 b-d.

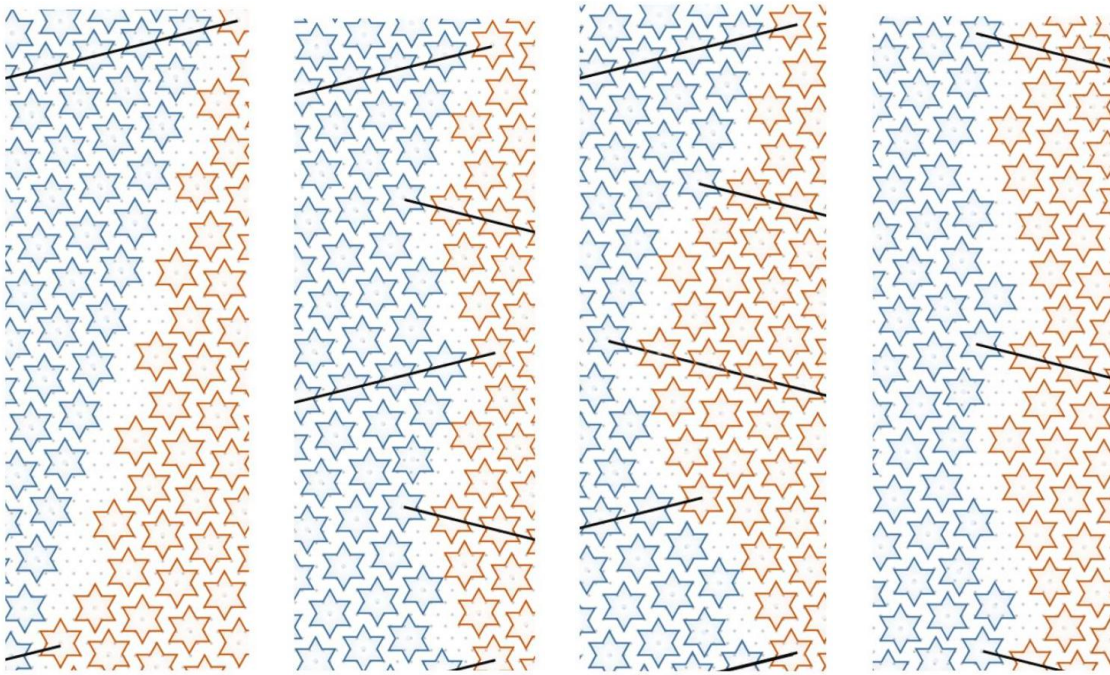


Figure S12. various attempts of creating a domain wall between differently oriented domains, while keeping some form of symmetry. a) One domain has a straight boundary, while the other one completely adapts. b), c) and d) The domain wall is symmetric and aligned with lattice direction. Both domains adapt to keep the symmetry. d) The domain wall is aligned with the lattice direction, but is not symmetric. Black lines are drawn as guidelines to mark where one domain could extend into the other domain.

Appearance of mirror domains for different annealing times.

By changing the simulated annealing time as described in [9] we can influence the probability of the presence of mirror domains. When the annealing time is short, there is a much higher chance to observe both kinds of domains, with an expected average distribution of 50% each. This is dictated by random direction nucleation growth of the domains and simultaneous locking due to the fast annealing times. Additionally, with short annealing times, sometimes even $\sqrt{12} \times \sqrt{12}$ domains are present, which were not previously seen in any experimental case [1]. When annealing the system slowly, we mostly observe only one type of the domains when the low temperature is reached. This implies that the energy of the domain walls between different domains is larger than the energy between the domains of the same type, as they always tend to relax to a group of single-orientation domains when given enough time. This can be confirmed by calculating the final energy of the system in both cases, following the energy calculations as

performed in [10]. The source of the difference in energies can be simply pointed out by looking at the figures and consists of two contributions: the domain walls between two domains with the same orientation are in most cases only one polaron spacing thick and perfectly straight, while the domain walls between mirrored domains are thicker and very rugged. In other words, when domains of both orientations are present, the overall coverage of the sample with the $\sqrt{13} \times \sqrt{13}$ superlattice (which is energetically the most favorable for this filling) is smaller, because more of the space is taken by the energetically costly domain walls.

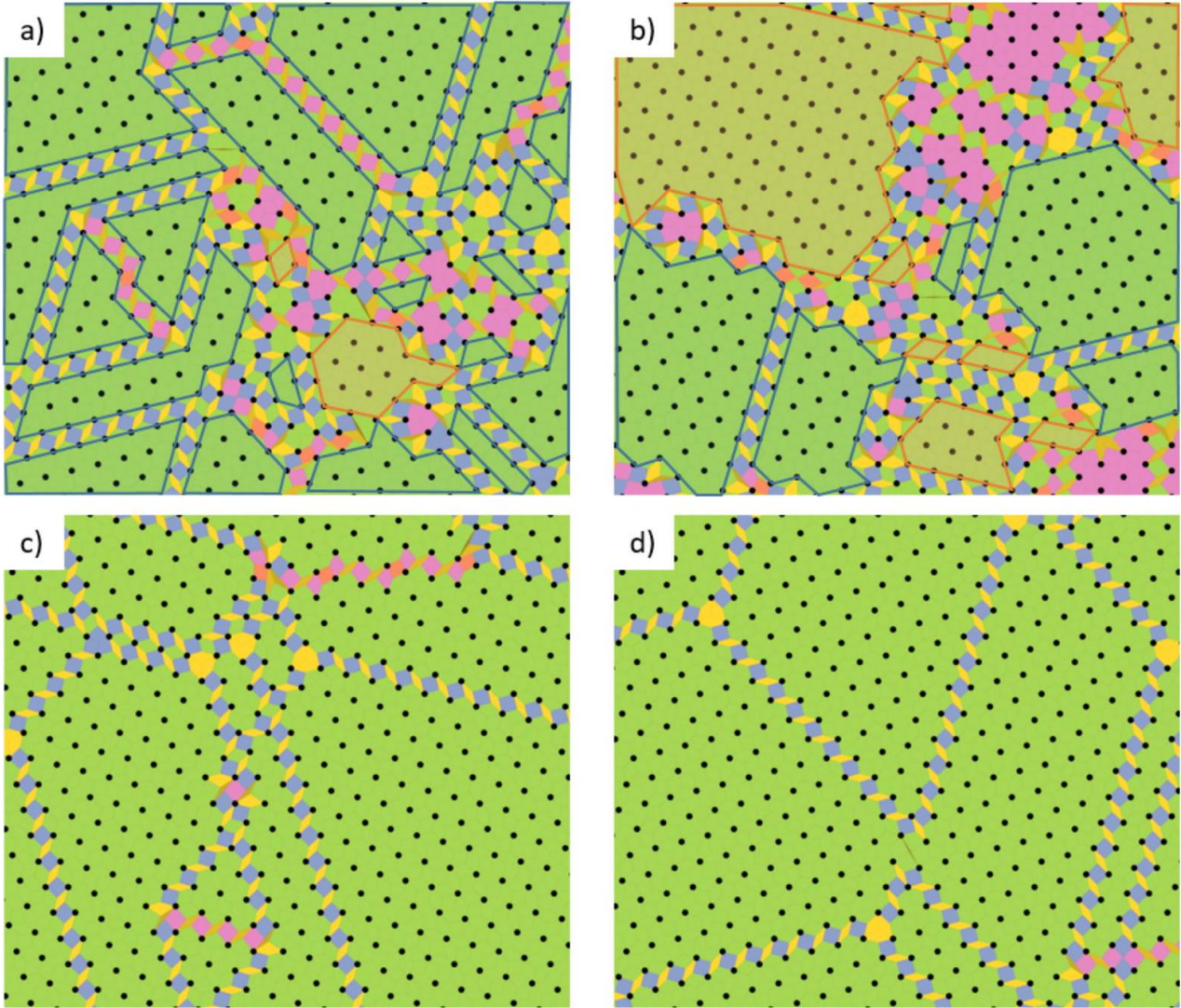


Figure S13. Comparison of different annealing times at $f = 12.6$. a) 90 sweeps, b) 100 sweeps, c) 200 sweeps, d) 300 sweeps.

For 100 or less sweeps, we very likely see mirrored domains and sometimes even the $\mathbf{V}12 \times \mathbf{V}12$ domains. When performing longer sweeps, we very rarely observe more than one type of domains. Different domain orientations were marked with blue and orange shapes in a) and b). The $\mathbf{V}12 \times \sqrt{12}$ domains are tiled with pink. In c) and d) no domains were marked as they are all of the same type.

Direction of the domain walls between the domains with different SL orientations.

Both the experimentally observed and simulated domain walls between mirrored domains are too short to indicate whether they follow a general direction. However, it roughly seems

that they tend to align with the atomic lattice direction. To verify this claim and see how longer domain walls would behave, we have employed fixed boundary conditions to the model to simulate two large domains with mirrored superlattice orientations (Fig. S14a). We have used the same model as before, but pinned down the polarons at the two boundaries (highlighted blue, marked with B and C) of the model to form the two distinct chiralities. We put additional unpinned polarons in the empty region between them, and kept the other two boundaries (highlighted yellow, marked with A) of the model periodic. Then, we observed the ordering of the polarons through the same annealing process as originally [10].

As the observed experimental samples are too small to calculate the appropriate filling (number of polarons per number of lattice sites) for this state, we used the filling of the C state (13 sites per polaron) as a basis and simulated the behavior for relatively large deviations (± 0.4) from this filling. The observed filling for the H state is 12.6 , which is covered in this range. The filling close around 13 shows only one domain wall and a small deviation of filling does not affect the results qualitatively. However for larger deviations (> 0.1), more domains and domain walls start forming, and a domains form over all of the available area. We stick to the fillings where only one domain wall appears (close to 13) for easier analysis of the domain wall direction. What we can see is that the domain wall in all cases aligns very close to the lattice direction, making the domains almost symmetrical. A potential problem arises from periodic boundary conditions for two of the unpinned borders (top and bottom borders on Fig. S14a), which define the direction of the shortest possible domain wall. In our case, this shortest possible domain wall follows the lattice direction, making it unclear, whether the domain wall tends to align with the lattice direction, or simply looks for the shortest path. In order to clarify that this does not happen due to the periodic boundary conditions, we shifted the boundary in the model (Fig. S14b)). Doing this, the shortest possible domain wall was not anymore along the lattice direction. With the new boundary conditions, the annealing did not result in one simple domain wall, as it did in the case shown in Fig. S14a). In this case we always arrive to a minimum, which is a messy mixture of domains with different orientation and even with some 12×12 domains. The result is the same for a variety of fillings (shown in Fig. S15 and S16). It appears that this kind of the domain wall is more energetically costly when it does not follow the lattice direction and thus tries to relax its energy by breaking into smaller pieces through formation of many smaller domains. We can assume that the same physical laws govern the formation of domain walls between mirrored domains, as they do in formation of the walls between two domains of the same chirality. It is generally accepted that the free energy of the domain walls includes a linear contribution of the length of the domain wall, which forces the domain walls to form straight lines, in order to achieve the lowest energy state [8]. We conclude that the walls between domains with different orientation tend to orient along the direction of the atomic lattice, as this is the way to lower their energy.

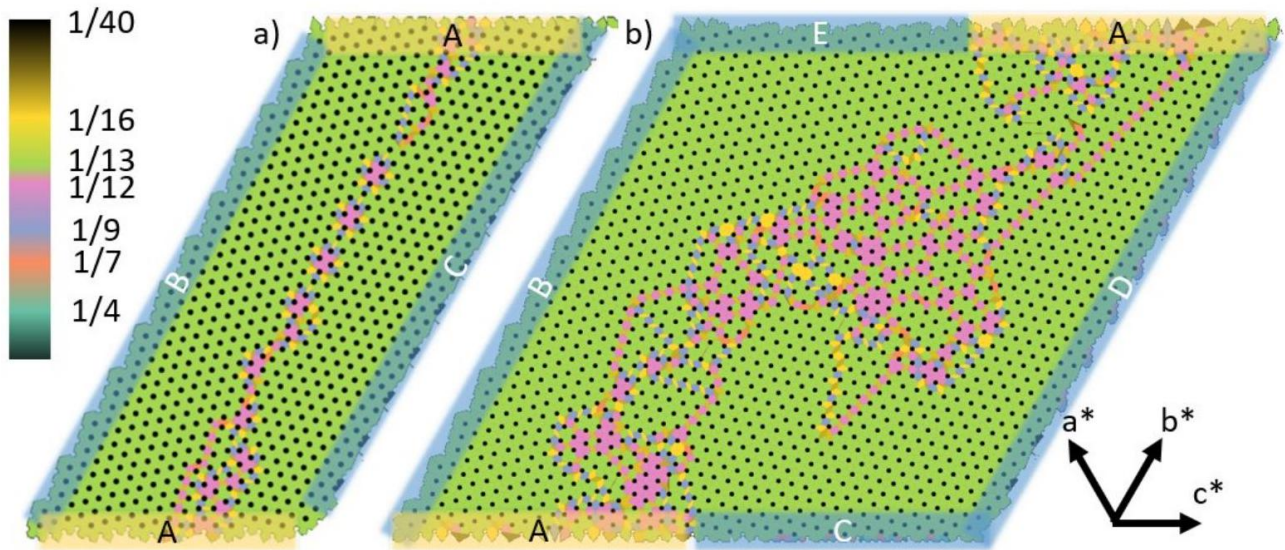


Figure S14. (a) Simulation of the polaron ordering with PBC only in the vertical direction (borders are marked with A), whereas on the left and right borders the polarons were pinned, to fix the two different superlattice orientations (borders B and C). (b) Similar as (a), but with shifted borders to model the domain wall which is not parallel to the lattice direction.

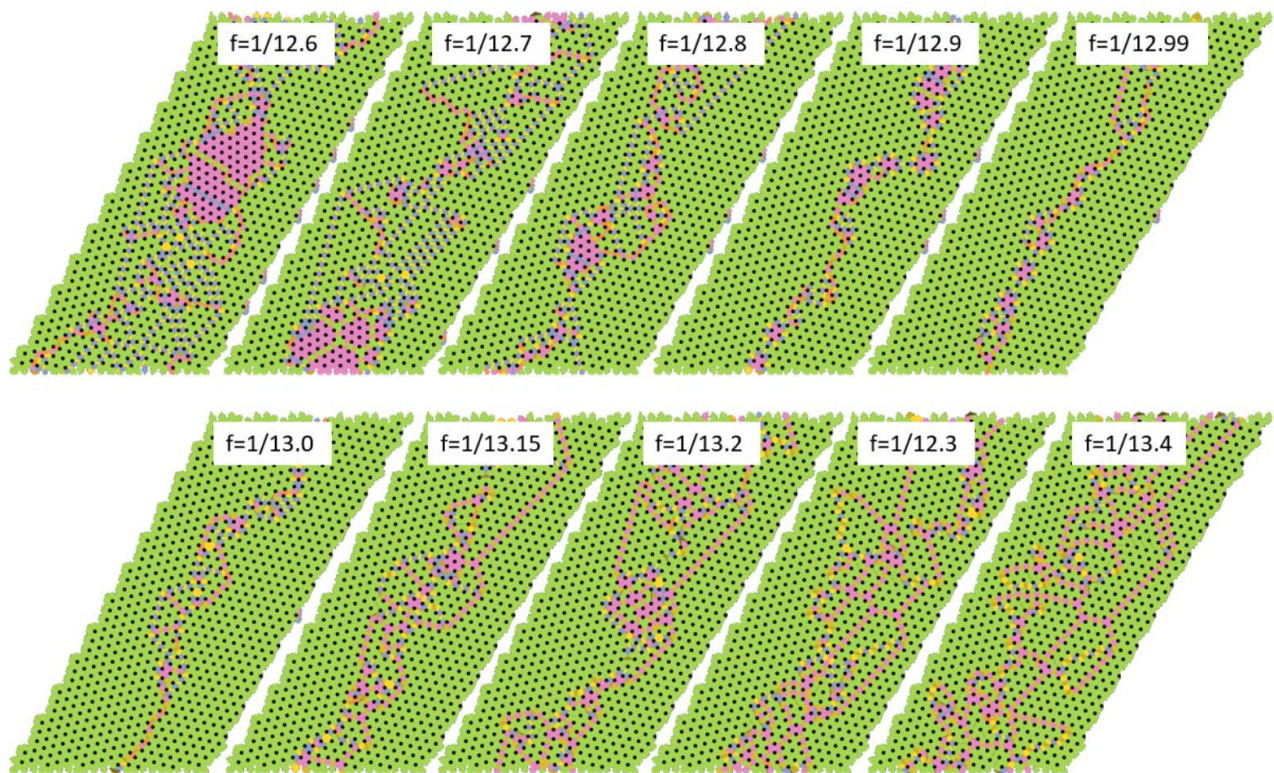


Figure S15. (a) Domain walls between mirrored domains for different fillings. For fillings close to $1/13$ the domain wall between the mirrored domains is close to straight and rarely some other domains appear. For larger deviations, the area becomes covered with various domains.

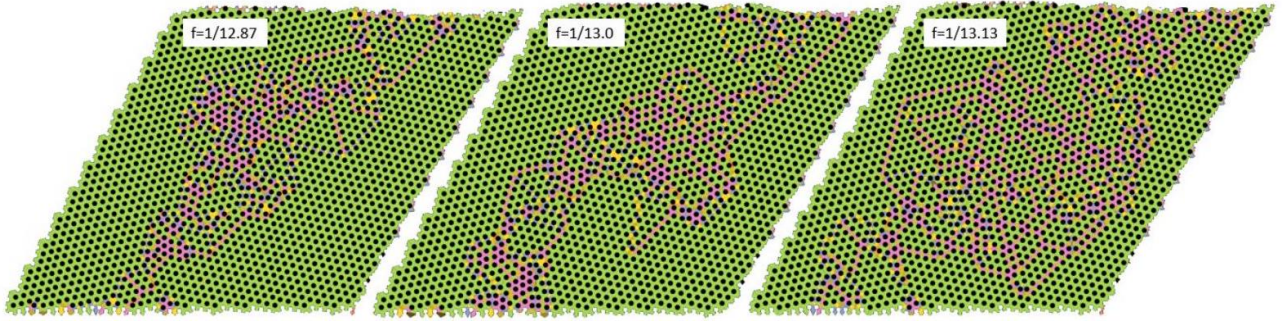


Figure S16. Domain walls between mirrored domains with shifted periodic boundary conditions for different fillings. We observe no conceptual difference of the domain wall formation when changing the filling of the system. We do not observe a single domain wall for any filling.

Modelling of the periodic lattice distortion in the double CDW state

To obtain a qualitative picture of the atomic lattice displacements in the superposition (S) state, we consider a model consisting of atoms that interact via Lennard-Jones potential and are subject to an underlying CDW potential. The periodic lattice distortion of the David star unit cells [11-13] is generally understood as the displacement of the outer twelve atoms towards the thirteenth atom in the center of the star. We assume that the Ta atoms interact via the Lennard-jones potential $V(r) = 4\varepsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right]$. Here r denotes the distance between two interacting particles, σ is the distance at which the potential energy is zero and ε is the depth of the potential. The interacting atoms on a 2D surface naturally form the energetically most favorable triangular lattice.

Next, we subject these particles to an external potential in form of the $\sqrt{13} \times \sqrt{13}$ CDW superlattice and perform a Monte-Carlo simulation to observe the formations that the particles will take to minimize the energy. We start with the single-direction CDW. The equation for minimizing the energy of the j -th particle in a left-handed CDW potential can be written as

$$V(r) = 4 \sum_{i \neq j} \left[\left(\frac{\sigma}{r_i - r_j} \right)^{12} - \left(\frac{\sigma}{r_i - r_j} \right)^6 \right] + U \operatorname{Re} \left(\sum_{d \in \{1,2,3\}} e^{i \vec{k}_d^T \vec{r}_j} \right),$$

where the first term sums over all of the particles i and calculates the pairwise potential energy between i -th and j -th particle. The second term adds the outside potential energy of the CDW. We show the different potentials in the Fig. S17. Note that in some cases we superimpose also the atomic lattice, for better understanding of the period of the potential.

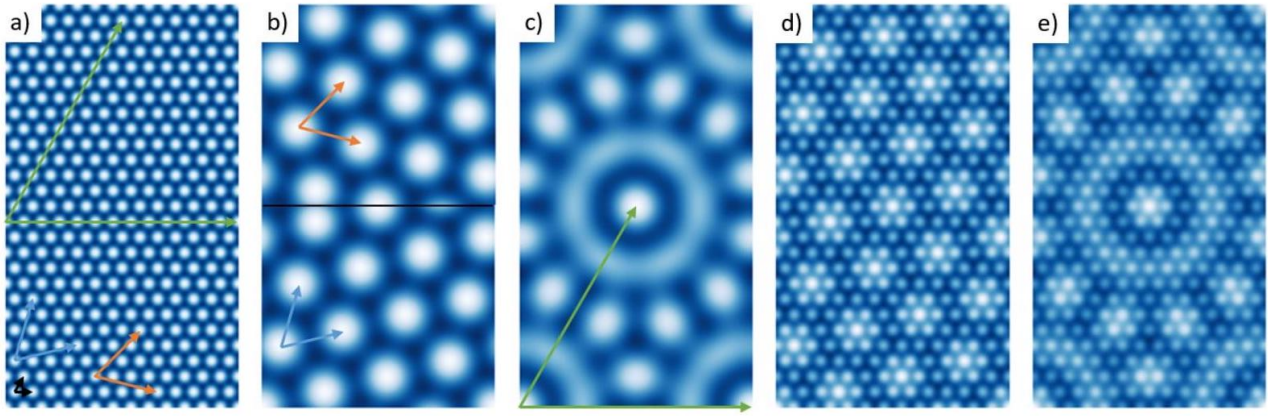


Figure S17. Different shapes of the potential as a sum of cosine terms. All figures are in the same scale. a) The atomic lattice (here the wavevectors k are taken to be the atomic lattice vectors), b) right (top) and left (bottom) handed CDW lattices, c) double CDW lattice (sum of both lattices in b), d) left-handed CDW lattice and atomic lattice (sum of a and b) and e) double CDW with atomic lattice modulation (sum of a, and c). The arrows Show the wavelengths of different waves: Black arrows show the a and b vectors of the atomic unit cell. Blue and orange arrows show the left and right handed CDW vectors and are equal to $3a + b$ and $4a - b$ respectively with their 60 degree equivalents. Green arrows show the size of the unit cell in the double CDW, which equals to $13a$ and $13b$. The atomic lattice is in this case assumed perfectly unperturbed and is shown in the figures just as a reference and not used in the further calculations.

In Fig. S18, we show results of the Monte-Carlo simulation for a single CDW potential with an exaggerated $U = 100$, where the displacements are clearly visible. We can see the formation of a $\sqrt{13} \times \sqrt{13}$ superlattice, where unexpectedly we do not observe the movement of 12 atoms towards the central atom, but only the inner 6 atoms of the expected David-star are displaced, while the outer 6 stay at their initial positions. This makes sense, considering the outer six atoms are sitting on a potential energy saddle, as opposed to the inner six atoms, which move towards the center of the valley in which they are located. Eventually, with an absurdly large U , the outer atoms move as well, but this case is not considered to be physically relevant anymore.

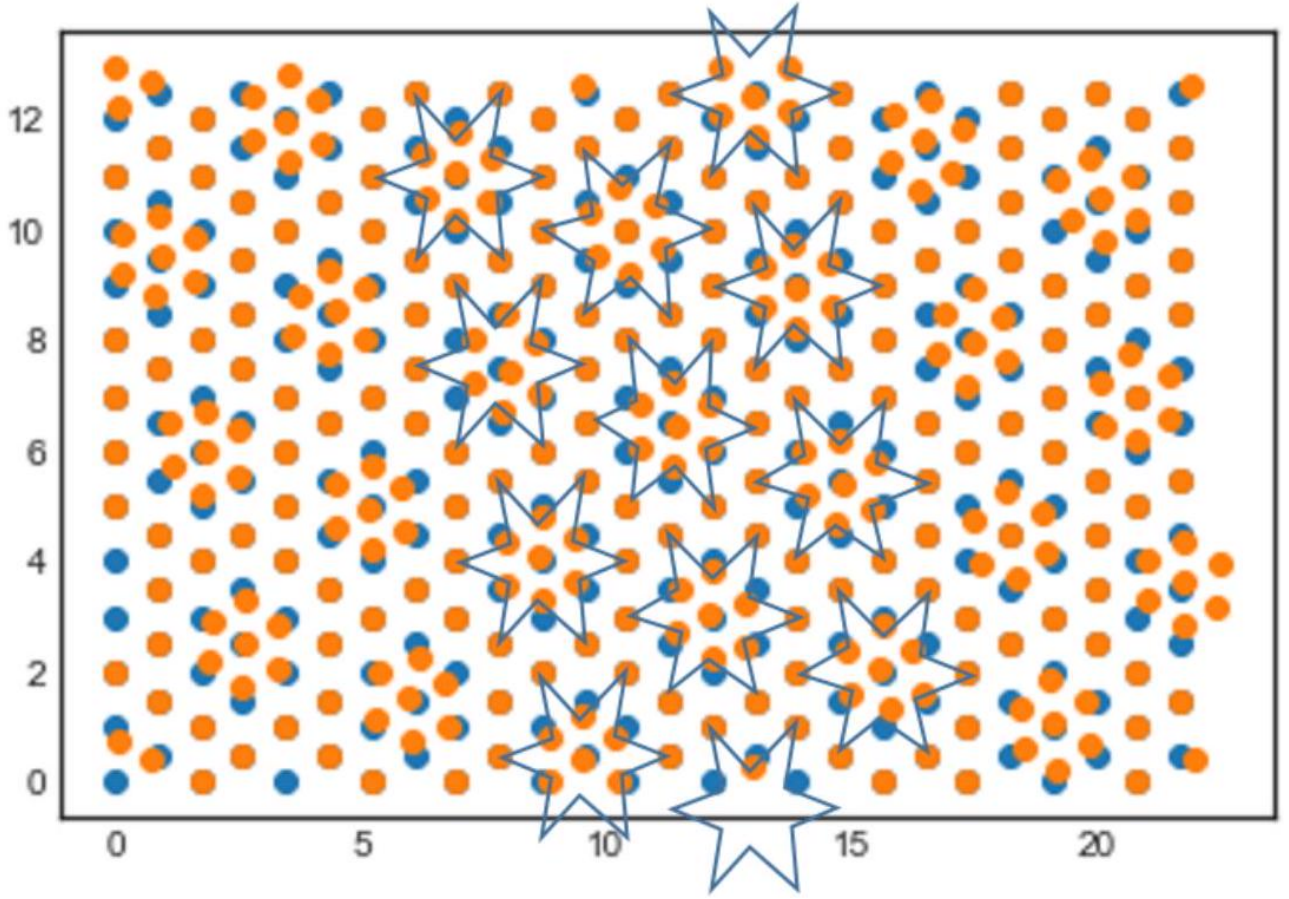


Figure S18. A result of a Monte-Carlo simulation for the particles interacting via Lennard-Jones potential, in an outside potential, which resembles the left handed $\sqrt{13} \times \sqrt{13}$ CDW superlattice (as shown in Fig S14 b). The blue and orange dots represent the equilibrium atomic positions and the displaced positions respectively.

We perform the same simulation using the potential energy of both CDW chiralities (as shown in Fig. S17g). Here we slightly change the equation to add the contribution of both directions of CDW.

$$V(r) = 4 \sum_{i \neq j} \left[\left(\frac{\sigma}{r_i - r_j} \right)^{12} - \left(\frac{\sigma}{r_i - r_j} \right)^6 \right] + U \operatorname{Re} \left(\frac{1}{2} \sum_{m \in \{+, -\}} \sum_{d \in \{1, 2, 3\}} e^{i \vec{k}_d^m \cdot \vec{r}_j} \right),$$

We also normalize the outside potential energy by a factor of $\frac{1}{2}$, as it now consists of two different contributions. The atomic displacements in this case follow a different pattern, which also closely resembles the pattern of the outside potential and is shown in Fig. S19.

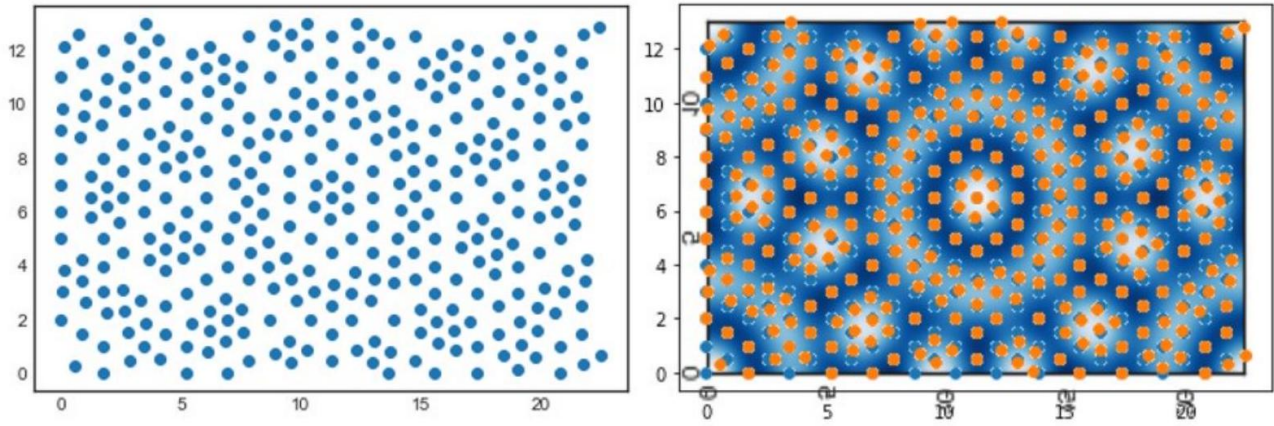


Figure S19. A result of a Monte-Carlo simulation for the particles interacting via Lennard-Jones potential, in an outside potential, which resembles the sum of the left and right handed $\sqrt{13} \times \sqrt{13}$ CDW superlattices. a) the displaced atoms, b) equilibrium and displaced atoms in blue and orange respectively, drawn on top of the double CDW potential energy surface.

To understand the displacements in the interfering CDW better, we compare them to a direct sum of displacements in two separate cases for the L and R CDW direction. For a clearer picture, we write down the atomic displacements in a vector form, assuming perfect atomic displacements (each atom is displaced by exactly the same value in one of the high-symmetry directions - towards the central atom of the star). By comparing the vector displacement with the Monte-Carlo simulation, one can see the best correspondence when we only displace the inner 6 atoms of the star, both for the single direction as well as for the double CDW. The simulated lattice distortions of the double CDW thus simply look like a sum of the displacements in both CDW directions.

We choose three different approaches to the atom displacements within a star: 1) all atoms are displaced equally towards the center of the star (Fig. S20), 2) The outer atoms are displaced twice as much as the inner atoms (this way the atoms in the star are at equal distances to their neighbors), (Fig. S21) and 3) only the inner 6 atoms in the star are displaced, to get the hexagonal shapes, similar to the ones obtained by the Monte-Carlo simulations (Fig. S22).

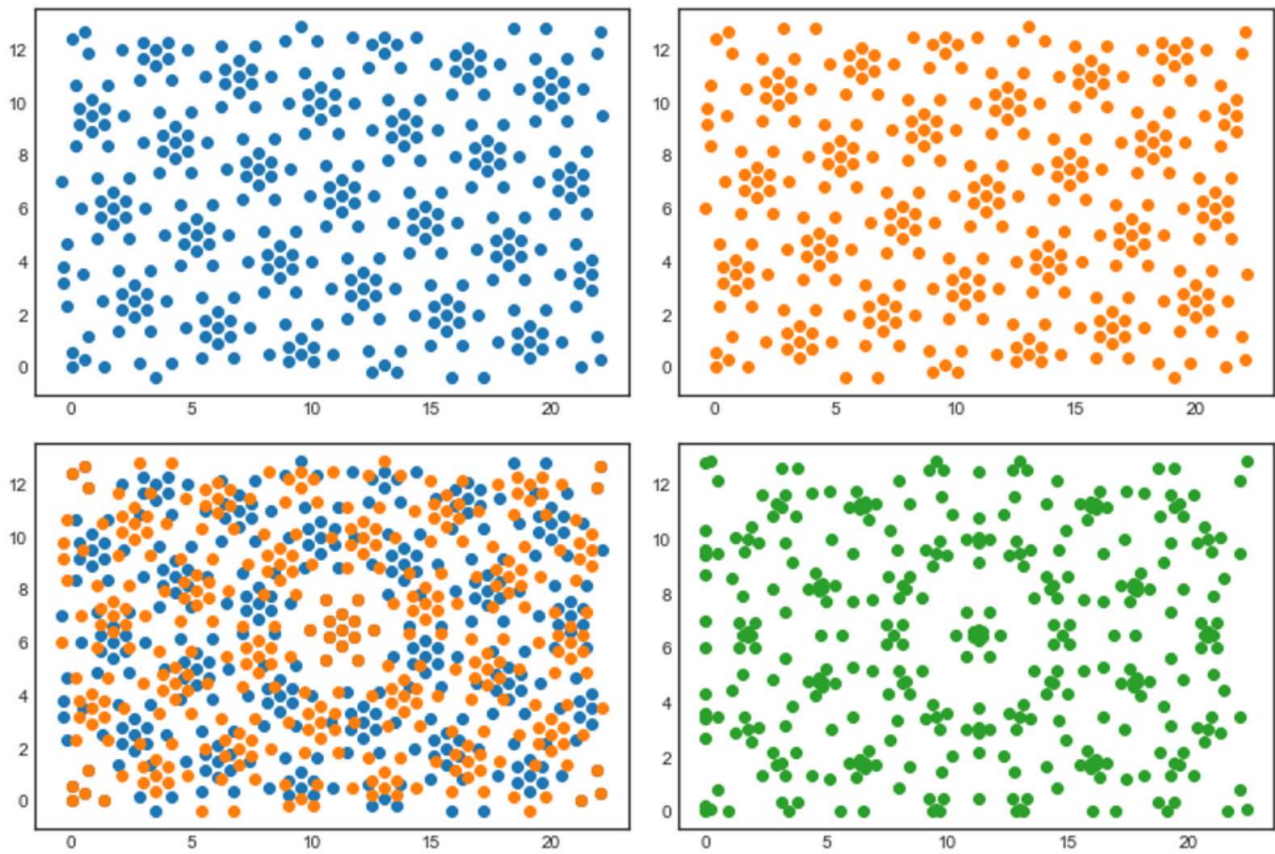


Figure S2O. Vector displacements of the atoms, where all 12 atoms are equally displaced towards the center atom, with the exaggerated displacements of 0.4 atomic unit cells. a) left-handed superlattice, b) right-handed superlattice, c) both left and right handed superlattices shown on the same plot and d) a sum of the displacements, calculated for each atom.

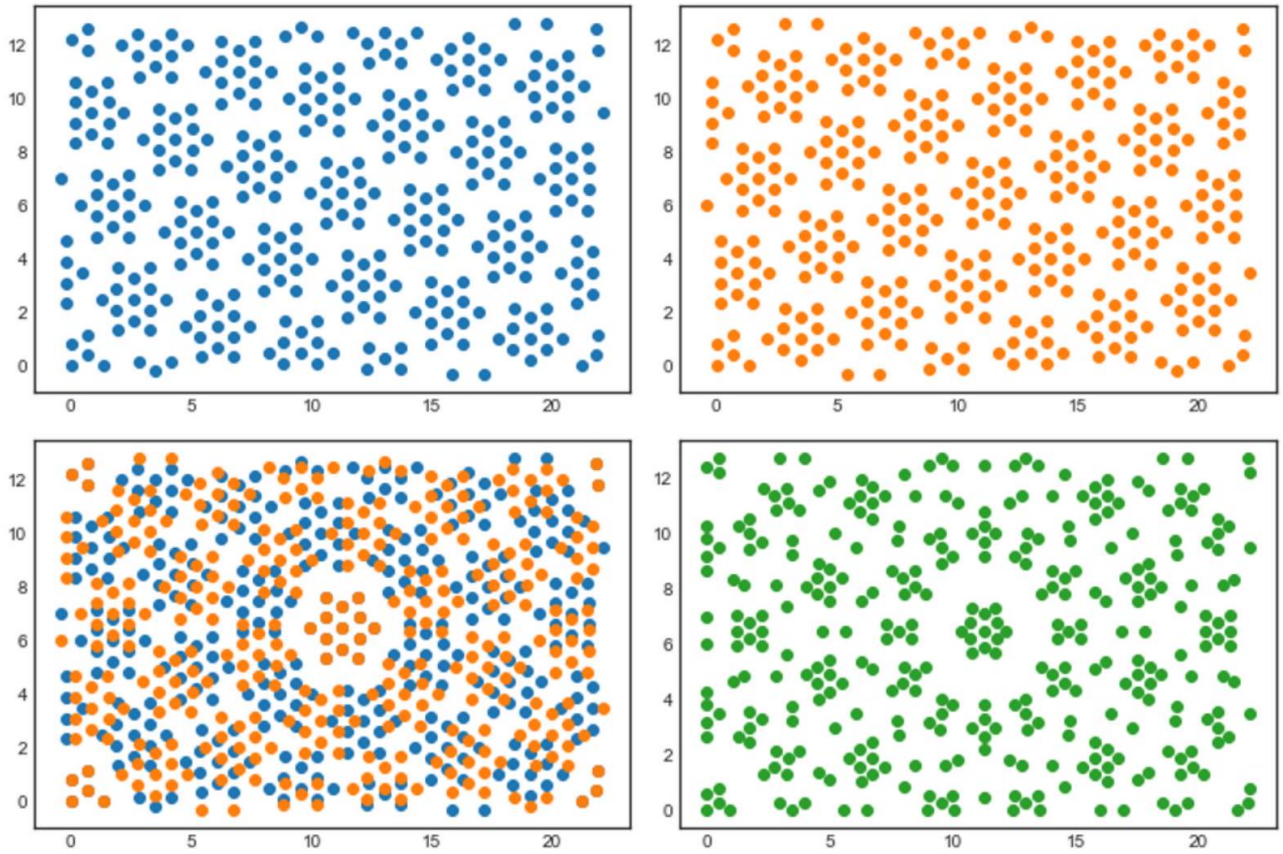


Figure S21. Vector displacements of the atoms, where the outer 6 atoms in the star are displaced twice as much as the inner atoms, for 0.4 and 0.2 atomic unit cells respectively. a) left-handed superlattice, b) right-handed superlattice, c) both left and right handed superlattices shown on the same plot and d) a sum of the displacements, calculated for each atom.

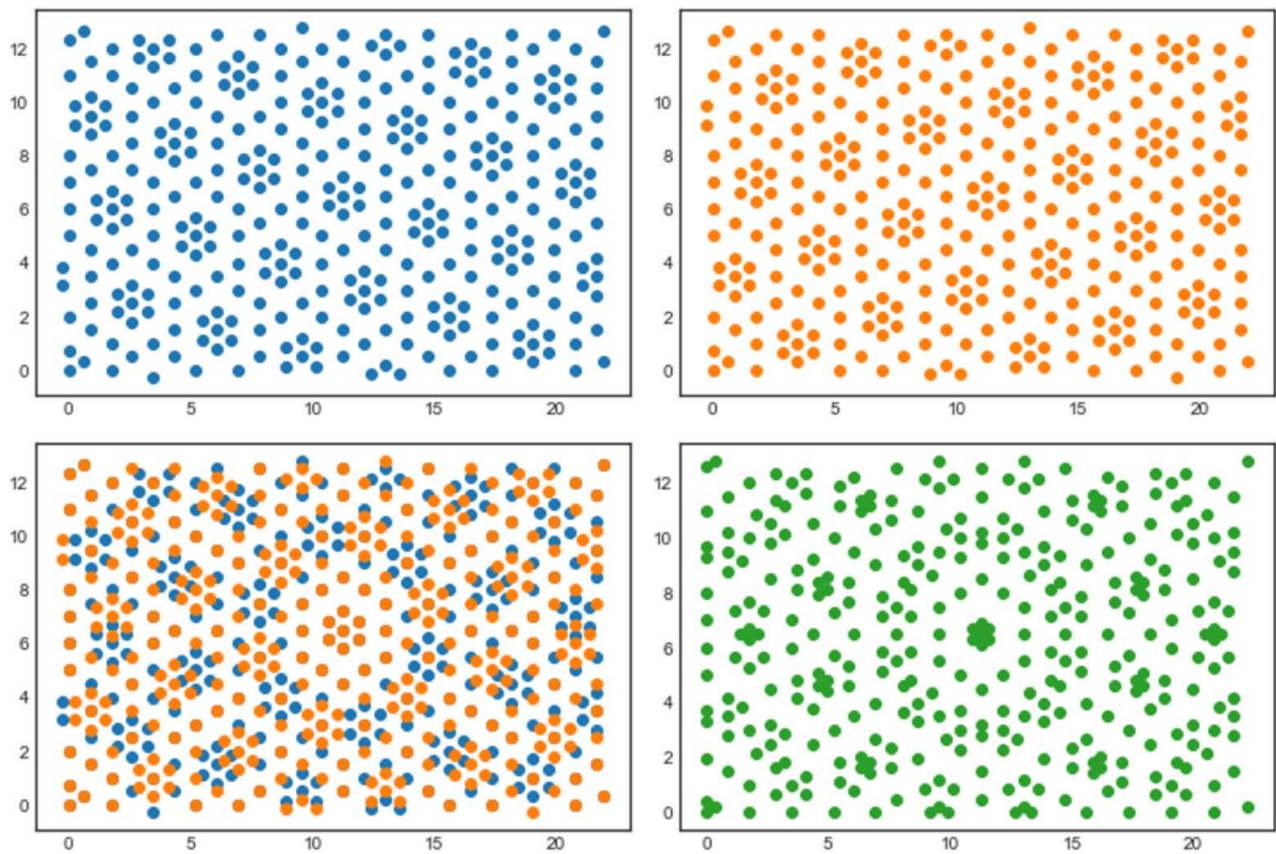


Figure S22. Vector displacements of the atoms, where only the inner 6 atoms of the star are displaced by 0.4 atomic unit cells towards the center atom, but the outer 6 stay unperturbed. a) left-handed superlattice, b) right-handed superlattice, c) both left and right handed superlattices shown on the same plot and d) a sum of the displacements, calculated for each atom.

In Fig. S23 we plot together the Monte-Carlo simulation (blue) and the vector displacement (green). By closely examining the images, we can see that the pattern is indeed very similar.

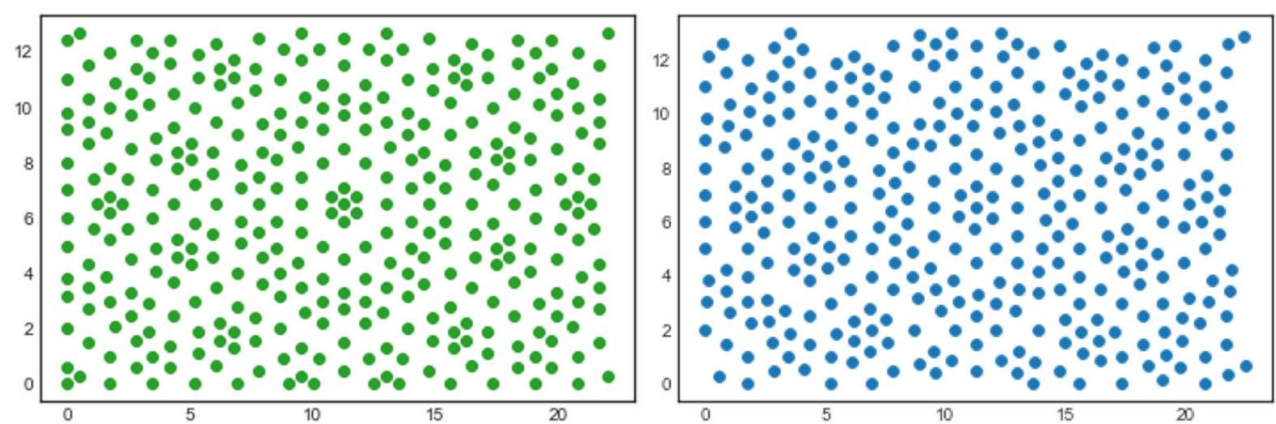


Figure S23. Comparison of the atomic displacements calculated as a vector sum of the two CDWs (the vector displacements are 0.3 atomic units for each CDW direction), shown in green, and the atomic displacements as obtained with the Monte Carlo simulation, shown in blue.

24.2 My Discussion

24.2.1 My Conclusion

24.2.2 Most Important General Questions

24.2.3 My Questions about Their Methods, Statements and Results

24.2.4 Questions about Assumed Knowledge

24.2.5 Things That I Maybe Understood Wrongly

24.2.6 Potential Future Research Directions

25 Band Structures of Transition-Metal-Dichalcogenide Layer Compounds by Mattheiss (1973)

(Jaka said that he took a value of ϵ_0 from here, I'll read it, also looks like a useful article)
(what is the $2H - NbSe_2$ Fermi-surface topology???)

Abstract

The nonrelativistic augmented-plane-wave (APW) method is applied to calculate the electronic band structures of several transition-metal-dichalcogenide (TX_2) layer compounds, including materials with the $C6$ ($1T - HfS_2$, $1T - TaS_2$), $C27$ ($2H - TaS_2$, $2H - NbSe_2$), and $C7$ ($2H - MoS_2$) structure types. These calculations involve crystal potentials that are derived from neutral-atom charge densities. The results of these calculations confirm that the group-IVB ($1T - HfS_2$) and group-VIB ($2H - MoS_2$) compounds are semiconductors; the calculated indirect band gaps of 2.7 and 1.2 eV are in reasonable agreement with the observed values of 2.0 and 1.4 eV, respectively. Metallic behavior is predicted for the intermediate group-VB compounds $1T - TaS_2$, $2H - TaS_2$, and $2H - NbSe_2$. A novel feature of the metal d bands in the $2H - TX_2$ compounds is the occurrence of a 1-eV hybridization gap within the d_{z^2} and d_{xy} , $d_{x^2-y^2}$ manifolds. This splits off a pair of hybridized d bands which are half-filled in $2H - TaS_2$ and $2H - NbSe_2$ and completely filled in $2H - MoS_2$. As a result of this hybridization gap, the valence or conduction bandwidths in each of these $2H - TXX_2$ compounds are reduced to about 1 eV.

25.0.1 I. INTRODUCTION

During the past few years, a widespread interest in the structural, optical, electrical, magnetic, and superconducting properties of the transition-metal-dichalcogenide layer compounds has evolved. These compounds have the formula TX_2 , where T is a transition-metal atom from the group IV B , VB, or VI B columns of the Periodic Table and X is one of the chalcogens, sulfur, selenium, or tellurium. The diverse physical properties of this broad class of materials have been reviewed in a recent article by Wilson and Yoffe.¹ In general, the dichalcogenides formed from the groups IVB and VI B transition-metal atoms exhibit semiconducting or insulating properties whereas the group VB compounds tend to be metallic.

Structurally, these compounds can be regarded as strongly bonded two-dimensional $X - T - X$ layers or sandwiches which are loosely coupled to one another by relatively weak Van der Waals-type forces. Within a single $X - T - X$ sandwich, the T and X atoms form two-dimensional hexagonal arrays. Depending on the relative alignment of the two X -atom sheets within a single $X - T - X$ sandwich, two distinct two-dimensional crystal structures are obtained.

In one, the metal atoms are octahedrally coordinated by six neighboring X atoms, whereas in the other, the coordination of the metal atoms is trigonal prismatic.

Variations in the stacking sequence and registry of successive $\mathbf{X}-\mathbf{T}-\mathbf{X}$ sandwiches along the hexagonal c axis lead to a large number of crystal structures or polytypes in three dimensions. These are referred to as the $1T$, $2H$, $3R$, $4Ha$, $4Hb$, and $6R$ phases. In this abbreviated notation, the integer indicates the number of $\mathbf{X}-\mathbf{T}-\mathbf{X}$ sandwiches per unit cell along the hexagonal c axis and T , H , and

R denote trigonal, hexagonal, and rhombohedral symmetries, respectively. The $1T$ phase contains $\mathbf{X}-\mathbf{T}-\mathbf{X}$ sandwiches in which the metal atoms are octahedrally coordinated, whereas the coordination is trigonal prismatic in the $2H$, $3R$, and $4Ha$ phases. In the $4Hb$ and $6R$ polytypes, the coordination within successive sandwiches alternates between octahedral and trigonal prismatic.

It is not surprising that the physical properties of these layer compounds are dominated by these two-dimensional structural characteristics. For example, it is found that single crystals usually grow in the form of thin platelets, and these are readily cleaved to yield samples that are only a few hundred angstroms thick along the c axis. Electrical and thermal conductivities are found to be significantly lower along the c axis than they are within the basal plane. One can often prepare intercalation compounds of the form A_xTX_2 , where A is an atom or molecule which occupies the interstitial sites between neighboring $\mathbf{X}-\mathbf{T}-\mathbf{X}$ sandwiches. The semiconducting group IVB and VIB compounds are found to exhibit metallic conductivity when intercalated with alkali atoms. The metallic group VB compounds can often be intercalated with organic molecules. Depending on their size, these molecules can increase the interlayer separations by as much as 50Å. Most of these metallic compounds superconduct at low temperatures, even when the layers are separated by these organic spacers.

Several semiempirical band-structure and ligand-field models have been proposed to describe the electronic states in these TX_2 layer compounds. Wilson and Yoffe¹ have proposed schematic energy-band models for several groups of TX_2 compounds. Relying heavily on systematic trends that are observed in the optical data, they

estimate valence and conduction bandwidths and band gaps, and correlate these with the observed electrical and structural properties. In a recent series of papers, Bromley, Murray, and Yoffe²⁻⁶ have applied a semiempirical tight-binding method³ to calculate the band structures for several groups of compounds, including the octahedrally coordinated $1T-TX_2$ compounds ($T = \text{Ti, Zr, Hf}; X = \text{S, Se, Te}$)^{4,6} as well as the trigonal-prismatic $2H-TX_2$ group VI B compounds ($T = \text{Mo, W}; X = \text{S, Se, Te}$).^{2,5} The calculations for the $2H$ compounds were carried out in a two-dimensional approximation, though some estimates of interlayer interactions were made in the case of $2H-\text{MoS}_2$. Edmondson⁷ has carried through a similar calculation for $2H-\text{MoS}_2$ in the two-dimensional limit. On the other hand, Goodenough⁸ and Huisman et al.⁹ have utilized the ligand-field or molecular-orbital approach to derive schematic energy-band models for several of these layer-type compounds.

The purpose of the present investigation is to apply the augmented-plane-wave (APW) method to determine the electronic energy bands for several of the less complicated TX_2 polytypes and to compare these results with the experimental data as well as the earlier semiempirical band models. This study involves four TX_2 compounds with three different crystal structures, including compounds with the C6 ($1T-\text{HfS}_2$, $1T-\text{TaS}_2$), C27 ($2H-\text{TaS}_2$, $2H-\text{NbSe}_2$), and C7 ($2H-\text{MoS}_2$) structure types in the "Strukturbericht" classification. Unlike the earlier calculations,²⁻⁷ the present investigation utilizes no empirical results other than the crystal-structure data. The present APW calculations involve approximate crystal potentials that are derived from neutral-atom charge densities. They include corrections to the muffin-tin potential in the unit cell volume that lies outside the APW spheres. A brief summary of the present APW results for $2H-\text{NbSe}_2$ and $2H-\text{MoS}_2$ has been reported in an

earlier publication.¹⁰

The present paper is divided into six sections. In Sec. II we review the physical properties of the various compounds that are considered in this investigation. The computational details of the present study are described in Sec. III, and the APW results are presented in Sec. IV. The APW results for the metal-atom d bands are analyzed in Sec. V in terms of a tight-binding model. Section VI includes a discussion of these results as well as a comparison with experiment. It also contains some comments on previous band and ligand-field models for these compounds.

TABLE I. Atom positions in the $1T - TX_2$ and $2H - TX_2$ layer compounds.

C6 structure type (D_{3d}^3); $1T - \text{HfS}_2$ (ξ, η, ζ) _{Hf} = (0, 0, 0) (ξ, η, ζ) _S = $\pm (\frac{1}{3}, \frac{2}{3}, z)$, $z \sim \frac{1}{4}$.
C27 structure type (D_{6h}^4); $2H - \text{TaS}_2$ (ξ, η, ζ) _{Ta} = $\pm (0, 0, \frac{1}{4})$ (ξ, η, ζ) _S = $\pm (\frac{1}{3}, \frac{2}{3}, z)$ $\pm (\frac{1}{3}, \frac{2}{3}, \frac{1}{2} - z)$, $z \sim \frac{1}{8}$
C7 structure type (D_{6h}^4); $2H - \text{MoS}_2$ (ξ, η, ζ) _{Mo} = $\pm (\frac{1}{3}, \frac{2}{3}, \frac{1}{4})$ (ξ, η, ζ) _S = $\pm (\frac{1}{3}, \frac{2}{3}, z - 1)$ $\pm (\frac{1}{3}, \frac{2}{3}, \frac{1}{2} - z)$, $z \sim \frac{5}{8}$

25.0.2 II. PHYSICAL PROPERTIES

The $1T - TX_2$ and $2H - TX_2$ layer compounds that are involved in this investigation have the $D_{3d}^3(P\bar{3}m1)$ and $D_{6h}^4(P6_3/mmc)$ space groups, respectively. Although the D_{3d}^3 space group belongs to the trigonal system, the Bravais lattice is hexagonal for both space groups. Following Slater,¹¹ we choose the primitive vectors that generate the hexagonal lattice as

$$\vec{t}_1 = \frac{1}{2}a(\sqrt{3}\hat{i} - \hat{j}), \quad \vec{t}_2 = a\hat{j}, \quad \vec{t}_3 = c\hat{k}, \quad (1)$$

so that an arbitrary vector $\vec{r}$ can be written in the form $\vec{r} = \xi \vec{t}_1 + \eta \vec{t}_2 + \zeta \vec{t}_3$. Using this coordinate system, we list in Table I the position coordinates of the T and X atoms in the corresponding unit cells for the $C6$, $C27$, and $C7$ crystal structures. The symmetric primitive unit cells are illustrated in Fig. 1. These are drawn approximately to scale, using the observed values for the lattice parameters that are listed in Table II. It is noted that crystal-structure refinements have been carried out only in a few cases so that precise values for the positional parameter z are generally unavailable.

It is emphasized that these crystal structures represent the high-temperature phases, particularly in the case of the metallic group-VB compounds. Recent data that are summarized below indicate the occurrence of low-temperature phase transitions in most of the metallic group-VB compounds. Furthermore, large variations are often found to exist in the results of independent latticeparameter determinations for the same compound. These are due, presumably, either to deviations from perfect stoichiometry or to the coexistence of several phases in at least some samples.

A. $1T - \text{HfS}_2$

Based on a simple ionic model, it is reasonable to anticipate that the TX_2 compounds involving the group-IV B transition-metal atoms would be semiconductors or insulators in which the fundamental band gap separates the filled X -atom p bands and the empty T -atom d -band states. Among the group-IV B compounds, $1T - \text{HfS}_2$ is an example of

one such material that can be prepared with sufficient stoichiometry to allow an electrical determination of the intrinsic gap. From the temperature dependence of the resistivity, Conroy and Park¹² infer a 2.1-eV gap for $1T - \text{HfS}_2$ that is in good agreement with the 1.95-eV indirect optical gap that is reported by Greenaway and Nitsche.¹³ The latter also observe structure in the reflectivity between 3 and 10 eV. Similar structure has also been observed in transmission spectra^{1,14} below 6 eV.

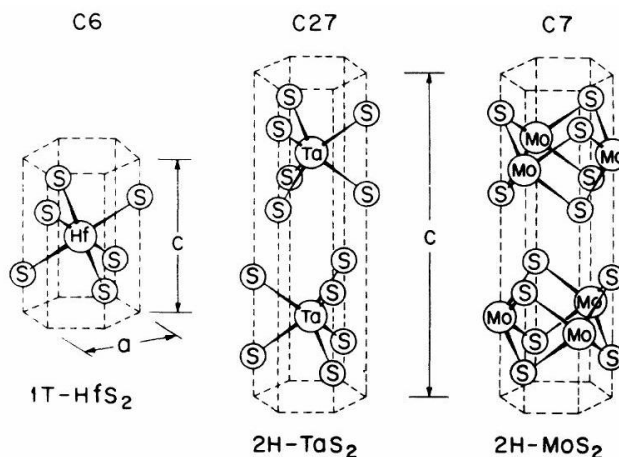


FIG. 1. Symmetric unit cells for the C6 ($1T - \text{HfS}_2$), C27 ($2H - \text{TaS}_2$), and C7 ($2H - \text{MoS}_2$) crystal structures.

B. $1T - \text{TaS}_2$

If this band model is extended to the group- VB compounds, then it predicts that metallic behavior will result from the added electron that now partially fills the T -atom d bands. It is found that the $1T - \text{TaS}_2$ polytype is stable only at temperatures above 1050°K . However, this phase can be maintained at lower temperatures by quenching. Resistivity measurements¹⁵ show that $1T - \text{TaS}_2$ is metallic above 350°K . They reveal that a metalinsulator transition occurs at about 350°K and that a second transition, involving two semiconducting phases, takes place near 190°K . Anomalies in the magnetic susceptibility are also reported¹⁶ at these temperatures. Estimates of the activation energy below the metal-insulator transition range from 0.02^{15} to 0.1eV .¹⁷ Recent photoemission studies¹⁸ indicate that the occupied portion of the tantalum $5d$ conduction band is about 1.5 eV wide and the sulfur $3p$ valence bandwidth is $6 - 7\text{eV}$.

Wilson and Yoffe¹ were the first to suggest semiconducting behavior for $1T - \text{TaS}_2$ at room temperature. They observed that the optical transmission tends to rise rather than fall off at photon energies below 1 eV . Recent room-temperature electron diffraction studies¹⁹ reveal the presence of a superlattice in $1T - \text{TaS}_2$. It is believed¹⁵ that the early reports^{1,20} of superconductivity in $1T - \text{TaS}_2$ below 0.8°K are due to mixed-phase ($1T$ and $2H$) samples.

C. $2H - \text{TaS}_2$

In contrast to the $1T$ phase, $2H - \text{TaS}_2$ remains metallic at low temperatures and becomes superconducting below 0.8°K . Heat-capacity measurements²¹ below 10°K yield an electronic contribution $\gamma = 8.5\text{ mJ/mole}^\circ\text{K}^2$. When organic molecules such as pyridine (py) are introduced between the S-Ta-S sandwiches to form the intercalation compound $2H - \text{TaS}_2(\text{py})_{1/2}$, the system remains metallic and the superconducting transition temperature is raised to 3.5°K . The heat capacity γ 's for the intercalated compounds are found to increase by $5 - 10\%$.²¹ Thompson et al.²² have measured the resistivity, magnetic susceptibility, and Hall effect in $2H - \text{TaS}_2$. They observe anomalies in these properties at about 70°K , and these are attributed to a phase transition.

D. $2H - \text{NbSe}_2$

Evidence for low-temperature phase transitions have also been observed in $2H - \text{NbSe}_2$. Lee et al.²³ have observed a peak in the susceptibility and a sign reversal in the Hall coefficient near $T \approx 40^\circ\text{K}$ which they attribute to antiferromagnetic ordering. Subsequent nuclear-magnetic-resonance (NMR) studies by Ehrenfreund et al.²⁴ rule out the existence of magnetic ordering below 40°K but suggest rather that a change in crystal structure has occurred, since they find evidence for the existence of two inequivalent niobium sites below 40°K . The results of x-ray studies by Marezio et al.²⁵ at 15°K are consistent with the room-temperature structure. However, they are also compatible with a distorted structure that involves a slight displacement of the niobium atoms, and this distorted

TABLE II. Structure parameters for TX_2 layer compounds.

Type	TX_2	a (Å)	c (Å)	z
1T	HfS ₂	3.635 ^a	5.837 ^a	...
	TaS ₂	3.365 ^b	5.853 ^b	...
2H	TaS ₂	3.316 ^b	12.070 ^b	...
	NbSe ₂	3.440 ^c	12.482 ^c	0.1163 ^c
2H	MoS ₂	3.160 ^d	12.294 ^d	0.621 ^e

structure is consistent with the NMR results.

Superconductivity is observed below 7.0°K in $2H - \text{NbSe}_2$, and heat-capacity measurements²⁶ yield $\gamma = 20.5 \text{ mJ/ mole } ^\circ\text{K}^2$, or about twice the value for $2H - \text{TaS}_2$. From these superconductivity and heat-capacity data, it is estimated²⁷ that the phonon enhancement factor $(1 + \lambda) \approx 1.6$. Photoemission studies¹⁸ indicate an occupied niobium $4d$ conduction bandwidth of less than 0.7 eV and a selenium $4p$ valence bandwidth of $6 - 7 \text{ eV}$. From a study of the optical anisotropy in $2H - \text{NbSe}_2$, Liang²⁸ has determined a rough estimate of the free-carrier mass anisotropy. He finds roomtemperature mass ratios of 5.3 and 3.4 for electron motion parallel and perpendicular to the hexagonal c axis, respectively.

E. $2H - \text{MoS}_2$

Although most crystals of the TX_2 layer-type compounds are synthetic, natural MoS₂ crystals with the $2H$ and $3R$ phases are quite common. In 1923, Dickinson and Pauling²⁹ first determined the crystal structure of $2H - \text{MoS}_2$, the mineral molybdenite. Along with the other group-VI B layer compounds, $2H - \text{MoS}_2$ samples exhibit semiconducting behavior. There is some disagreement concerning the magnitude of the band gap in $2H \text{ MoS}_2$. Wilson and Yoffe¹ attribute a weak indirect edge at 0.2 eV to the semiconducting energy gap. Huisman, DeJonge, Haas, and Jellinek (HDHJ)⁹ believe that this $0.2 - \text{eV}$ structure is extrinsic and propose that the intrinsic gap in $2H - \text{MoS}_2$ is about 1.4 eV . Recent photoemission studies^{18,30} suggest that this gap is at least 1 eV . The low-energy optical properties of $2H - \text{MoS}_2$ (as well as the other group-VIB compounds) are dominated by a pair of sharp exciton lines. In $2H - \text{MoS}_2$, these occur at about 2 eV and are separated by about 0.2 eV .^{1,31}

Information about the states near the top of the valence band in $2H - \text{MoS}_2$ has been provided by electron paramagnetic resonance studies on Asdoped samples.³² These results

^{0a} F. K. McTaggart and A. B. Wadsley, Aust. J. Chem. 11, 445 (1958).

^b Reference 17.

^c Reference 25.

^d J. C. Wilderwanck and F. Jellinek, Z. Anorg. Allgem. Chem. 328, 309 (1964).

^e Reference 29.

suggest that the holes near the valence-band edge involve molybdenum $4d$ wave functions with d_{z^2} symmetry. Somoano et al.³³ find that the intercalation compounds which are formed by adding alkali-metal atoms to $2H - \text{MoS}_2$ are both metallic and superconducting, with transition temperatures as high as 6.5°K .

25.0.3 III. COMPUTATIONAL DETAILS

APW programs that were developed earlier for the hexagonal-close-packed (hcp) structure³⁴ have been modified in this investigation to handle a variety of binary hexagonal compounds, including those with the C6, C27, and C7 crystal structures. The C27 and C7 structures have the same nonsymmorphic space group (D_{6h}^4) as the hcp structure, so in these cases, the program modification involves primarily changes in the number and location of the atoms in the unit cell. The space group for the C6 crystal structure is symmorphic (D_{3d}^3) and includes those symmetry operations in D_{6h}^4 that do not involve nonprimitive translations.¹¹ Thus, by omitting this class of symmetry operations, one can easily treat the C6 structure as a special case of the D_{6h}^4 space group.

As noted previously,³⁴ the fact that each of the crystal structures which is considered here has an inversion center helps to simplify the APW calculation considerably. If one chooses the origin of coordinates so that it coincides with the inversion center, then the APW energy-overlap matrix can be set up so that it is real rather than complex. With this choice, the structure factors $e^{i\vec{\mathbf{r}}_n \cdot \vec{\mathbf{k}}}$ that occur in the APW matrix³⁵ reduce either to 1 or $2 \cos \vec{\mathbf{k}} \cdot \vec{\mathbf{r}}_n$, depending on whether the atomic position vector $\vec{\mathbf{r}}_n$ is at the origin or not.

In each of the $1T$ and $2H$ phases, the X -atom sites have C_{3v} point symmetry. The symmetry of the T -atom sites is different in the $1T$ and $2H$ phases. In $1T - \text{HfS}_2$, the Hf sites have D_{3d} symmetry, whereas in $2H - \text{TaS}_2$ and $2H - \text{MoS}_2$, the Ta and Mo sites both have D_{3h} symmetry. It is noted that the $C6 (1T - \text{TX}_2)$ phase coincides with the NiAs structure (which also has the D_{6h}^4 space group) if a second T atom is inserted in the Van der Waals gap at $\vec{\mathbf{r}}_n = (0, 0, \frac{1}{2})$ and $z = \frac{1}{4}$. The partial filling of these sites produces Phillips's "bridge" compounds.³⁶

The present APW calculations involve ad hoc crystal potentials that are derived from the Har-tree-Fock-Slater atomic charge densities of Herman and Skillman.³⁷ In each case, the atomic configuration of the metal and chalcogen atoms are assumed to be $d^n s^1$ and $s^2 p^4$, respectively. Slater's original³⁸ free-electron exchange approximation is used. The methods for calculating the muffintin potentials and treating the muffin-tin corrections in the region outside the APW spheres are analogous to those applied previously in similar calculations for ReO_3 ,³⁹ the $3d$ monoxides,⁴⁰ and several perovskite-type compounds.⁴¹

The values assumed for the metal- and chalcogen-atom APW sphere radii (R_T and R_X , respectively) are listed in Table III, along with the observed (or assumed) values for the positional parameter z . As in the earlier calculations,³⁹⁻⁴¹ the values for R_T and R_X are chosen so that the T - and X -atom spheres touch along the nearestneighbor direction and $R_T/R_X \approx \frac{7}{6}$. It is found that this choice optimizes the convergence of both the T -atom d and the X -atom p energy-band states³⁵ and minimizes the corrections to the muffin-tin potential in the region between the APW spheres. This table includes an entry for a hypothetical form

^a Hypothetical compound in which the c axis is expanded from ~ 12.5 to $15.5\text{\AA}$ to simulate intercalation.

of $2H - \text{NbSe}_2$ in which the c lattice parameter has been expanded by about $3\text{\AA}$ to simulate in a very crude way the effects of intercalation.

In Table IV we summarize the sandwich heights, interlayer distances, and $T - T$, $X - X$, and $T - X$ bond lengths in these compounds. Here, it is shown that the parameter z for the hypothetical form of $2H \text{ NbSe}_2$ in Table III is such that the sandwich height is unchanged and the interlayer separation is increased by about $1.5\text{\AA}$. We note that the intralayer X -atom bond

TABLE III. APW sphere radii for TX_2 layer compounds.

Type	TX_2	z	R_T (a.u.)	R_X (a.u.)
1T	HfS ₂	0.25	2.60	2.23
	TaS ₂	0.25	2.47	2.12
2H	TaS ₂	0.118	2.53	2.17
	NbSe	0.1163	2.64	2.26
	NbSe ₂ ^a	0.1423	2.64	2.26
2H	MoS ₂	0.621	2.46	2.11

lengths are not equal, so unlike the earlier band calculations,^{4–6} the octahedral or trigonal-prismatic coordination of the metal atoms is slightly distorted rather than "ideal"

The only new feature of the present APW calculations is that they exploit the approximate linear dependence of the logarithmic derivatives on energy for $l \geq 4$ to simplify the APW programs and increase their computational efficiency.³⁵ Test calculations that apply this linear fit over a 1.6 Ry energy range demonstrate that this approximation yields energy eigenvalues that agree with the standard APW results to better than four decimal places.

The reciprocal lattice vectors for the hexagonal lattice generated by Eq. (1) are given by

$$\vec{b}_1 = (2/\sqrt{3}a)\hat{i}, \quad \vec{b}_2 = (1/\sqrt{3}a)(\hat{i} + \sqrt{3}\hat{j}), \quad \vec{b}_3 = (1/c)\hat{k}. \quad (2)$$

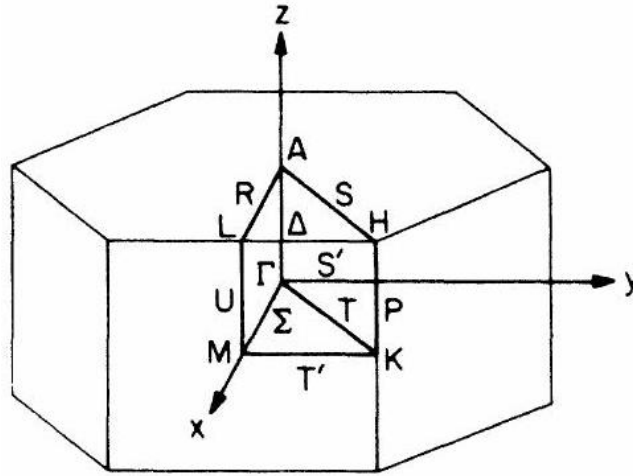


FIG. 2. Brillouin zone for the hexagonal Bravais lattice with symmetry points and lines labeled according to the standard notation.

An arbitrary lattice vector in k space can be written

$$\vec{K}_n = 2\pi \left(n_1 \vec{b}_1 + n_2 \vec{b}_2 + n_3 \vec{b}_3 \right), \quad (3)$$

where the n_i are integers. The corresponding Brillouin zone is shown in Fig. 2, where the symmetry points and lines are labeled in accordance with Herring's notation.⁴² The scale of the Brillouin zone shown in Fig. 2 corresponds roughly to the c/a ratio for 1T – HfS₂. The corresponding dimensions along the z axis are reduced by about a factor of 2 for the 2H compounds.

As in previous APW calculations for transitionmetal compounds,^{39–41} the scope of the present study has been limited to high-symmetry points in the Brillouin zone by the large

number of APW basis functions that are required to achieve adequate convergence of the energy eigenvalues. The present calculations for the $1T - TX_2$ and $2H - TX_2$ compounds include approximately 160 and 280 APW basis functions, respectively. It is estimated that these yield energy-band results which are converged to within a few thousandths of a rydberg. The maximum dimensions for the symmetrized APW matrix was arbitrarily set at 60×60 , and this proved to be sufficient to achieve satisfactory convergence at the six symmetry points in the

TABLE IV. Tabulation of sandwich heights, interlayer distances, and bond lengths (Å) in TX_2 layer compounds.

Type	TX_2	Sandwich height	Interlayer distance	$d(T - X)$	Intralayer $d(X - X)$	$d(T - T) =$
1T	HfS ₂	2.92	2.92	2.56	3.60	3.64
	TaS ₂	2.93	2.93	2.43	3.51	3.37
2H	TaS ₂	3.19	2.85	2.49	3.19	3.32
	NbSe ₂	3.34	2.90	2.59	3.34	3.44
	NbSe ₂ ²	3.34	4.41	2.59	3.34	3.44
2H	MoS ₂	3.17	2.98	2.42	3.17	3.16

Brillouin zone (Γ, M, K, A, L , and H). One exception involves the L_1 states in the $2H$ compounds, where convergence errors could be as large as 0.01 Ry . Limited calculations were performed along symmetry lines. These usually involved fewer than the optimum number of APW basis functions, especially in the ALH plane where only a subgroup of the full wave-vector group is utilized in the symmetrized calculations.³⁴

The character tables for the D_{6h}^4 space group were first worked out by Herring.⁴² Slater¹¹ has tabulated the irreducible representations for both the D_{3d}^3 and D_{6h}^4 space groups. In the case of the D_{6h}^4 space group, Slater's notation agrees with that of Herring if the H_2 and H_3 irreducible representations are interchanged. The present notation includes this interchange and is therefore consistent with Herring's original notation.

The D_{6h}^4 space group is nonsymmorphic. With the origin of coordinates at the inversion center,¹¹ those space-group operations $\{\alpha | \vec{R}_n\}$ whose rotational parts α are included in the D_{3d} point group are associated only with primitive translations $\vec{R}_n = n_1 \vec{t}_1 + n_2 \vec{t}_2 + n_3 \vec{t}_3$, where n_i are integers and the $\vec{t}_i$ are given by Eq. (1). The remaining twelve space-group operations have the form $\{\alpha | \vec{R}_n + \vec{\tau}\}$, where the nonprimitive translation $\vec{\tau} = \frac{1}{2}\vec{t}_3 = \frac{1}{2}c\hat{k}$. For ease in programming the symmetrized APW method so that it can be applied to both the D_{3d}^3 and D_{6h}^4 space groups, it is convenient to order these symmetry operations in such a way that the twelve D_{3d} point-group operations have odd indices and the remaining operations have even indices. One can then arrange to include or skip the even operations, and thereby treat either the D_{6h}^4 or D_{3d}^3 space groups in a systematic manner.

The notation adopted here for the D_{3d}^3 irreducible representations is identical with that of Murray et al.⁴ This notation coincides with that introduced by Fong and Cohen⁴³ if the + superscripts are ignored and the - superscripts are replaced by primes.

Using standard group-theoretical techniques, we have determined the symmetry properties of Bloch sums formed from s, p , and d orbitals localized about the T and X sites in both the $1T - TX_2$

and $2H - TX_2$ compounds. The results of this analysis at the six symmetry points in the Brillouin zone are included in Table V. For each structure, we identify the appropriate

^{0a} See Ref. a in Table III.

TABLE V. Symmetry properties of Bloch sums formed from s, p , and d orbitals at the metal and sulfur sites in $1T - \text{HfS}_2$, $2H - \text{TaS}_2$, and $2H - \text{MoS}_2$.

(a) $1T - \text{HfS}_2$	Γ	M	K	A	L	H
Hf s	1^+	1^+	1	1^*	1^+	1
p_z	2^-	2^-	2	2^-	2^-	2
p_x, p_y	3^-	$1^-, 2^-$	3	3^-	$1^-, 2^-$	3
d_{z^2}	1^+	1^+	1	1^+	1^+	1
$d_{xy}, d_{x^2-y^2}$	3^+	$1^+, 2^+$	3	3^+	$1^+, 2^+$	3
d_{xz}, d_{yz}	3^+	$1^+, 2^+$	3	3^+	$1^+, 2^+$	3
S s	$1^+, 2^-$	$1^+, 2^-$	3	$1^+, 2^-$	$1^+, 2^-$	3
p_z	$1^+, 2^-$	$1^+, 2^-$	3	$1^+, 2^-$	$1^+, 2^-$	3
p_x, p_y	$3^+, 3^-$	$1^\pm, 2^\pm$	1, 2, 3	$3^+, 3^-$	$1^\pm, 2^\pm$	1, 2, 3
(b) $2H - \text{TaS}_2$						
Ta s	$1^+, 4^-$	$1^+, 2^-$	1, 3	1	1	1
p_g	$3^+, 2^-$	$3^+, 4^-$	2, 4	1	1	1
p_x, p_y	$5^+, 6^-$	$1^+, 4^+, 2^-, 3^-$	5, 5	3	1, 2	2, 3
d_{z^2}	$1^+, 4^-$	$1^+, 2^-$	1, 3	1	1	1
$d_{xy}, d_{x^2-y^2}$	$5^+, 6^-$	$1^+, 4^+, 2^-, 3^-$	5, 5	3	1, 2	2, 3
d_{xz}, d_{yz}	$6^+, 5^-$	$2^+, 3^+, 1^-, 4^-$	6, 6	3	1, 2	2, 3
S s	$1^+, 3^+, 2^-, 4^-$	$1^+, 3^+, 2^-, 4^-$	5, 6	1, 1	1, 1	2, 3
p_z	$1^+, 3^+, 2^-, 4^-$	$1^+, 3^+, 2^-, 4^-$	5, 6	1, 1	1, 1	2, 3
p_x, p_y	$5^\pm, 6^\pm$	$1^\pm, 2^\pm, 3^\pm, 4^\pm$	1, 2, 3, 4, 5, 6	3, 3	1, 1, 2, 2	1, 1, 2, 3
(c) $2H - \text{MoS}_2$						
Mo s	$1^+, 4^-$	$1^+, 2^-$	5	1	1	3
p_g	$3^+, 2^-$	$3^+, 4^-$	6	1	1	2
p_x, p_y	$5^+, 6^-$	$1^+, 4^+, 2^-, 3^-$	1, 3, 5	3	1, 2	1, 2
d_{z^2}	$1^+, 4^-$	$1^+, 2^-$	5	1	1	3
$d_{xy}, d_{x^2-y^2}$	$5^+, 6^-$	$1^+, 4^+, 2^-, 3^-$	1, 3, 5	3	1, 2	1, 2
d_{xz}, d_{yz}	$6^+, 5^-$	$2^+, 3^+, 1^-, 4^-$	2, 4, 6	3	1, 2	1, 3
S s	$1^+, 3^+, 2^-, 4^-$	$1^+, 3^+, 2^-, 4^-$	5, 6	1, 1	1, 1	2, 3
p_z	$1^+, 3^+, 2^-, 4^-$	$1^+, 3^+, 2^-, 4^-$	5, 6	1, 1	1, 1	2, 3
p_x, p_y	$5^\pm, 6^\pm$	$1^\pm, 2^\pm, 3^\pm, 4^\pm$	1, 2, 3, 4, 5, 6	3, 3	1, 1, 2, 2	1, 1, 2, 3

irreducible representation by its subscript. Thus, the entries 1^* and 2^- at the point M denote the M_{1+} and M_{2-} irreducible representations, respectively. Duplicate entries indicate that the same representation occurs twice within a given set of Bloch functions. Since the D_{3d}^3 and D_{6h}^4 space groups contain a unique z axis, we subdivide the p functions into those with p_g and p_x, p_y symmetry. In the case of the d functions, a similar separation results in three groups, including (a) d_{z^2} ; (b) $d_{xy}, d_{x^2-y^2}$; (c) d_{xz}, d_{yz} . These results are useful for identifying the atomic symmetry of particular bands or groups of bands in the following sections.

25.0.4 IV. APW RESULTS

A. $1T - \text{HfS}_2$ and $1T - \text{TaS}_2$

The APW results for the $1T$ -phase HfS_2 and TaS_2 compounds are shown in Figs. 3 and 4, respectively. The results of the APW calculations are indicated with open circles and the band profiles are rough estimates that are determined to a large extent by the compatibility

relations.⁴³ In both compounds, the lower group of six bands are derived primarily from the sulfur $3p$ orbitals. In $1T - \text{HfS}_2$, these are separated by an $0.2 - \text{Ry}$ gap from the empty hafnium $5d$ bands. The dashed bands in the upper portion of Fig. 3 correspond to the bottom of the hafnium $6s - 6p$ bands. A similar ordering of bands is found in $1T - \text{TaS}_2$, though in this case, the $3p - 5d$ band separation is reduced

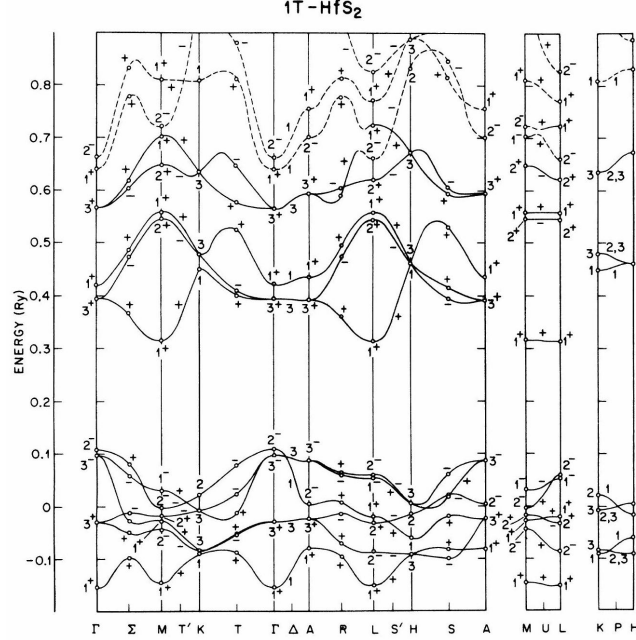


FIG. 3. APW energy-band results (open circles) for $1T - \text{HfS}_2$. Energies are relative to the muffin-tin constant, $V_0 = -0.842\text{Ry}$.

to about 0.1 Ry and the Fermi-level (indicated by the dashed horizontal line) now lies in the lower portion of the tantalum $5d$ bands. The energy scale for these (as well as the following) results is such that the muffin-tin constant is zero.

It is found that the $5d$ bands in these octahedrally coordinated compounds are split into nonoverlapping subbands. Based on tight-binding arguments that are described in Sec. V, we identify the $5d$ orbitals associated with the lower triply degenerate subband as those with d_{x^2} , d_{xy} , and $d_{x^2-y^2}$ type symmetry and refer to this lower manifold as the t_{2g} subband. Because of the close proximity of the dashed metal $6s - 6p$ bands in Figs. 3 and 4, hybridization effects blur the actual width of the upper doubly degenerate e_g subband formed from the d_{xg} and d_{yg} orbitals. We arbitrarily associate the lowest states with the correct symmetry to these d_{xg} and d_{yg} orbitals. This leads to t_{2g} (e_g) bandwidths of 0.25 (0.15) and 0.30 (0.20) Ry in $1T - \text{HfS}_2$ and $1T - \text{TaS}_2$, respectively. The larger sulfur $3p$ and tantalum $5d$ bandwidths in $1T \text{ TaS}_2$ are due undoubtedly to increased overlapcovalency effects that result from the smaller lattice parameter in the basal plane (see Table II).

The differences between the energy-band results in the ΓMK and ALH planes in Figs. 3 and 4 are due to interlayer interactions. Within the sulfur $3p$ and metal $5d$ manifolds, these bandwidths are usually less than 0.05 Ry . Two noticeable exceptions involve the bands joining the Γ_{2-} , A_{2-} , and Γ_{1+} , A_{1+} states within the $3p$ manifold. This is not surprising, since according to Table V, these states correspond to sulfur p_g orbitals for which significant interlayer coupling is expected.

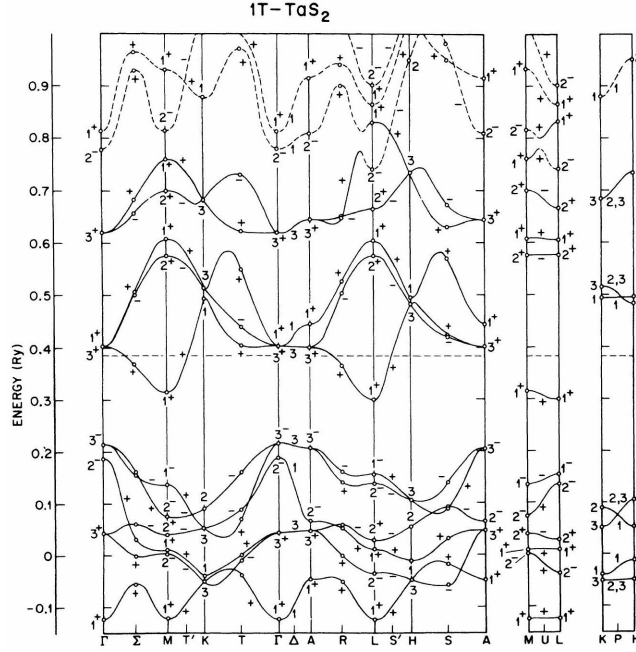


FIG. 4. APW results for $1T - \text{TaS}_2$, where $V_0 = -0.945\text{Ry}$.

B. $2H - \text{NbSe}_2$ and $2H - \text{TaS}_2$

The corresponding APW results for the group-VB $2H$ compounds TaS_2 and NbSe_2 are shown in Figs. 5 and 6, respectively. It is clear that these results are considerably more complicated than those for the $1T$ phase, mainly because the number atoms in the unit cell has doubled. In both compounds, the lowest group of twelve bands evolve from X -atom p orbitals. Above these, we find the ten metal d bands, and finally, near the top of each figure, the (dashed) metal $s - p$ bands. In each compound, the ten metal d bands are split by a gap of about 0.1 Ry into a lower pair of d subbands and a group of eight d bands at higher energies. In these group-VB compounds, the dashed Fermi level occurs within this lower splitoff d subband, thereby predicting metallic behavior for these materials. As we shall show in Sec. IV C, the group-VI B compounds such as $2H - \text{MoS}_2$ possess a similar band structure. In this case, the lower d subband is completely filled and this leads to semiconducting behavior in the group-VIB compounds.

At first sight, these results appear to be consistent with the Wilson-Yoffe model,¹ which con-

tains a nonbonding d_{ξ^2} subband that is partially filled in $2H - \text{TaS}_2$ and $2H - \text{NbSe}_2$ and totally filled in $2H - \text{MoS}_2$. However, we note from the results of Table V that, while the lowest subband contains d_{z^2} type orbitals at Γ , it has the symmetry of d_{xy} , $d_{x^2-y^2}$ orbitals at K . The d_{x^2} subband actually extends up to K_1, K_3 , the lowest pair of bands at K in the upper d complex. In terms of a tight-binding model that is described in Sec. V, we show that strong hybridization between the d_{ξ^2} and d_{xy} , $d_{x^2-y^2}$ subbands is responsible for the 0.1 – Ry energy gap that exists within the d manifold of these $2H$ compounds. Thus, the small (0.075 Ry) width of the lowest subband is an artifact of this hybridization gap and is not to be interpreted as a measure of the strength of the metal-chalcogen $s - d$ or $p - d$ interactions or the direct metal-metal $d - d$ interactions.

Because of the additional symmetry of the D_{6h}^4 space group, a double degeneracy exists everywhere in the ALH plane when spin-orbit coupling is neglected.³⁴ As in the case of the $1T$ compounds, the bandwidths along the Δ, U , or P lines of the Brillouin zone reflect the strength of the interlayer interactions. Among the metal d -band states, these are largest for

the d_{z^2} orbitals ($\Gamma_{1+}, A_1; \Gamma_{4-}$,

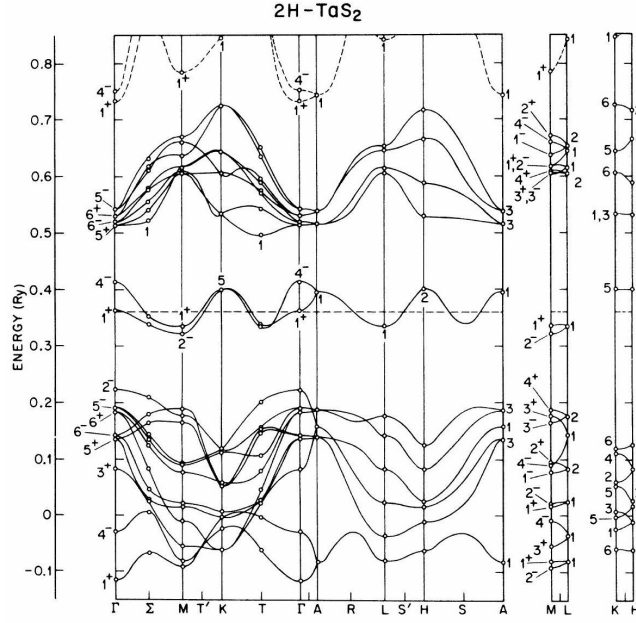


FIG. 5. APW results for $2H - \text{TaS}_2$, where $V_0 = -0.938$ Ry.

A_1). Within the chalcogen p manifold, the bands associated with the p_g -type orbitals ($\Gamma_{2-}, A_1; \Gamma_{3+}, A_1; \Gamma_{4-}, A_1; \Gamma_{1+}, A_1$) again reflect rather substantial interlayer interactions.

To help distinguish between the interlayer and intralayer contributions to the band profiles, we show in Fig. 7 the energy-band results for "intercalated" $2H - \text{NbSe}_2$. As discussed previously (see Tables III and IV), this calculation involves a hypothetical form of $2H - \text{NbSe}_2$ in which the interlayer separation is increased by about $1.5\text{\AA}$. It is clear from a comparison of the results shown in Figs. 6 and 7 that the interlayer interactions are substantially reduced in the latter calculation. It is noted that the energy scales for the two $2H - \text{NbSe}_2$ calculations will nearly coincide if those in Fig. 7 are shifted by 0.189 Ry; this is in fact the difference in the values of the corresponding muf-fin-tin constants. In Fig. 7, it is found that the bands in the ΓMK and ALH planes are nearly identical, so that the band structure is nearly that of a two-dimensional compound.

C. $2H - \text{MoS}_2$

The APW results for $2H - \text{MoS}_2$ are shown in Fig. 8. Neglecting interlayer interactions, $2H - \text{MoS}_2$

has the same two-dimensional crystal structure as the group-VB $2H$ compounds. Therefore, it is not surprising that the band structures for these two groups are similar. According to Table V, some changes take place in the symmetry properties of metal s, p , and d bands at the K and H points, and these are reflected in the results shown in Fig. 8. We note that the lowest pair of d bands at K now has $K_1 - K_3$ symmetry, so it still corresponds to $d_{xy}, d_{x^2-y^2}$ type orbitals. Although there are now two K_5 states in the upper d manifold, a comparison with the results for the group-VB compounds and the analysis in Sec. V suggests that the lower one corresponds to the d_{z^2} orbitals. Thus, these results predict an 0.085 -Ry indirect gap that results from intralayer hybridization between the d_{x^2} and $d_{xy}, d_{x^2-y^2}$ subbands.

D. Sulfur 3s and Selenium 4s Core States

We have calculated the sulfur 3s bands in $2H$ TaS₂ and the selenium 4s bands in $2H$ -NbSe₂. In the former compound, these bands have a width of 0.12 Ry and are centered about an energy of -0.7 Ry on the energy scale of Fig. 5. In the case of NbSe₂ (Fig. 6), the selenium 4s bands are slightly broader (0.13 Ry) and slightly higher in energy

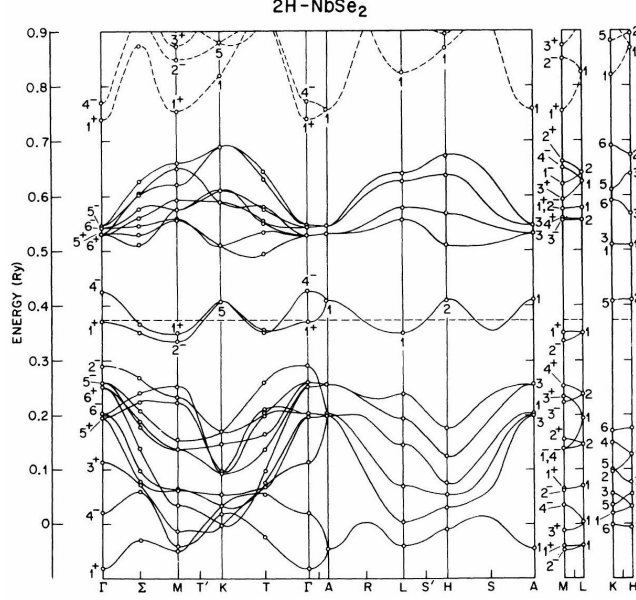


FIG. 6. APW results for $2H$ - NbSe₂, where $V_0 = -0.931\text{Ry}$.

(-0.65 Ry) relative to the muffin-tin constant. Thus, it is expected that the X -atom s bands will lie about 0.9 Ry below the top of the p bands in both the sulfides and the selenides. This is reasonably close to the 0.8 Ry difference between the atomic 3s(4s) and 3p(4p) levels in sulfur (selenium).³⁷

E. Muffin-Tin Corrections

To illustrate the effect of the muffin-tin corrections on the present APW results, we compare in Table VI the APW muffin-tin (MT) eigenvalues at Γ for $1T$ -TaS₂ and $2H$ -NbSe₂ with those obtained when the corrections between the APW spheres are included (muffin-tin corrections). It is found that individual eigenvalues change by as much as $\pm 0.08\text{Ry}$. It is believed that two competing mechanisms combine to produce these changes. The gross features of these results can be understood by considering the nature of these muffin-tin corrections.

In the muffin-tin approximation, the constant V_0 is chosen so that the average potential in the region outside the APW spheres is zero. As a result, the corrections are found to be negative in the regions just outside the T - and X -atom spheres and positive in the more remote corners of the unit cell. Thus, one effect of these corrections is to lower the energies of both the semilocalized

metal d -type and chalcogen p -type states whose charge densities are concentrated primarily in those regions where the muffin-tin corrections are negative. The wave functions of the more extended metal $s - p$ states correspond to a more uniform charge density, one that extends into the corners of the unit cell. In this case, the corrections can be either positive or negative, depending on

the symmetry of the wave function.

The second mechanism involves metal-chalcogen overlap-covalency effects. The muffin-tin cor-

TABLE VI. APW eigenvalues at Γ for $1T - \text{TaS}_2$ and $2H - \text{NbSe}_2$ in the muffin-tin approximation (MT) and including muffin-tin corrections (MTC).

$1T - \text{TaS}_2$			$2H - \text{NbSe}_2$		
State	MT (Ry)	MTC (Ry)	State	MT (Ry)	MTC (Ry)
Γ_{1+}	-0.070	-0.123	Γ_{1+}	-0.033	-0.082
Γ_{1+}	0.446	0.403	Γ_{1+}	0.395	0.371
Γ_{1+}	0.731	0.816	Γ_{1+}	0.716	0.740
Γ_{3+}	0.127	0.044	Γ_{3+}	0.120	0.114
Γ_{3+}	0.480	0.402	Γ_{3+}	0.878	0.937
Γ_{3+}	0.655	0.622	Γ_{5+}	0.254	0.197
Γ_{2-}	0.249	0.189	Γ_{5+}	0.555	0.532
Γ_{2-}	0.804	0.780	Γ_{6+}	0.298	0.251
Γ_{3-}	0.276	0.216	Γ_{6+}	0.559	0.531
			Γ_{2-}	0.349	0.290
			Γ_{2-}	0.875	0.905
			Γ_{4-}	0.104	0.020
			Γ_{4-}	0.459	0.427
			Γ_{4-}	0.780	0.771
			Γ_{5-}	0.309	0.259
			Γ_{5-}	0.579	0.547
			Γ_{6-}	0.261	0.203
			Γ_6^-	0.567	0.543

rections lower the potential barriers along the near-est-neighbor metal-chalcogen bond directions. This enhances the formation of metal-chalcogen σ and π bonds involving the chalcogen $s - p$ and the metal $s - p - d$ orbitals. This enhancement in the strength of the metal-chalcogen bonds causes the energies of the bonding (primarily chalcogen $s - p$) states to be further lowered but raises the energies of the corresponding antibonding (metal $s - p - d$) states.

25.0.5 V. TIGHT-BINDING INTERPRETATION

The present energy-band results for the layertype TX_2 compounds possess many of the same general characteristics as those found previously for the cubic transition-metal oxides.^{39–41} An important feature shared by all of these compounds is the fact that the metal $s - p$ bands lie well above the Fermi level. As emphasized earlier,^{40,44} this is caused by strong overlap and covalent-bonding effects between the metal and chalcogen $s - p$ orbitals. This results in the formation of metalchalcogen bonding and antibonding $s - p$ states, with the energy of the latter increased by 5–10eV. The energy separation between the bonding and antibonding $s - p$ orbitals is generally referred to as the $\sigma - \sigma^*$ gap.^{1,8} Thus, while the valence bands in Figs. 3-8 are often described as chalcogen p (or s) bands, they are more properly identified as bonding combinations of both metal and chalcogen $s - p$ orbitals. The dashed bands in the upper parts of Figs. 3-8 are antibonding combinations of these same orbitals.

There are similar but weaker overlap-covalency interactions between the metal d and chalcogen $s - p$ orbitals. Unlike the transition metals where the $s - p$ and d bands overlap, the metal d bands usually fall within the $\sigma - \sigma^*$ gap in the transitionmetal compounds. Except perhaps in the case of the rocksalt structure,⁴⁰ these overlap-covalency effects are primarily responsible for the d bandwidth and topology in such compounds.

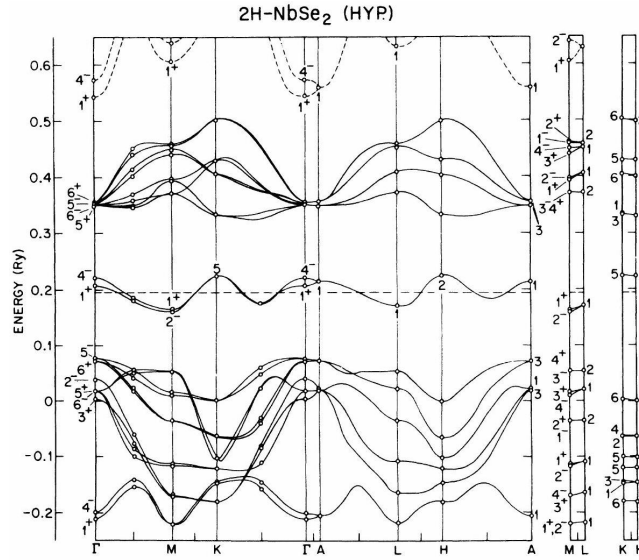


FIG. 7. APW results for a hypothetical form of $2H - \text{NbSe}_2$ in which the interlayer separation is increased by $1.5\text{\AA}$ ($V_0 = -0.742Ry$.)

In order to provide additional insight into the nature of the d -band states in the present $1T$ and $2H - \text{TX}_2$ compounds, we apply the Slater and

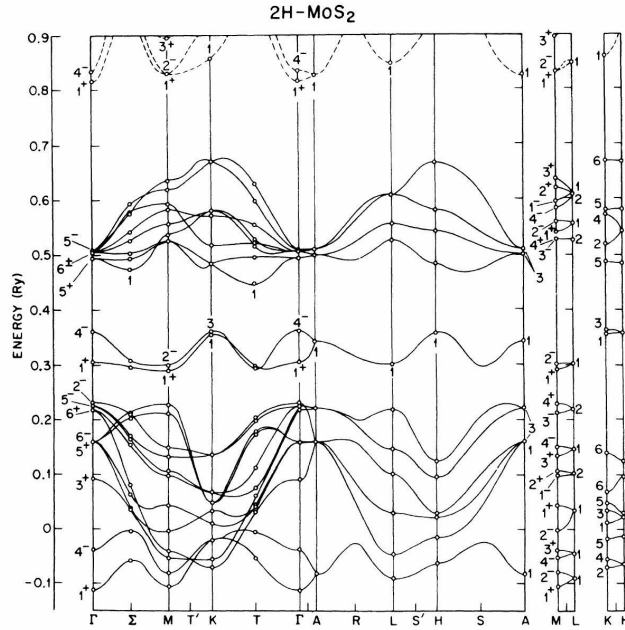


FIG. 8. APW results for $2H - \text{MoS}_2$, where $V_0 = -0.961Ry$.

Koster⁴⁵ linear-combination-of-atomic-orbitals (LCAO) interpolation method to fit the APW d -band results of Figs. 3-8. The LCAO matrix elements for the molybdenum $4d$ bands in $2H - \text{MoS}_2$ are available from the work of Egorov et al.⁴⁶ and Miasek.⁴⁷ The corresponding LCAO d -band Hamiltonian matrices for the $1T - \text{TaS}_2$ and $2H - \text{TaS}_2$ structures are easily derived using the group-theoretical techniques of Egorov et al.⁴⁶

As discussed previously in the case of the rocksalt structure,⁴⁰ the application of the SlaterKoster LCAO interpolation method to fit the d bands in a transition-metal compound where over-lap-covalency effects are substantial yields "effective" LCAO parameters $\mathcal{E}_{\alpha,\beta}(\vec{r}_n)$.

These effective parameters contain a direct $d-d$ interaction term $E_{\alpha,\beta}(\vec{r}_n)$ between an α orbital at the origin and a β orbital at $\vec{r}_n$ as well as indirect terms (i.e., additional contributions to the d bandwidth that result from overlap-covalency interactions involving the metal d and neighboring chalcogen $s-p$ orbitals).

In the present LCAO fit to the d bands for the $C6$ and $C7$ structure types (Table I), both nearestneighbor intralayer and interlayer $d-d$ interactions are included. In the case of the $C27$ structure, these are supplemented by a few second-neighbor interlayer interactions. The need for the latter is clear from the results shown in Figs. 5 and 6 as well as those in Table I. In Figs. 5 and 6, it is found that the interlayer splitting of the d_{ξ^2} bands is much greater at Γ (Γ_{4-}, Γ_{1+}) than it is at K (K_1, K_3). According to Table I, nearest-neighbor interlayer $d-d$ interactions produce a splitting within the d_x^2 subband that is constant throughout the ΓMK plane so that any dependence of this splitting on k_x and k_y must arise from second-neighbor interlayer effects.

The centers of gravity of the various (covalently mixed) d subbands are given by the effective one-center LCAO orbital energies $\mathcal{E}_{\alpha,\alpha}(0,0,0)$. These energies are equivalent to the molecular-orbital or ligand-field one-electron levels of an isolated transition-metal complex.^{40,44} where the effects of the lattice periodicity are ignored. Consequently, they provide a useful means for comparing the band and ligand-field models for these TX_2 compounds.

A. Band versus Ligand-Field Models

Previous attempts to describe the electronic structure of the TX_2 layer-type compounds have involved either band¹⁻⁷ or ligand-field^{8,9} models. Although the former method undoubtedly provides the correct description of the electronic states in the present compounds, it is nevertheless useful to compare the present results for the metal d band states in both the band and ligand-field limits.

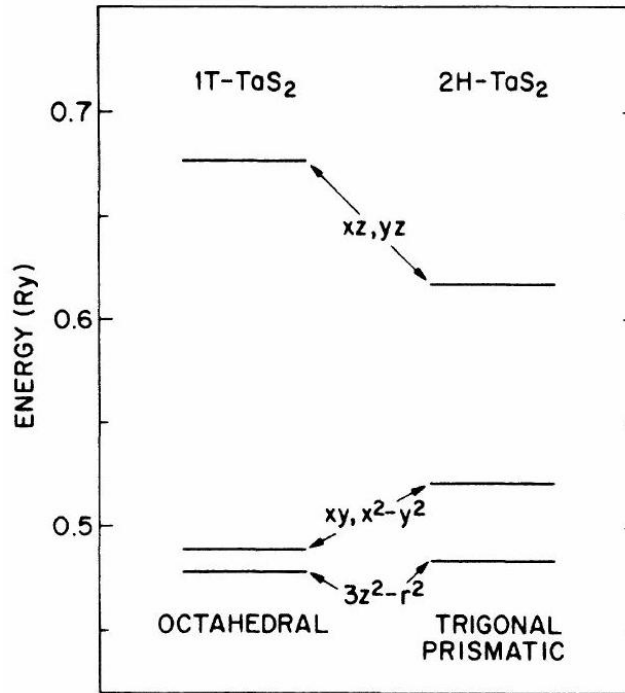


FIG. 9. Comparison between the ligand-field d levels for octahedral and trigonal-prismatic TaS_6 complexes, as derived from the present energy-band results for $1T-TaS_2$ and $2H-TaS_2$, respectively.

It is important to emphasize that the ligand-field levels correspond to the centers of gravity of the appropriate d subbands in the periodic crystal and not (as is often assumed ⁸) to the band energies at $\vec{k} = 0$.

HDHJ⁹ have analyzed a simplified model for the ligand-field splitting of d levels in both octahedral and trigonal-prismatic environments. According to their results, the d -type ligand-field levels for an ideal octahedral TX_6 complex include a lower triply-degenerate t_{2g} level [$\mathcal{E}_{\alpha,\alpha}(0,0,0)$ with $\alpha = z^2, xy$, and $x^2 - y^2$ in the present coordinate system] and an upper doubly degenerate e_g state ($\alpha = xz, yz$). In the case of a trigonal-prismatic TX_6 complex, their results show that the octahedral t_{2g} level is split into a singly degenerate ($\alpha = z^2$) and a doubly-degenerate ($\alpha = xy, x^2 - y^2$) level.

In Fig. 9 we compare the ligand-field splittings of the $5d$ levels in $1T$ - TaS₂ (octahedral) and $2H$ TaS₂ (trigonal-prismatic), as determined by the present APW-LCAO method. These represent the centers of gravity of the various d subbands shown in Figs. 4 and 5, respectively. These ligand-field results are in excellent agreement with those shown in Fig. 3 of the paper by HDHJ.⁹ The existence of a small splitting between the d_{g2} and $d_{xy}, d_{x^2-y^2}$ levels in Fig. 9 for the octahedral coordination is consistent with the fact that the present calculation for $1T$ - TaS₂ involves a slightly distorted octahedron with edges of 3.37 and 3.51 Å, respectively.

A second similarity between the present results and those of HDHJ concerns the fact that the split-

ting between the d_{xz}, d_{yz} , and d_{z^2} levels is smaller in the case of the trigonal prism than it is for the octahedral TX_6 complex. In the trigonal-prismatic complex, the ordering of the d_{z^2} and $d_{xy}, d_{x^2-y^2}$ levels agrees with that proposed by HDHJ,⁹ but is opposite to that of Goodenough.⁸

Finally, we note that the 0.1 Ry hybridization gap within the tantalum $5d$ manifold in $2H$ - TaS₂ (Fig. 5) is larger than and not related directly to the 0.04-Ry ligand-field splitting between the $d_{xy}, d_{x^2-y^2}$ and d_{z^2} levels shown in the right-hand portion of Fig. 9. HDHJ⁹ assume that this ligand-field splitting must be at least 1.4 eV in $2H$ - MoS₂ in order to explain the observed optical gap. Goodenough's model⁸ involves a somewhat larger splitting since he assumes a reversed order for the $d_{xy}, d_{x^2-y^2}$, and d_{z^2} levels and assigns the optical gap to the spin-orbit split $d_{xy}, d_{x^2-y^2}$ level. The corresponding APW-LCAO results for $2H$ - MoS₂ yield a ligand-field splitting between the $d_{xy}, d_{x^2-y^2}$, and d_{k^2} levels of 0.045 Ry, which is about one-half the 0.09 -Ry hybridization gap shown in Fig. 8.

It is useful to apply these techniques to compare the gross features of the present APW-LCAO results for the group-IV B and group-VI B compounds with the semiempirical band structures of Bromley, Murray and Yoffe (BMY).²⁻⁶ For example, while MBY⁴ assume ideal octahedral coordination in their calculation for $1T$ - HfS₂, the corresponding energy-band results suggest an 0.1 -Ry splitting between the centers of gravity of the d_{z^2} and $d_{xy}, d_{x^2-y^2}$ subbands. This is about ten times larger than the present APW-LCAO estimate of 0.01 Ry for this splitting in $1T$ - HfS₂. A similar discrep-

ancy is found in the results for $2H$ - MoS₂. In this case, the results of BMY⁵ suggest an 0.12 - Ry splitting between the $d_{xy}, d_{x^2-y^2}$, and d_{x^2} levels whereas the present APW-LCAO estimate is about one-third as large.

B. LCAO D Bands

We now apply this LCAO model to trace the manner in which the various d subbands evolve in these $1T$ - TX_2 and $2H$ - TX_2 compounds when the effects of the lattice periodicity are taken into account. By setting the effective $d-d$ parameters $\mathcal{E}_{\alpha,\beta}(\vec{r}_n)$ for interlayer interactions equal to zero, we can determine the "two-dimensional" band structures for these materials. In addition, by either omitting or including various $d-d$ hybridization parameters

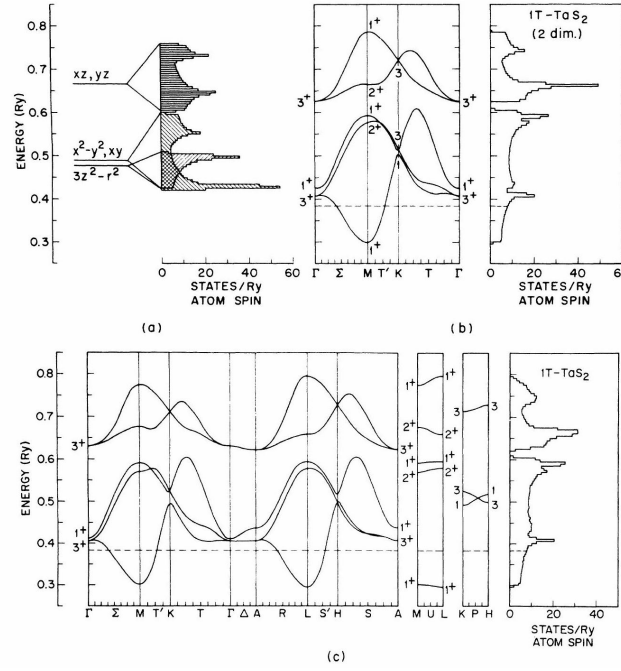


FIG. 10. (a) Ligand-field levels and LCAO density-of-states curves for unhybridized d bands in $1T\text{-TaS}_2$. LCAO results for $1T\text{-TaS}_2$ with hybridization, first neglecting (b) and then including (c) interlayer interactions.

[such as $\mathcal{E}_{\alpha,\beta}(\vec{r}_n)$ with $\alpha = z^2$ and $\beta = xy$ or $x^2 - y^2$], we can indicate rather graphically the importance of interband hybridization effects in determining the APW energy-band results for these compounds.

The LCAO results for the tantalum $5d$ bands in $1T\text{-TaS}_2$ are shown in Fig. 10. The results shown in Figs. 10(a) and 10(b) neglect interlayer interactions. In Fig. 10(a) we relate the ligand-field levels to the density-of-states curves for the corresponding d subbands, neglecting interband hybridization. The effects of hybridization on the $E(\vec{k})$ and density-of-states curves are shown in Fig. 10(b). Finally in Fig. 10(c) the corresponding results for three-dimensional $1T\text{-TaS}_2$ are shown. By comparing these results with those in Fig. 10(b), one concludes that interlayer interactions play a relatively minor role in smearing the sharp singularities that occur in the two-dimensional density-of-states curve.

Similar APW-LCAO results for the d bands in $2H\text{-MoS}_2$ are shown in Fig. 11. Again, the histograms joining the various ligand-field levels in Fig. 11(a) represent the density-of-states curves for the individual molybdenum $4d$ subbands, neglecting interband hybridization and interlayer interactions. The corresponding $E(\vec{k})$ and total density-of-states curves are shown to the right. The dashed Fermi level indicates that $2H\text{-MoS}_2$ would be metallic in this approximation. The labeling of these two-dimensional energy-band states is in accordance with the notation of BMY.⁵ We note that the widths of the various $4d$ subbands in $2H\text{-MoS}_2$ are comparable to those in $1T\text{-TaS}_2$ when interband hybridization is omitted.

The effect of including interband hybridization is illustrated in Fig. 11 (b). In this two-dimensional limit, reflection symmetry in the basal plane permits hybridization only between the (effective) d_{xy} , $d_{x^2-y^2}^2$, and d_x^2 orbitals. According to Fig. 11(b), these hybridization effects result in the formation of a narrow d subband which is half-filled in the group- $VB2H\text{-TX}_2$ compounds and completely filled in $2H\text{-MoS}_2$. The additional effect of including interlayer interactions is shown in Fig. 11(c).

Similar $E(k)$ and density-of-states results for three-dimensional $2H\text{-TaS}_2$ and $2H\text{-NbSe}_2$

are contained in Figs. 12(a)-12(c). In each case, the Fermi level occurs quite close to a slightly rounded logarithmic-type singularity in the conduction-band density-of-states curve. For convenience, the energy scale in Fig. 12(c) has been adjusted so that it coincides with that in Fig. 12(b).

A comparison between the LCAO results in Figs. 10-12 and the corresponding APW results in Figs. 4-8 reveals some qualitative as well as quantitative differences, particularly in the band profiles within the upper d -band complexes. The source of these differences is not fully understood, though they may be due to $s - d$ hybridization. In any case, the object of this simplified LCAO model is to achieve a qualitative understanding of the present APW results for the metal d bands. To achieve increased accuracy, one must include explicitly the chalcogen $s - p$ orbitals in the LCAO basis set.^{39-41,44}

25.0.6 VI. DISCUSSION

Previous experience with the APW method suggests that this technique is particularly accurate in representing the internal structure of the d bands in transition metals and compounds. However, it is found that such calculations are somewhat less reliable in predicting the relative energies of the $s - p$ and d bands in the transition metals or the correct ligand-metal $p - d$ band separation in transition-metal compounds. As is well known, these aspects of a band calculation are particularly sensitive to the details of the crystal potential and depend on such factors as the assumed atomic (or ionic) configuration, the method used to treat exchange and correlation, and self-consistency effects. For example, APW calculations for transition-metal oxides³⁹⁻⁴¹ involving neutral-atom potentials tend to overestimate the observed $p - d$ gap by 1 - 3eV.

One might expect similar errors in the present APW calculations for the transition-metal dichalcogenides since these results are based on the same neutral-atom model for the crystal potential. The present results for $1T - \text{HfS}_2$ provide a direct means for comparing the calculated and observed $p - d$ gaps in these dichalcogenide layer compounds. The APW results for $1T - \text{HfS}_2$ in Fig. 3 yield a $p - d$ indirect gap of 2.7 eV, which is 0.6 - 0.7eV larger than the observed value.^{12,13} If one attributes this error entirely to ionicity effects, then the present results suggest that the sulphides (and probably the selenides) are less ionic than the oxides. How-

ever, it is interesting to note that the HermanSkillman³⁷ estimate of the Darwin and mass-velocity corrections for the atomic $\text{Hf}5d$ level is -0.05 Ry, or precisely the value that is required to bring the calculated and observed band gaps in $1T - \text{HfS}_2$ into complete agreement.

White and Lucovsky⁴⁸ present arguments based on the results of infrared reflectivity measurements that the octahedral group-IV $B1T - \text{TX}_2$ compounds are purely ionic whereas the trigonal-prismatic group-VI $B2H - \text{TX}_2$ compounds are covalent. The present APW results for these materials suggest no such clear cut change in either the bonding or ionicity in passing from the group-IV B to the

group-VIB compounds. The fact that the calculated $p - d$ band separation decreases as one proceeds from the group-IV B to the group-VI B compounds certainly increases the extent of the covalent bonding as one moves to the right in the Periodic Table. However, it seems unlikely that the ionicity would decrease from +4 to 0 within this sequence of compounds. Based on the results of self-consistent calculations on somewhat analogous transition-metal compounds such as NbN ⁴⁹ and the MnO_4^- cluster,⁵⁰ I would estimate that the effective metalatom charge is never greater than about +1 in the dichalcogenides.

As a result of these difficulties and uncertainties, the present APW calculations are unable to provide a reliable prediction as to whether or not the metal d bands overlap the top of

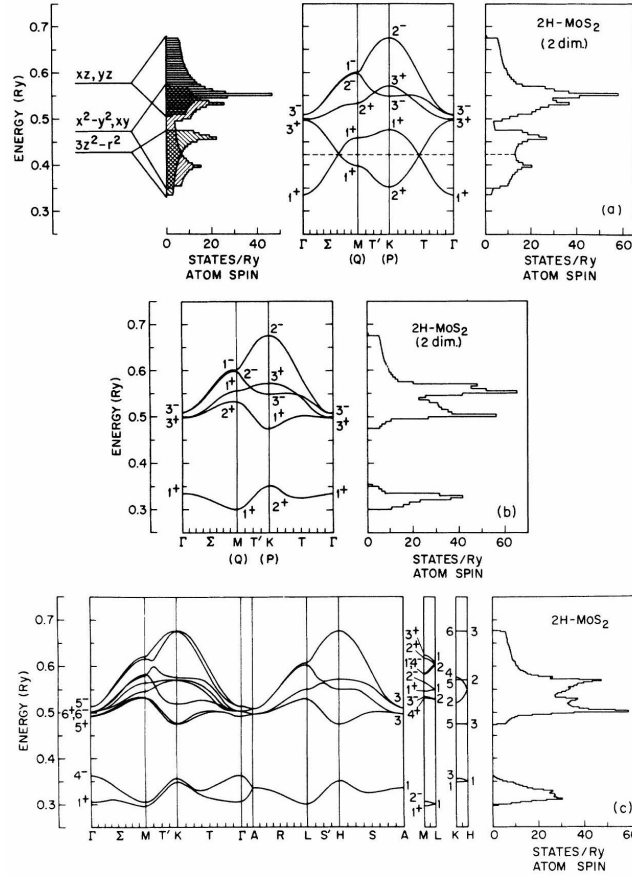


FIG. 11. (a) Ligand-field levels, LCAO $E(\vec{k})$, and density-of-states curves for $2H - \text{MoS}_2$ neglecting interband hybridization and interlayer interactions. (b) LCAO results for $2H - \text{MoS}_2$ with hybridization effects included. (c) LCAO results for $2H - \text{MoS}_2$ including interlayer interactions.

the chalcogen p bands in the group-VB and group-VIB compounds. HDHJ⁹ were the first to suggest a model with overlapping d and p bands for these compounds. Originally, this was done to explain the fact that the transport measurements²³ on $2H - \text{NbSe}_2$ and $2H - \text{TaSe}_2$ samples indicate that the conductivity changes from n to p type as a function of tempera-

ture. However, as Title and Shafer³² point out this model is no longer necessary since the NMR²⁴ and x-ray²⁵ data show that this anomaly is associated with a structural transformation. In addition, Bromley⁵¹ has shown that conduction via both holes and electrons can occur in $2H - \text{NbSe}_2$ if interlayer interactions are considered. The present APWLCAO results predict that the $2H - \text{NbSe}_2$ Fermi surface contains only holelike carriers.

There are several aspects of Bromley's bandstructure model for $2H - \text{NbSe}_2$ that deserve comment. In two dimensions, this model is simply the d_z^2 band shown in Fig. 11(a) connecting the states with Γ_1^+ , M_1^+ , and K_1^+ symmetry. Unlike the results shown in this figure, Bromley assumes that this d_z^2 band is split off in energy from the other d subbands. The present APW-LCAO results provide reliable estimates of Bromley's tightbinding parameters D and δ . These parameters represent the effective $d - d$ interactions between nearest-neighbor d_z^2 orbitals within a single layer and in adjacent layers, respectively. The LCAO results shown in Fig. 12(b) correspond to $D = 0.0114\text{Ry}$ and $\delta = 0.0044\text{Ry}$, or $\delta/D = 0.39$. As discussed in Sec. V, second-neighbor interlayer effective interactions are significant in $2H - \text{NbSe}_2$ for the d_z^2 -type orbitals. It is found that these second-neighbor interlayer parameters are about $\frac{1}{3}$ the magnitude of δ . However, their effect on the band structure is enhanced by the fact that there

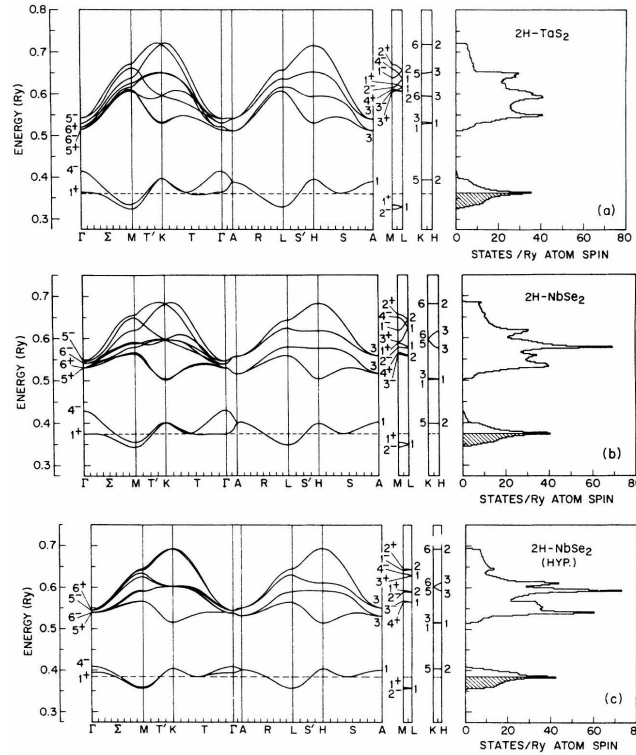


FIG. 12. LCAO results for (a) $2H-TaS_2$; (b) $2H-NbSe_2$; (c) hypothetical $2H-NbSe_2$ with expanded interlayer separation.

are six times as many of these second neighbors as there are nearest neighbors in $2H-NbSe_2$.

The present APW results for $2H-NbSe_2$ predict a Fermi surface that includes four separate holelike sheets. In the first zone, these include a closed hole-type surface centered about the point A in Fig. 2 and an open cylindrical surface along the KH line. The closed surface extends close to but fails to contact the ΓMK plane if Γ_1+ lies below the Fermi level, as shown in Fig. 6. Otherwise, this sheet would also be open along the c axis. The second zone contains two open cylindrical hole surfaces that are centered about the ΓA and KH lines, respectively, and enclose the first-zone sheets. These first- and second- zone sheets are degenerate in the ALH plane if spin-orbit coupling is neglected. According to Fig. 5, a similar Fermi surface is predicted for $2H-TaS_2$, though in this case, all the sheets are open.

Graebner⁵² has observed magnetothermal oscillations in $2H-NbSe_2$. The angular dependence of the data suggests that it arises from orbits on a closed pancake-shaped Fermi-surface sheet whose diameter is at least five times its thickness. Neither the present APW-LCAO results nor Bromley's tight-binding model provides a reasonable explanation for these data. It seems likely that one must consider the effects of the 40°K phase transition²³⁻²⁵ on the $2H-NbSe_2$ band structure in order to interpret these Fermi-surface results. This represents a serious complication since, according to Marezio et al.,²⁵ the size of the $2H-NbSe_2$ unit cell is quadrupled at temperatures below the 40°K phase transition. When the undistorted energy bands shown in Fig. 6 are folded into the reduced low-temperature Brillouin zone, the number of conduction bands increases from two in the high-temperature phase to eight in the distorted phase. As a result, one expects significant changes in both the Fermi-surface dimensions and topology in $2H-NbSe_2$ at low temperatures.

The most direct empirical information concerning the relative positions of metal d and chalcogen p bands in the group-VB and group-VI BTX_2 compounds is obtained from optical and photoemission data. We consider first the optical properties and attempt to understand

the gross features of the low-energy data in terms of a joint-density-of-states (JDS) model for direct transitions within the d manifold, assuming constant interband matrix elements.

The JDS curve for direct $d-d$ transitions in $2H-MoS_2$ is shown in Fig. 13. These results are derived from the LCAO band structure of Fig. 11(c). The energies at which structure is observed in the transmission spectrum are labeled, using the notation of Wilson and Yoffe¹ and Beal et al.³¹ The vertical arrow indicates the energy at which transitions from the sulfur $3p$ to the unoccupied molyb-

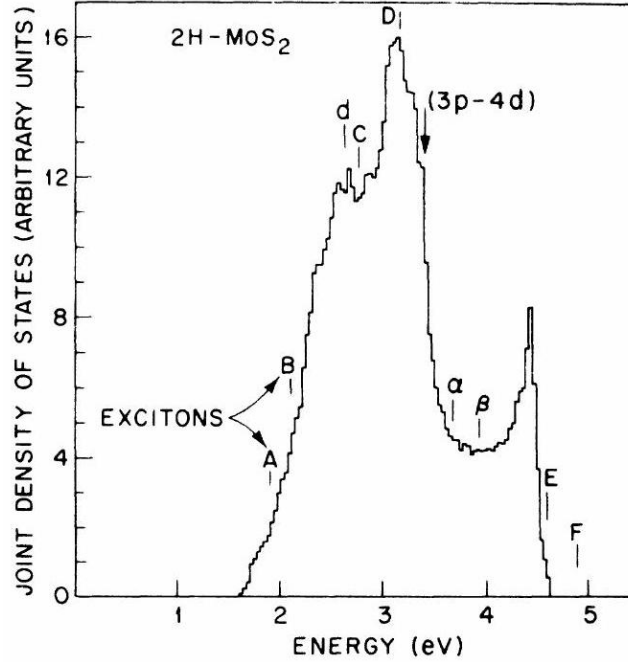


FIG. 13. Joint-density-of-states curve for direct transitions within the $2H-MoS_2$ manifold. The arrow indicates the energy at which sulfur $3p$ -molybdenum $4d$ transitions commence, according to the results of Fig. 8.

denum $4d$ bands are expected to commence, according to the APW results of Fig. 8.

A comparison of this JDS curve with the $2H-MoS_2$ transmission spectrum [(Figs. 22(a) and 1 of Refs. 1 and 31, respectively)] suggests that the main absorption peak that is centered at 3 eV is due to $d-d$ transitions. This differs from previous interpretations,^{1,5,31} which attribute this structure to $p-d$ transitions. It is interesting to note that Zeppenfeld's $^{53}\epsilon_2$ curve (imaginary part of the dielectric constant) for $2H-MoS_2$ exhibits peaks at 3.0 and 4.5 eV, which is in good agreement with the JDS curve shown in Fig. 13. We conclude that there is no direct evidence in the $2H-MoS_2$ optical data for the occurrence of $p-d$ transitions at energies below 3-4 eV. This suggests that the A and B excitons that are observed^{1,31} at energies of 1.9 and 2.1 eV, respectively, in $2H-MoS_2$ involve $d-d$ ^{8,9} rather than $p-d$ transitions.^{1,5,31}

The results of similar JDS calculations for the group-VB $2H-TX_2$ compounds are shown in Fig. 14. Though there are no optical data available for $2H-TaS_2$, Wilson and Yoffe¹ compare the transmission spectra of $2H-NbSe_2$ and $2H-TaS_2$. These data exhibit prominent absorption peaks that begin at energies of 2.0 and 2.3 eV and rise to well-defined maxima at 2.8 and 3.2 eV, respectively. This behavior is in qualitative agreement with the JDS results for $2H-NbSe_2$ and $2H-TaS_2$ which are shown in Figs. 14(b) and 14(a), respectively.

We note in Fig. 14 that a 1.5 – 2.0 – eV window occurs in the JDS curves for $2H-NbSe_2$ and $2H-TaS_2$ between 0.5 and 2.3 eV. According to the optical data, the absorption is small but finite within this energy range. We attribute this absorption to $p-d$ transitions from the filled chalcogen p -type valence bands to the empty

metal d bands just above the Fermi level, in agreement with the interpretation of Wilson and Yoffe.¹ Although these transitions are omitted from the JDS curves of Fig. 14, we indicate the threshold energies where these transitions are expected to commence, using the energy-band results of Figs. 5 and 6. From the fact that the optical absorption remains finite throughout this energy range, we infer that the $p-d$ band separation is very nearly zero in both $2H-TaS_2$ and $2H-NbSe_2$.

This is consistent with the results of ultraviolet photoemission (PE) studies on these compounds.^{18,30,54-56} These data suggest that the $p-d$ band overlap is about $0.1-0.2\text{eV}$ in both $2H-NbSe_2$ and $2H-MoS_2$. The PE data also resolve the controversy^{1,9} regarding the magnitude of the semiconducting gap in the group-VIB compounds. These results demonstrate that this gap is at least 1eV in $2H-MoS_2$ ^{18,30,55} and $2H-MoTe_2$,^{18,56} which is consistent with the present APW results for $2H-MoS_2$. These PE data¹⁸ also provide estimates of the occupied $4d$ bandwidths in $2H-NbSe_2$ that agree well with the present calculated results.¹⁰ Similar agreement is obtained for the chalcogen p bandwidths.

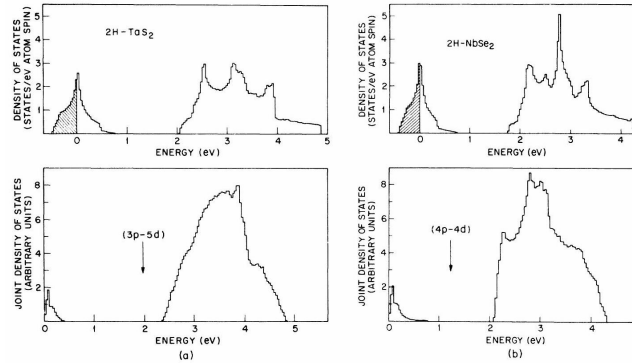


FIG. 14. Density-of-states and joint-density-of-states results for (a) $2H-TaS_2$ and (b) $2H-NbSe_2$. The vertical arrows indicate the threshold energies where $p-d$ transitions are expected to commence.

If the $p-d$ band separation in Figs. 4-8 is reduced until these bands overlap by $0.1-0.2\text{eV}$, then the top of the p valence band will be close to but below the Fermi level in the group-VB $2H-TX_2$ compounds. In $2H-MoS_2$, where the valence bandwidth is about 1eV , a $0.1-0.2\text{eV}$ overlap would leave the valence-band maximum at Γ , where the orbitals have d_x^2 type symmetry. This result is consistent with the results of electron paramagnetic resonance studies on doped $2H-MoS_2$ samples by Title and Shafer.³² It provides additional support for interpreting the $1.9-$ and 2.1eV excitons in $2H-MoS_2$ in terms of $d-d$ transitions.

In the case of the metallic group-VB $2H-TX_2$ compounds, we can compare the experimental and theoretical values for the band density of states at the Fermi energy, $N(E_F)$. In the case of $2H-NbSe_2$, the agreement is quite good. The empirical value of $2.8\text{ states/eV spin Nb atom}$ is derived from heat-capacity²⁶ and superconductivity²⁷ data, using McMillan's formula.⁵⁷ This agrees well with the value of $3.0\text{ states/eV spin Nb atom}$ that is shown in Fig. 14(b) for $2H-NbSe_2$. This implies that the low-temperature phase transition^{24,25} in $2H-NbSe_2$ has a small effect on the density of states at the Fermi level. This is consistent with the fact that the magnetic susceptibility is essentially unchanged as the temperature is lowered through the 40°K phase transition.²⁵

On the other hand, the susceptibility data for $2H-TaS_2$ exhibits a sharp decrease just below the 70°K phase transition.^{16,22} The simplest interpretation of this result involves a structural transformation that reduces the band density of states at the Fermi level. According to the heat-capacity data,²¹ the phonon-enhanced density of states is $1.8\text{ states/eV spin Ta atom}$,

which is smaller than the calculated band density of states $N(E_F) = 2.3$ states/eV spin Ta atom. The effects of phonon enhancement of the thermal density of states will only increase this discrepancy.

The present APW-LCAO calculations for the group-VB $2H - TX_2$ compounds suggest that the lattice instabilities that have been observed in these compounds may be caused by the very sharp peak in the density of states at the Fermi energy, as shown in Figs. 12 and 14. As Labbé and Friedel⁵⁸ have shown, the existence of fine structure in the density of states near the Fermi energy can lead to a Jahn-Teller-type distortion which splits this density-of-states peak and thereby reduces the free energy of the system at low temperatures.

Ehrenfreund et al.²⁴ estimate that the upper limit to the possible charge redistribution between the two niobium sites in $2H - NbSe_2$ below 40°K is about 0.1 electron. This suggests a splitting of the density-of-states peak $\delta E = \Delta n / N(E_F) = 0.03$ eV, which is comparable with the calculated 0.07 – eV

peak width. If this splitting were somewhat larger in $2H - TaS_2$, then one would expect a lower minimum between the occupied and unoccupied peaks, and this could explain the relatively small value for $N(E_F)$ that is derived from the low-temperature heat-capacity data for this compound. This model suggests that $N(E_F)$ (and probably the superconducting transition temperature) should increase if one could suppress the 70°K phase transition in $2H - TaS_2$ by quenching or some other means.

The present APW-LCAO results for $1T - TaS_2$ provide little insight into the nature of the metalsemiconductor transition that is observed at 350 °K. The calculated conduction bandwidth of 4 eV suggests that this transition is caused by a lattice distortion rather than a Mott transition. A complete determination of the low-temperature crystal structure for $1T - TaS_2$ would be required before one could speculate further on this matter. Recent electron-diffraction studies¹⁹ suggest that the room-temperature phase is very complex. Superlattice patterns indicate that $1T - TaS_2$ is pseudohexagonal at room temperature, with $a' \approx 37\sqrt{13}a$.

Finally, HDHJ⁹ have applied a ligand-field model to determine the relative stability of the trigonalprismatic and octahedral TX_6 complexes for systems with d^0 , d^1 , and d^2 configurations. In this calculation, they assume that the electron-interaction terms are identical for both geometries so that the difference in total energies is proportional to the difference in the sums of the one-electron energies for each system. The present results show that band-structure effects represent an important factor in the stabilization process, particularly the 1 – eV hybridization gap that occurs in the conduction band of the $2H$ phase.

We can show that this hybridization gap is relatively unimportant in the case of the group-VB compounds. From the present APW-LCAO results for $1T - TaS_2$ and $2H - TaS_2$, we find that the Fermi energies for these phases agree to within 0.2 eV. Relative to the vacuum, the average band energies per d electron in $1T - TaS_2$ and $2H - TaS_2$ are -0.60 and -0.59 Ry, respectively. The similarity in these values is consistent with the fact that both polytypes are metastable at low temperatures.

In the group-VI B compounds, the hybridization gap lowers substantially the average d -band energy for the $2H - TX_2$ compounds relative to that for the $1T$ phase. This probably accounts for the fact that the group-VI B compounds never form with the $1T$ phase. This argument can also be extended to more complicated polytypes. For example, we note that the group-VIB compounds form only the $2H$ and $3R$ polytypes where the coordination is trigonal prismatic whereas the group-VB compounds include structures where the coordination is octahedral ($1T$), trigonal prismatic ($2H, 3R, 4Ha$), or a combination of the two ($4Hb, 6R$).

Note added in manuscript. Kasowski⁵⁹ has recently published energy-band results for $2H - MoS_2$ and $2H - NbS_2$. These were calculated using the simplified linear-combination-of-muffin-tin-orbitals (LCMTO) method.⁶⁰ Although both the present APW and Kasowski's LCMTO calculations involve crystal potentials that should in principle be identical, the energy-

band results are in fact quite different. The most significant difference concerns the width of the valence and conduction bands in $2H - \text{MoS}_2$ and $2H - \text{NbS}_2$. Kasowski finds that these bandwidths are about 2.7 and 3.1 eV, respectively. These values are about $2\frac{1}{2}$ times larger than those obtained in the present APW calculation for $2H - \text{MoS}_2$ and $2H - \text{NbSe}_2$. He attributes these differences to the "non-muffin-tin part of the potential."

I believe that this explanation for these discrepancies is incorrect. As discussed in Sec. III, the present APW calculations include the corrections to the muffin-tin potential in the region outside the APW spheres exactly.³⁹ Thus, the only remaining simplifying assumption in the APW potential involves the nonspherical terms within the APW spheres. By means of a calculation that will be discussed shortly, I find that these nonspherical corrections in $2H - \text{NbSe}_2$ are about 10 times smaller than the 1.8–2.0-eV discrepancy between the calculated LCMTO and APW bandwidths. In fact, it is found that these nonspherical corrections further reduce the APW bandwidth in $2H - \text{NbSe}_2$ by 0.18 eV, thereby enhancing this discrepancy. Therefore, I believe that the origin of this discrepancy lies in the LCMTO calculation.

There is a second feature in Kasowski's LCMTO results for $2H - \text{NbS}_2$ that deserves comment. This concerns the changes in the conduction-band states when the potential in the region between the layers is set equal to zero. Although one would expect that this artificial potential barrier would reduce the strength of the effective $d - d$ interlayer interactions, Kasowski's results imply that these interlayer interactions are actually enhanced in this situation. In particular, he finds that the conduction-band splittings at $\Gamma [E(\Gamma_{4-}) - E(\Gamma_{1+})]$ and $M [E(M_{2-}) - E(M_{1+})]$ increase rather than decrease when this zero-potential barrier is imposed between the layers. This is opposite to the trend shown in Figs. 6 and 7, where these splittings decrease as the interlayer separation (and consequently, the interlayer potential barrier) is increased.

In order to estimate the magnitude of the nonspherical corrections in these layer-type compounds, I have performed an additional APW calculation for $2H - \text{NbSe}_2$ in which the niobium and selenium APW sphere radii of Table III were reduced by 15%. In the original calculation, the nonspherical terms of the potential just inside the niobium spheres varied from -0.45 to +0.20 Ry relative to the spherical average. The corresponding deviations within the selenium spheres were about $\frac{2}{3}$ as large. By shrinking these radii, one reduces the maximum nonspherical corrections just inside both spheres to the range -0.16 to +0.09 Ry. Of course, this increases the peak-to-peak variation of the nonconstant terms of the potential in the region outside the APW spheres (from 1.3 to 1.8 Ry), but this is not serious since these corrections are treated exactly in the APW method.

Relative to the results shown in Fig. 6, it is found that these nonspherical corrections shift the energies of the conduction-band states with Γ_{1+} , Γ_{4-} , M_{1+} , and M_{2-} symmetry by +0.004, -0.003, +0.007, and +0.010 Ry, respectively. Of course, there may be large percentage errors associated with these estimates since they involve energy differences which are comparable in magnitude to the estimated convergence of the APW eigenvalues in either calculation. With this in mind, let us summarize the over-all effect of these nonspherical corrections on the $2H - \text{NbSe}_2$ band structure of Fig. 6. In general, it is found that these corrections lower the energies of states within the selenium $4p$ manifold by less than 0.02 Ry. One exception involves the valence-band state with Γ_{2-} symmetry, where the shift is -0.04 Ry. This causes a slight increase in the $4p - 4d$ energy separation and leaves Γ_{2-} about 0.005 Ry above Γ_{5-} . The corresponding corrections within the niobium $4d$ manifold tend to be positive and less than 0.01 Ry.

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26 Orbital textures and charge density waves in transition metal dichalcogenides by Ritschel, Trinckauf, Koepernik, Büchner, Zimmermann, Berger, Joe, Abbamonte, Geck

(I forgot why was I opening this article at all?)

Abstract

Low-dimensional electron systems, as realized in layered materials, often tend to spontaneously break the symmetry of the underlying nuclear lattice by forming so-called density waves [1]; a state of matter that currently attracts enormous attention [2, 3, 4, 5, 6]. Here we reveal a remarkable and surprising feature of charge density waves (CDWs), namely their intimate relation to orbital order. For the prototypical material 1T-TaS₂ we not only show that the CDW within the two-dimensional TaS₂-layers involves previously unidentified orbital textures of great complexity. We also demonstrate that two metastable stackings of the orbitally ordered layers allow manipulation of salient features of the electronic structure. Indeed, these orbital effects provide a route to switch 1T-TaS₂ nanostructures from metallic to semiconducting with technologically pertinent gaps of the order of 200 meV. This new type of orbitronics is especially relevant for the ongoing development of novel, miniaturized and ultra-fast devices based on layered transition metal dichalcogenides [7, 8].

26.1 Theory

Among the various transition metal dichalcogenides (TMDs), 1T-TaS₂ stands out because of its particularly rich electronic phase diagram as a function of pressure and temperature [9]. This phase diagram not only features incommensurate, nearly commensurate and commensurate CDWs, but also pressure-induced superconductivity below 5 Kelvin. In addition to this, it was proposed early on that the low-temperature commensurate CDW (C-CDW), which is illustrated in Fig. 1 (a),(c), also features many-body Mott-physics [10]. Experimental evidence

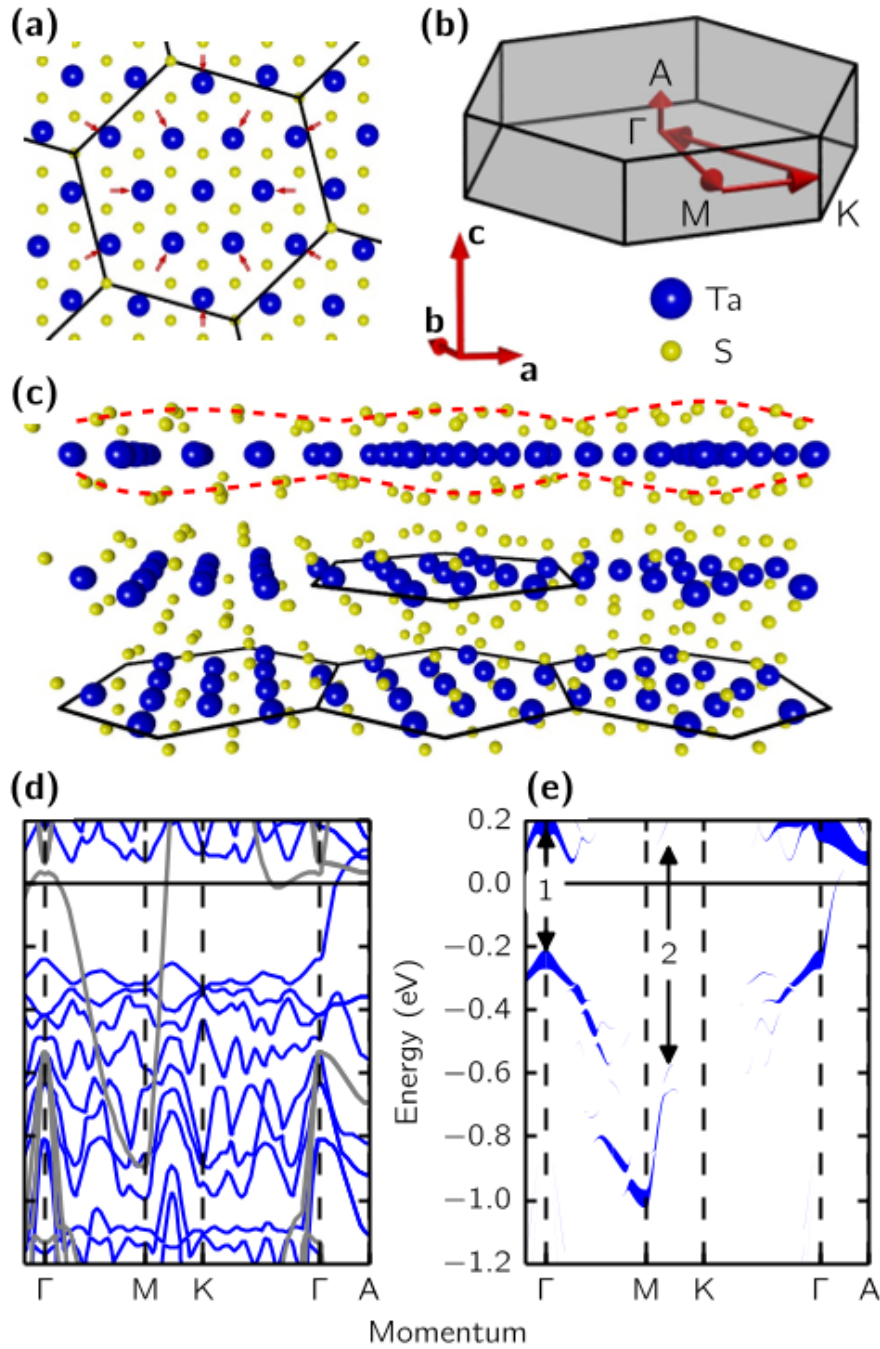


Figure 26.1: **The $\sqrt{13} \times \sqrt{13}$ supercell structure of 1T-TaS₂.** (a) and (c): View along the *c*-axis and parallel to the *ab*-planes, respectively (**a, b, c**: lattice vectors of the undistorted $P\bar{3}m1$ crystal structure). The Ta-displacements indicated by red arrows in (a) are mainly parallel to the *ab*-planes, resulting in clusters containing 13 Ta-sites. Red dashed lines in (c) highlight the breathing of the S-sites perpendicular to the *ab*-plane. (d): LDA supercell band structure along the high symmetry direction in the Brillouin zone shown in (b). The gray lines indicate the unreconstructed band structure. (e): Unfolded band structure. The thickness of bands measures the spectral weight at this position. Arrows indicate the gaps at Γ and between M and K which are commonly named Mott-gap (1) and CDW-gap (2), respectively.

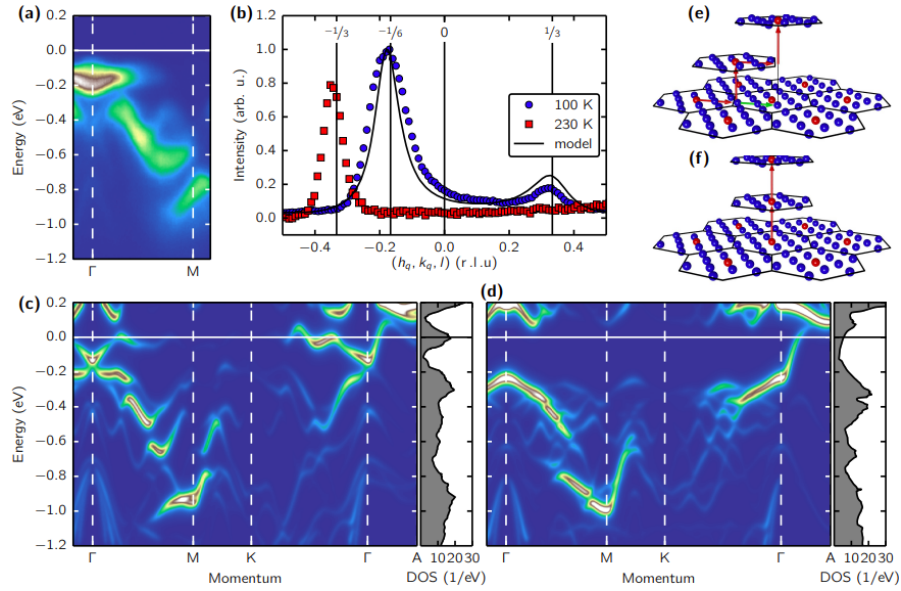


Figure 26.2: **Different layer stackings and their impact on the band structure.** (a): ARPES data of 1T-TaS₂ measured at 1 K. (b): XRD intensity of 1T-TaS₂ measured along the l -direction for the C-CDW and NC-CDW phase. The in-plane q -vector corresponds to $h_q = 16/13$, $k_q = 1/13$ for the C-CDW phase at 100 K and $h_q = 1.248$, $k_q = 0.068$ for the NC-CDW phase at 230 K. The single reflection observed for the NC-CDW implies a well-ordered stacking along c , fully consistent with previous results [15]. On entering the C-CDW phase, the XRD pattern changes markedly and two broad peaks appear owing to the presence of an alternating c -axis stacking (see text). A numerical simulation of the XRD (solid line) further reveals a finite correlation length of the alternating c -axis stacking of approximately $10 \times c$. (c) and (d): Calculated band structure for $\mathbf{T}_S = 2\mathbf{a} + \mathbf{c}$ and $\mathbf{T}_S = 1\mathbf{c}$, respectively. To facilitate the comparison with ARPES data shown in (a) the bandweights have been convolved with a Lorentzian shaped resolution function. (e) and (f): Visualization of the stacking with $\mathbf{T}_S = 2\mathbf{a} + \mathbf{c}$ and $\mathbf{T}_S = 1\mathbf{c}$, respectively. Red arrows indicate the stacking vectors that connect the central Ta-sites (shown in red) in successive layers.

for the presence of Mott-physics in 1T-TaS₂ has indeed been obtained recently by time-resolved spectroscopies, which observed the ultra-fast collapse of a charge excitation gap, which has been interpreted as a fingerprint of significant electron-electron interactions [11, 12, 13].

Even though the above scenario for the C-CDW is widely accepted, important experimental facts remain to be understood: the very strong suppression of the C-CDW with external pressure is puzzling. Already above 0.6 GPa, the C-CDW is no longer stable, although nesting conditions, band widths as well as the lattice structure remain essentially unchanged. It is also not clear how ordered defects within the C-CDW order, which emerge in the nearly commensurate phase (NC-CDW) upon heating [14, 15] and which do not cause significant changes in the bandwidths, can render the electron-electron onsite interaction U completely ineffective [16]. In the following we will show that all these issues are explained consistently in terms of orbital textures that are intertwined with the CDW. In addition to this, we also demonstrate that this new twist to the physics of CDWs also provides a new and powerful device concept for future applications based on TMDs.

An important feature of the C-CDW is its partially disordered stacking along the c -axis: characterizing the relative alignment of the C-CDW in adjacent ab -planes in terms of stacking vectors $\mathbf{T}_S$, which connect the central Ta-sites in successive layers (cf. Figs. 2 (e) and (f)), the c -axis stacking is given by an alternation of $\mathbf{T}_S = 1\mathbf{c}$ with a random choice from the three symmetry equivalent vectors $\mathbf{T}_S = 2\mathbf{a} + \mathbf{c}$, $2\mathbf{b} + \mathbf{c}$ or $-2(\mathbf{a} + \mathbf{b}) + \mathbf{c}$ [17, 18]. The effect of the

different $\mathbf{T}_S$ on the electronic structure so far remained unexplored. Our highly efficient DFT approach (see methods), however, enables us to study these effects for the first time within the local density approximation (LDA).

For our *ab initio* calculations, we chose two superstructures with $\mathbf{T}_S = 1\mathbf{c}$ and $\mathbf{T}_S = 2\mathbf{a} + \mathbf{c}$, respectively, which represent the two metastable types of stacking found experimentally. The calculated total energy for both superstructures differs only by a few meV, implying that these two stacking types are indeed metastable. Fig. 1 (d) shows the band structures for the C-CDW with $\mathbf{T}_S = 1\mathbf{c}$ and the undistorted lattice, where the band dispersions are shown along high symmetry directions of the Brillouin zone of the unmodulated structure (Fig. 1 (b)). In good agreement with previous DFT results [19], the band structure in the plane through Γ , M and K is fully gapped and only along Γ -A a Fermi level crossing occurs. This yields a one-dimensional metal, in line with recent reports [20]. A major disadvantage of such supercell calculations is, however, that the additional backfolded bands only indicate for which momenta $\mathbf{k}$ and energies ω electronic states exist. There is no information about the spectral weight of these states. Exactly this information is provided by the so-called spectral function $A(\mathbf{k}, \omega)$ [21], which is the physically relevant quantity that can be accessed experimentally by e.g., angle-resolved photoemission spectroscopy (ARPES).

An approximation for $A(\mathbf{k}, \omega)$ within DFT, can be obtained using the so-called unfolding procedure [22]. The result of this unfolding procedure for the band structure shown in Fig. 1 (d) is presented in Fig. 1 (e), where the thickness of the individual bands reflects the spectral weight $|A(\mathbf{k}, \omega)|^2$. It is clearly visible that only a small fraction of the reconstructed band structure carries substantial spectral weight. Unlike the bands in Fig. 1 (d), the unfolded band structure allows to clearly identify dispersing bands and, correspondingly, the size and location of energy gaps. Specifically, our calculation yields two gaps around the Fermi level E_F , indicated by arrows in Fig. 1 (e). The gap at Γ is usually interpreted as a Mott-gap due to the electron-electron interaction U [13, 23], while the gap between M and K fits well to the Fermi surface nesting vector and is therefore commonly assigned to a CDW-gap due to the electron-phonon coupling. It is very important to note here, that our calculations do not include any onsite interactions U . The fact that the gap at Γ is obtained without including U is therefore surprising and already implies that this gap cannot be caused by Mott-physics alone.

In Fig. 2 we compare the unfolded LDA band structures for $\mathbf{T}_S = 1\mathbf{c}$ and $\mathbf{T}_S = 2\mathbf{a} + \mathbf{c}$, which yields the first major result of this study: the dramatic dependence of the electronic structure on the CDW-stacking. As can be observed in Figs. 2 (c) and (d), essential features of the low-energy electronic structure depend critically on the stacking. Most notably the bands around the Γ -point are strongly affected. While for $\mathbf{T}_S = 2\mathbf{a} + \mathbf{c}$ the in-plane dispersions show E_F -crossings along Γ -K and Γ -M, both crossings are completely absent for $\mathbf{T}_S = 1\mathbf{c}$. Therefore, a transition from an in-plane metal to an in-plane semiconductor occurs as a function of $\mathbf{T}_S$. Considering that the *ab*-planes of 1T-TaS₂ are usually thought to realize strongly two-dimensional metallic systems, these are most surprising results.

The comparison of the two DFT models to the ARPES data in Fig. 2 (a) shows that the calculation for $\mathbf{T}_S = 2\mathbf{a} + \mathbf{c}$ describes the experiment very well for binding energies below -0.3 eV. However, it is also obvious that both DFT models fail to describe the electronic states close to E_F and, in particular, the pseudo-gap observed experimentally [24]. Including an onsite U at Ta does not cure this discrepancy, implying that these effects are beyond LDA+ U . Indeed, the strong $\mathbf{T}_S$ -dependence of the electronic structure suggests that these deviations are related to the stacking disorder in the real material [18], which cannot be taken into account by our DFT-models. While this issue certainly deserves scrutiny in future work, here we focus on determining the origin of the dramatic effects of $\mathbf{T}_S$.

To this end we calculated the charge density distribution of the uppermost occupied states in real space. As can be seen in Fig. 3, for both stackings a complex orbital texture within

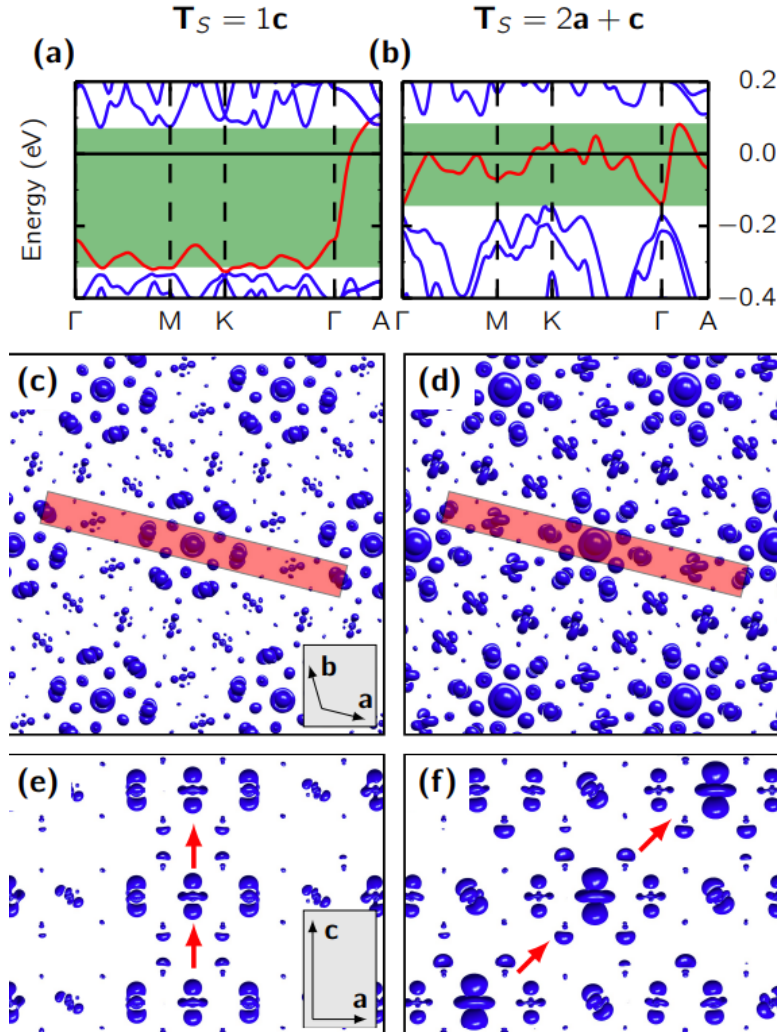


Figure 26.3: **Real space illustration of the electron density for the highest occupied band.** (a) and (b): The band structure near E_F . The energy window used to calculate the energy-resolved electron density is indicated by the green area. (c) and (d): A complex orbital texture emerges within the ab -plane for $\mathbf{T}_S = 1\mathbf{c}$ (c) and $\mathbf{T}_S = 2\mathbf{a} + \mathbf{c}$. (e) and (f), View of the ac -plane corresponding to the red areas in (c) and (d). (e): For $\mathbf{T}_S = 1\mathbf{c}$ significant hopping is allowed only along the c -direction. (f): A substantial ab -component of the hopping appears for $\mathbf{T}_S = 2\mathbf{a} + \mathbf{c}$.

the ab -plane emerges. This is the second major result of this work: the discovery of an orbital texture that is intertwined with a CDW. Note that not only the occupancy of a certain type of orbital changes spatially. Instead also the symmetry of the orbitals clearly changes from site to site, resulting in a complex orbital ordering pattern.

The orbital structure for $\mathbf{T}_S = 1\mathbf{c}$ permits significant charge hopping only along c , as illustrated in Fig. 3 (e). In other words, the charges flow along orbital stripes along c , corresponding to the quasi one-dimensional character of the uppermost band in Fig. 3 (a) and Fig. 2 (d). This drastically changes in the case of $\mathbf{T}_S = 2\mathbf{a} + \mathbf{c}$. Now there is a significant ab -component of the hopping as illustrated in Fig. 3(f), so that the uppermost band attains a larger in-plane dispersion and crosses E_F along Γ -M and Γ -K (Figs. 3 (b) and 2 (c)).

These results have important consequences: Firstly, the comparison of the ARPES data and the DFT results shows that the Γ -gap is obtained on a quantitative level without an onsite repulsion U on Ta. Although this result does not exclude the presence of electron-electron interactions, it strongly argues against U being the main cause for the Γ -gap. Instead, the band

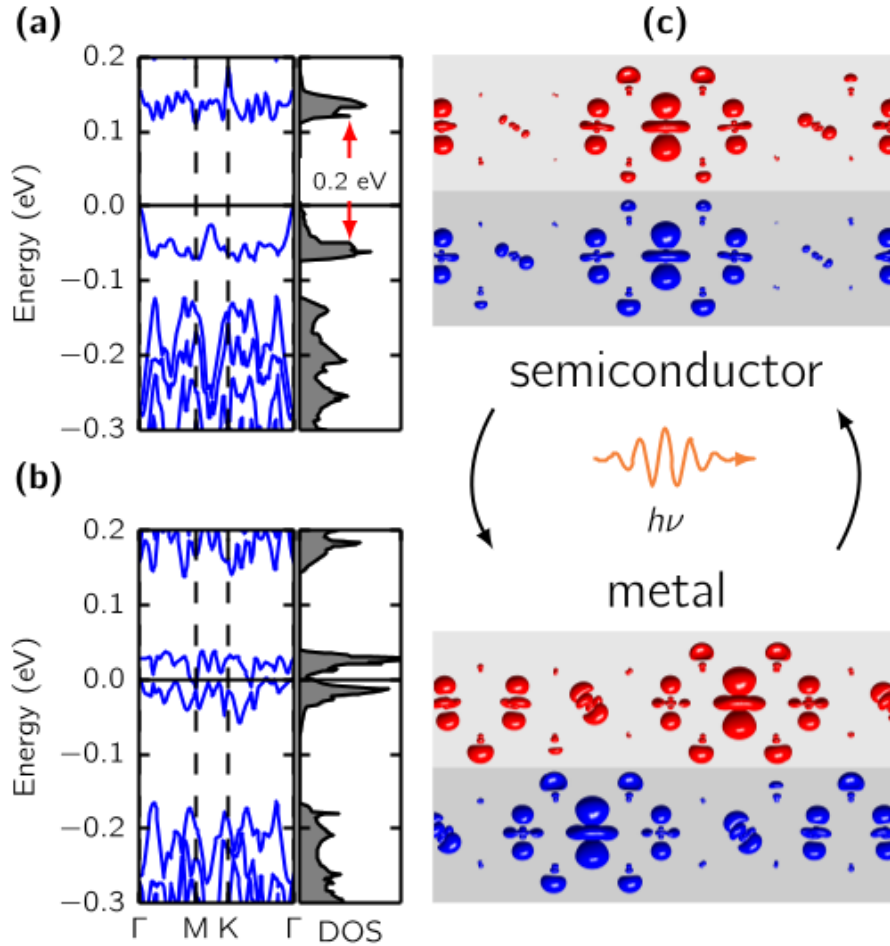


Figure 26.4: **Device concept based on the switching between metastable orbital orders.** Calculated band structure for a bilayer of 1T-TaS₂ with $T_S = 1c$ (a) and $T_S = 2a+c$ (b). A semiconductor-to-metal transition takes place upon changing the stacking of the two layers. (c): Orbital order corresponding to the semiconducting (top) and metallic state (bottom).

structure calculations reveal that this gap is for a large part due to the interlayer hybridization. The latter is in turn mostly caused by the $3z^2 - r^2$ -type orbitals pointing along c , i.e., the Γ -gap is directly coupled to the orbital texture. This result naturally explains the ultra-fast response of this gap observed in time-resolved ARPES experiments, since the disruption and reordering of the electronic orbitals can evolve on much faster time-scales than the lattice.

Secondly, the presence of orbital textures explains the strong pressure dependence of the CDW-order in 1T-TaS₂, because through the orbital texture pressure has a large effect on the stability of CDW-phases with different stackings in a way that goes well beyond traditional nesting scenarios. We also stress that the crucial role of the interlayer interactions is verified experimentally by the data in Fig. 2 (b), which shows that the stacking changes completely across the C-CDW/NC-CDW transition. This change in stacking together with our DFT-results also rationalizes the collapse of the gap at Γ upon entering the NC-CDW with warming.

Thirdly and most importantly, the relative orientation of the orbitals in adjacent ab -planes has a spectacular effect on the band dispersions. This can be readily understood in terms of the overlap integrals, which depend critically on the relative orientation of the orbitals in adjacent layers along c (cf. Figs. 2 (e),(f)). The above immediately yields a new device concept, which employs metastable orbital orders for controlling the electronic structure of nanostructures: As illustrated in Fig. 4 for a bilayer of 1T-TaS₂, switching between the metastable orbital configurations causes a complete semiconductor-metal transition. In other words, by changing

the orbital order in the direction *perpendicular* to the layers, one can control the conductivity *parallel* to the layers. Even though this effect has not yet been observed directly, a very recent experiment provides first evidence that this might be achieved reversibly and on ultra-fast timescales using optical laser pulses [25].

Orbital textures hence enable to manipulate the band dispersion and gap structure of 1T-TaS₂ in a very effective way. They therefore provide a new route to tailor and switch the electronic properties of TMDs, possibly on the femtosecond time scale. This concept of orbitronics may hence enable to create novel, small and ultra-fast electronics, which adds to the large potential of TMDs for future device applications.

26.2 Methods

The **DFT** calculations were done using the FPLO14 package [26], which has been developed at the IFW Dresden and supports unfolding of the band structure as outlined in Ref. [22]. Due to its small basis size it allows for calculations of large supercells extremely efficiently, which makes the presented calculations numerically affordable. The supercell structure for $\mathbf{T}_S = 1\mathbf{c}$ was derived from Ref. [27] and [15]. In order to simulate different layer stackings we transformed the hexagonal supercell into a triclinic supercell without changing the atomic displacements. It is important to note that a structural relaxation, which starts from the undistorted lattice, rapidly converges against the experimentally observed superstructure. In addition, the present DFT calculations reproduce the so-called Mott and CDW gap on a quantitative level. This verifies our approach and shows that the present DFT-models capture the important interactions present in the real material.

XRD data were obtained at the beamline BW5 at the Deutsches Elektronensynchrotron (DESY). We mounted a high-quality single crystal of 1T-TaS₂ in a dispex Helium cryostat sitting in an Euler cradle. The presented XRD data was obtained by measuring the diffracted intensity of the superstructure reflection while scanning along the crystallographic *l*-direction for two different temperatures.

ARPES measurements were conducted at the 1³-ARPES endstation at beamline UE112PG2 at the Berlin Synchrotron (BESSY). We used *p*-polarized light of 96 eV photon energy, so that the final state crystal momentum at normal emission corresponds to the Γ -point [28]. The sample temperature was kept at 1 K.

27 Nanoscale manipulation of the Mott insulating state coupled to charge order in 1T-TaS₂ by Cho et al.

(second cited paper in Jaka's thesis, I'll look later, maybe they also did something like Jaka did)

Quantum states of strongly correlated electrons are of prime importance to understand exotic properties of condensed matter systems [1, 2, 3] and the controllability over those states promises unique electronic devices such as a Mott memory [4]. As a recent example [8], a ultrafast switching device was demonstrated using the transition between the correlated Mott insulating state and a hidden-order metallic state of a layered transition metal dichalcogenides 1T-TaS₂. However, the origin of the hidden metallic state was not clear and only the macroscopic switching by laser pulse and carrier injection was reported. Here, we demonstrate the nanoscale manipulation of the Mott insulating state of 1T-TaS₂. The electron pulse from a scanning tunneling microscope switches the insulating phase locally into a metallic phase which is textured with irregular domain walls in the

charge density wave (CDW) order inherent to this Mott state. The metallic state is a novel correlated phase near the Mott criticality with a coherent feature at the Fermi energy, which is induced by the moderate reduction of electron correlation due to the decoherence in CDW. This work paves the avenue toward novel nanoscale electronic devices based on correlated electrons.

The electron motion as represented by the bandwidth W is strongly prohibited by the on-site Coulomb repulsion U and a Mott insulating state develops by the localization of electrons near Fermi energy (E_F) when the U/W exceeds a critical value [1]. In a unique Mott insulator of 1T-TaS₂, the correlated insulating state is brought by the spontaneous formation of the CDW order, which substantially reduces (increases) the bandwidth W (U/W) at E_F [16, 7]. Due to the entanglement, the Mott transition might be controlled by the CDW order. Indeed, the resistance abruptly decreases by one order of magnitude upon increasing the temperature above $T_c \sim 220$ K [8] where the CDW order melts to small domains textured by nearly commensurate (NC) domain wall networks [9]. The metallic phase with textured CDW can be generated not only by the thermal excitation but also by the chemical doping [10, 11, 12], the photoexcitation [13, 8], the pressure [7], the carrier injection [15, 23] and the reduction of thickness [17, 9].

While these studies demonstrate the macroscopic controllability of the correlated Mott insulating phase by the CDW order, the origin of the excited metallic phase, the textured CDW phase, has been elusive. The metallicity was attributed to the metallic domain wall themselves [7], the metallization of the Mott-CDW domains due to the screening by free carriers of domain walls [10], or the change of the interlayer stacking order [51]. However, there has been no experimental verification of these scenarios and no direct information on the electronic structure of the domain wall. The nature of the metallic phase is also in the center of the current debate on the mechanism of the superconductivity emerging at low temperatures [7, 20, 11, 12].

In the present study, we have succeeded in the nanoscale manipulation of the metal-insulator transition of the Mott insulating phase of 1T-TaS₂. A few tens of nanometer metallic patches can reversibly be formed and erased with an atomically abrupt phase boundary by applying voltage pulse from a scanning tunneling microscope tip. The spectroscopy measurements with atomic resolution rule out the existence of substantial free carriers along domain walls and unveil the novel correlated nature of the metallic phase.

Figure 1a illustrates the CdI₂-type crystal structure of 1T-TaS₂ with Ta atoms octahedrally coordinated by S atoms. A unit layer consists of one Ta layer sandwiched between two S layers. Within the insulating phase at low temperature, 1T-TaS₂ develops a long-range ordered CDW accompanied with the *David-star* distortion; 12 Ta atoms shrink toward the center Ta atom and S layers swell up along the c -axis. Such a deformation forms a commensurate $\sqrt{13} \times \sqrt{13}$ triangular superlattice ($a_{CDW} \sim 12.1$ Å) (Fig. 1b) [21]. The lattice deformation brings about the charge localization at the center of *David-stars*, which is clearly resolved in the STM image of the CDW phase (Fig. 1c) [22].

The manipulation of the Mott-CDW phase was realized by applying a positive voltage pulse ($V_s \geq +2.0$ V and $\Delta t = 100$ ms) within a typical scanning tunneling microscope (STM) set-up (Fig. 1c and Methods). A pulse creates a textured CDW domain of a few tens of nanometers with an irregular domain wall network inside. The additional pulse (solid arrows in Fig. 1d) can also reduce the size of a preexisting textured CDW domain (dashed arrows in Fig. 1d). The higher a pulse voltage is, the bigger patch is formed. At this temperature, the textured CDW patch can be very much stable but the STM imaging with a moderate tunneling current gradually reduces its size (from 5 to 8 of Fig. 1d). This indicates the metastability of the textured CDW phase and that we can reproducibly induce a textured CDW patch on a roughly desired position and erase it.

It has been shown that the Mott-CDW phase can be macroscopically turned into the metallic

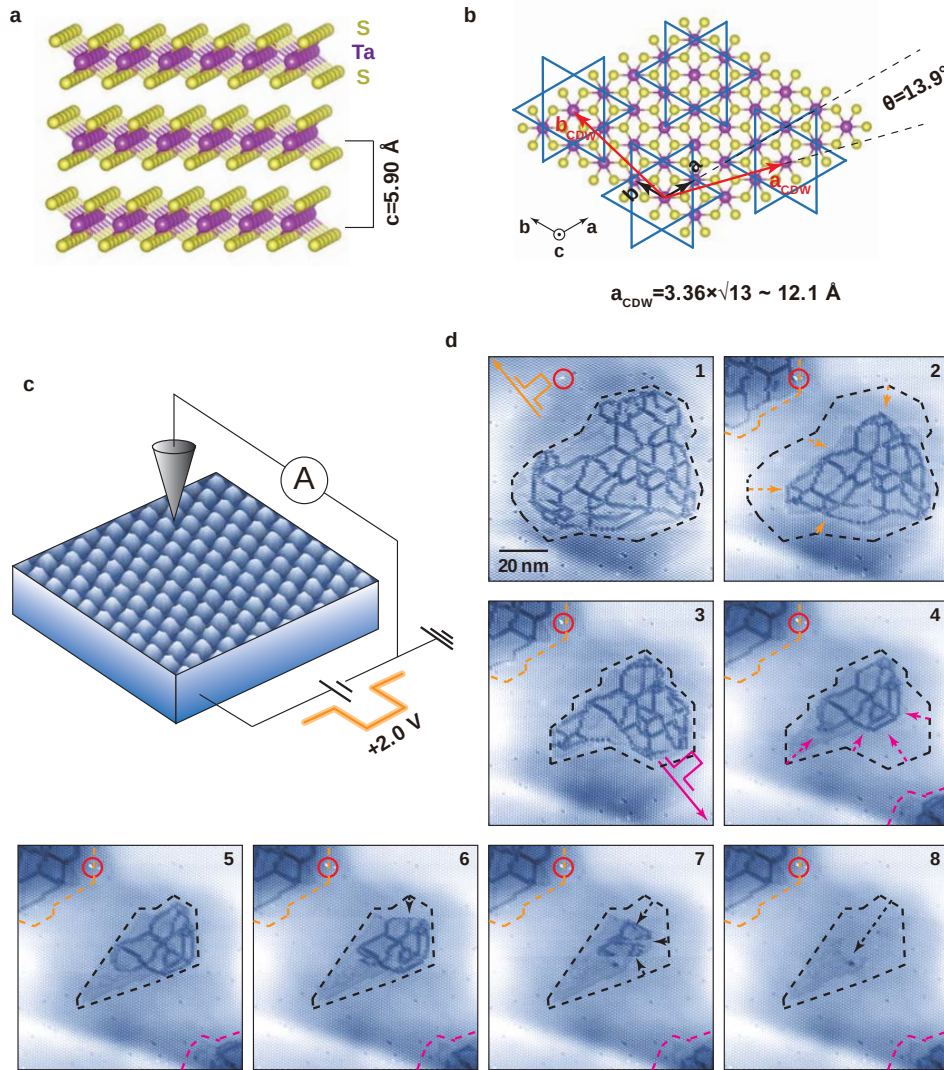


Figure 27.1: **Nanoscale manipulations via positive voltage pulses to the CDW domain.** **a**, Side and **b**, Top-view of the atomic structure of $1T\text{-TaS}_2$ with the *David-star* CDW pattern superimposed. **c**, STM set-up with an image of the CDW phase (tunneling current $I_t = 100$ pA, sample bias $V_s = -0.80$ V and scan size $L^2 = 12 \times 12$ nm 2) of $1T\text{-TaS}_2$ at $T = 4.3$ K. **d**, A series of STM images ($I_t = 100$ pA, $V_s = -1.20$ V and $L^2 = 92 \times 92$ nm 2) showing the time evolution of domains with the broken phase coherence of the CDW order by the domain wall network. An impurity (red circles) is used as a landmark for all images. Before the STM images of 1, 2 and 4, V-pulses are applied with an amplitude of +2.0 V, +2.10 and +2.35 V with a duration of 100 ms at the central, upper-left and lower-right sites (red and yellow arrows), respectively. The dashed lines and arrows indicate the pulse-induced evolution of domains.

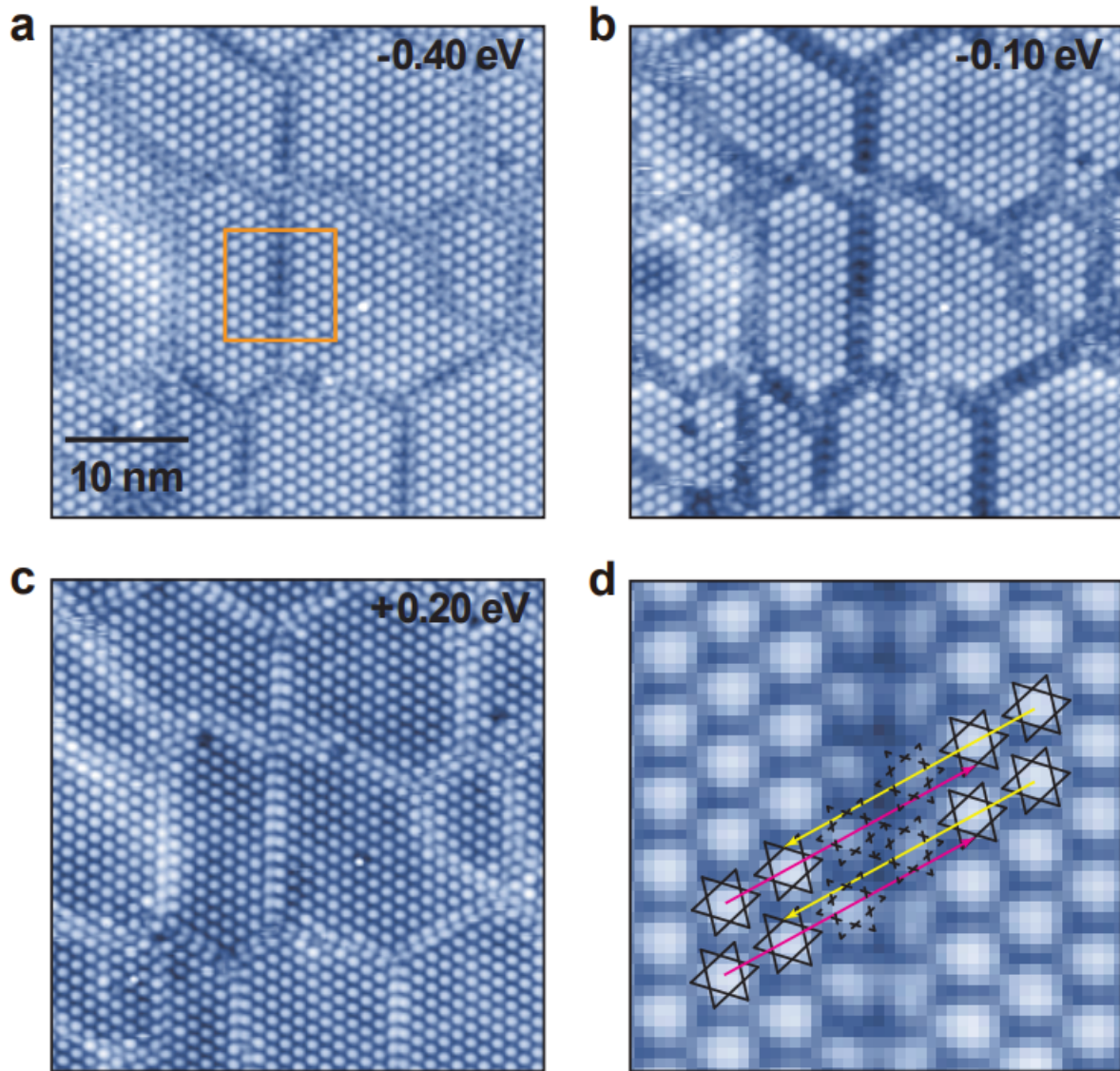


Figure 27.2: **STM images of the textured CDW phase with domain walls.** a–c, Bias dependent STM images showing the structure and electronic states of domain walls in the textured CDW phase ($I_t = 100$ pA, $V_s = -0.40, -0.10$ and $+0.20$ V and $L^2 = 40 \times 40$ nm²). d, Zoomed-in of the area in the orange box of Fig. 2a. The phase shift of the CDW ordering across the domain wall is illustrated with the arrows. The dashed *David-stars* cannot construct perfect CDW unit cells due to the misfit at the domain wall.

phase with textured CDW by thermal excitation [8] or carrier doping [15, 23, 17, 9]. They commonly introduced the crucial role of extra carriers and, in particular, the temperature-dependent Hall measurement [23] and the electric-field-effect study [23] indicated the direct role of hole carriers over the critical density in creating topological defects of domain walls. In the present case, only a positive V-pulse is active, where the local hole concentration under the STM tip is enhanced [24]. This is consistent with the hole-carrier mechanism, while we cannot completely exclude the local heating effect and the transient electron carrier injection by the tunneling current.

The topological defect itself is well resolved in the STM images (Fig. 2). The phase of the CDW changes abruptly across the domain wall as shown in Fig. 2d, which directly affects two adjacent rows of CDW maxima as shown by their reduced contrast. Two rows of reduced CDW maxima and the CDW phase shift is the most common domain wall configuration. While the details were not revealed, this domain wall is consistent with those of the thermally excited NC-CDW phase [9]. However, the NC-CDW phase has ordered Kagome lattices of domain walls [9, 25] while the present domain wall network is disordered. This difference is apparently related to the quenched nature of the present textured CDW patches, being far away from the thermal equilibrium. The present case would be close to the metallic phase induced by the laser excitation from the low temperature phase. This work calls the metallic phase a hidden, thermodynamically unreachable, order state and assumed a triangular lattice of the domain walls without any microscopic information [8].

Most of the previous works blamed the conducting channel along a domain wall as the origin of the metallic property, directly [7] or indirectly [10]. Nevertheless, there has been very little direct spectroscopic information on domain walls. The present study clearly rules out the dominating metallic nature of the domain wall denying most of the previous metallization scenarios for various textured CDW phases. In the STM image, the contrast of the domain walls is suppressed close to E_F (Fig. 2b) and enhanced at $V = +0.20$ eV (Fig. 2c). This indicates that the domain walls have little density of states near E_F with its own electronic state at $+0.20$ eV, which is more directly verified by the spatially resolved $dI/dV(r, V)$ curves (green curves in Figs. 3d and 3e) discussed below.

In stark contrast, the textured CDW patch has a clear metallic characteristic. We took the $dI/dV(r, V)$ curves starting from a textured CDW patch into the normal Mott-CDW background. In the ordered Mott-CDW region, two prominent peaks at $V = -0.19$ and $+0.23$ eV are resolved, which correspond to the lower and upper Hubbard bands, respectively, constituting the Mott gap of $\Delta_{Mott} = 0.42$ eV. Beyond the Mott gap, there is additional band splitting away from E_F , most importantly, around $V = -0.30$ eV. This band gap is known to come from the CDW formation [7] and the peak at -0.42 eV is ascribed to the top of the valence subbands. [10, 26, 27] This band splitting makes the necessary condition for the Mott insulating state, *i.e.* a narrow band at E_F . In contrast, within the textured CDW patch, the tunneling spectra unambiguously indicate finite density of states around E_F . The zero-bias conductance profile [$dI/dV(r, 0)$] in Fig. 3c contrasts sharply the metallic and insulating regions. Note that the zero-bias conductance or the E_F density of states is peaked on the CDW maxima within the texture CDW patch. These peaks are due to a pronounced spectral feature very close to E_F (white arrows in Fig. 3b, the grey bar in Figs. 3d, and the black arrow in Fig. 3e). In addition, the tunneling spectra in the textured CDW phase exhibit broad features centered at -0.12 and $+0.16$ eV. They are similar to the Hubbard states in the Mott-CDW phase but shifted slightly toward E_F with a substantial reduction of the intensity and a noticeable broadening. On the other hand, the top of the valence band is also shifted substantially toward E_F (Fig. 3e).

The spectral characteristics of the textured CDW phase within the Mott gap can be straightforwardly related to the breakdown process of a Mott insulating state. The present system has been effectively described by an one band Hubbard model on a triangular lattice at the half

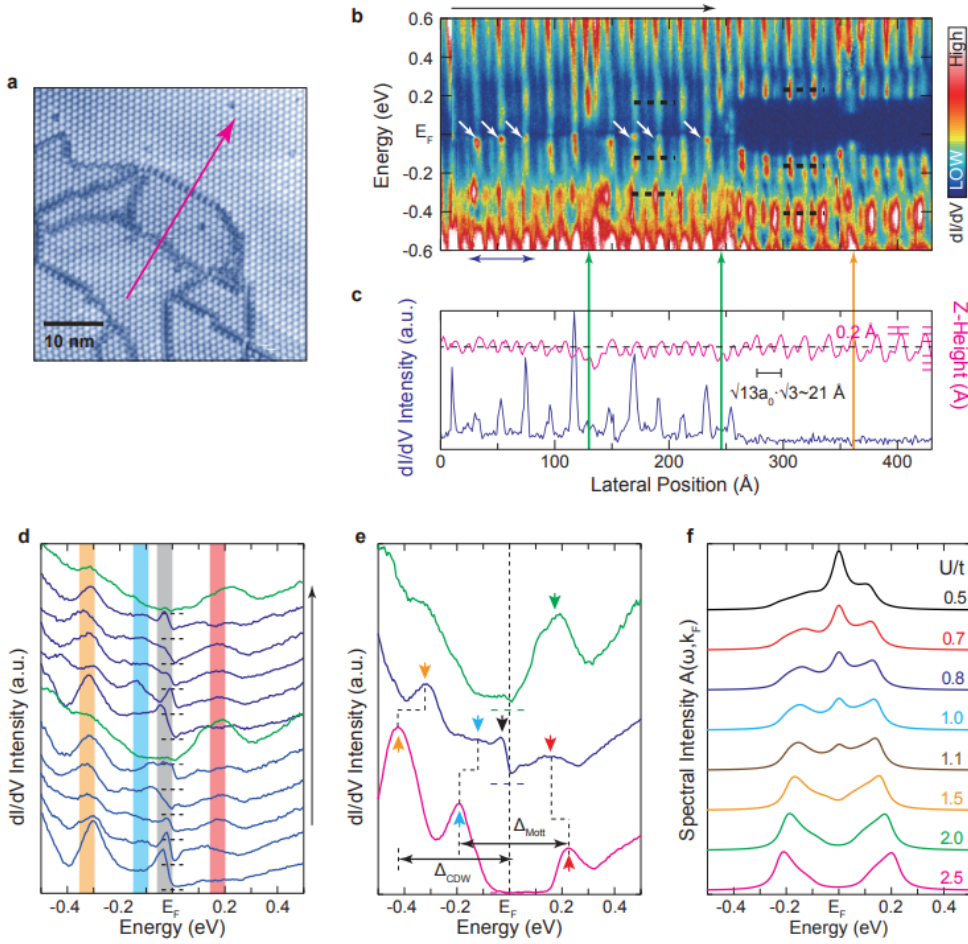


Figure 27.3: **Direct comparison of electronic structures between commensurate and textured CDW phases** **a**, STM image of a crossover region between the commensurate and textured CDW phase ($I_t = 10$ pA, $V_s = -1.20$ V and $L^2 = 45 \times 45$ nm²). **b**, The differential conductance $dI/dV(r, eV)$ data measured along the arrow in Fig. 3a. **c**, Z-height (magenta) and dI/dV intensity profiles at E_F (blue) taken together with the $dI/dV(r, eV)$ data. The vertical orange and green arrows indicate a point defect and domain walls, respectively. **d**, $dI/dV(eV)$ curves along the black arrow shown in Fig. 3b. Each curve is averaged within each CDW cluster and shifted for comparison. The spectra in green are for the domain walls in the textured CDW region. Colored vertical bars indicate the prominent peak positions, which are also marked with arrows in Fig. 3e. **e**, Spatially averaged $dI/dV(V)$ curves of the insulating commensurate CDW phase (magenta), the metallic domain (blue), and the domain wall (green). The horizontal dashed lines mark the zero conductance. Blue (red), yellow and green arrows indicate the lower (upper) Hubbard state, the topmost valence band, and the resonance peak, respectively. **f**, Theoretically calculated spectral function for different correlation U/t in a triangular lattice.

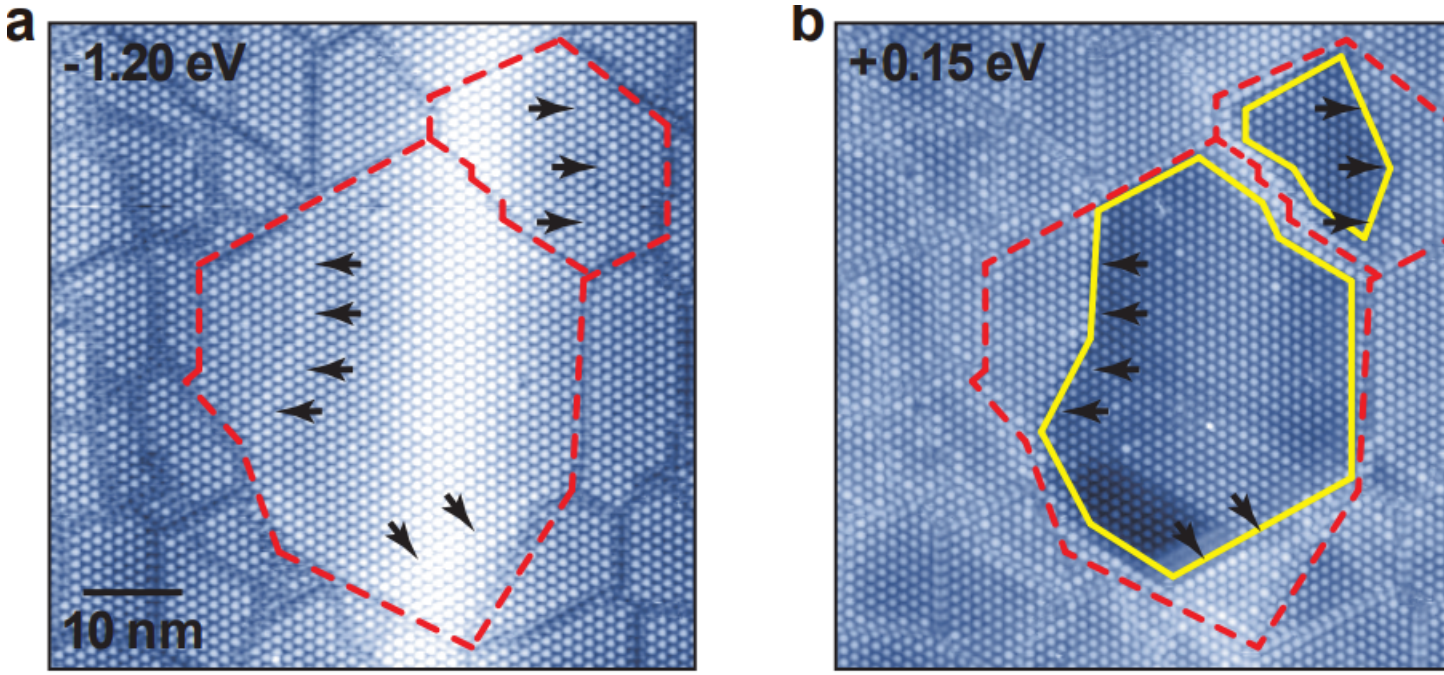


Figure 27.4: **Existence of the subdomains and the stacking order** High (a,) and low (b,) bias STM image of the textured CDW domain ($I_t = 10$ pA, $V_s = -1.20$ and $+0.15$ V and $L^2 = 90 \times 90$ nm²). The relatively large CDW domains (red lines) within a texture CDW patch and the insulating subdomains (yellow) within them. The black arrows indicate the domain walls in the sublayers.

filling (see Methods). Our own theoretical calculation based on spin-liquid physics [28] (see Methods) reveals a metal-insulator transition as a function of U/t (t , an intersite hopping integral proportional to W), which captures all the major experimental findings; weakening and broadening of the Hubbard states together with the reduction of the Mott gap (Fig. 3f) and the appearance of the coherent resonance peak near E_F . The coherent peak was assigned as the Abrikosov-Suhl resonance in the previous dynamic mean field theory calculation [29]. These theories assure that the present textured CDW phase is a correlated metallic state close to the critical regime of the Mott transition ($U/t \sim 1.4$ in Fig. 4f).

What remains to be explained is the origin of the reduced correlation U/W to drive the transition. The screening by free carriers of domain walls [10] is not likely due to the lack of substantial free carriers in the dI/dV data. Instead, we note that the long range CDW order is lost within the textured CDW patch. The reduced CDW order would naturally decrease the CDW band splitting, which is clearly evidenced by the substantial energy shift of the split valence band top in Fig. 4e. The effect of the reduced CDW band gap on the Mott state can be traced by calculating the evolution of the bandwidth at E_F . Our own calculations unambiguously show that the bandwidth at E_F is linearly increased by the decrease of the CDW order parameter (see supplementary information). The bandwidth increase of the Hubbard bands is evident in the experiment. This is close to the concept of the bandwidth-controlled Mott transition discussed previously [7, 30]. In addition, we can suggest that the domain walls act also as the disorder in the Mott system, which generally reduces the correlation energy U [31]. Thus, we conclude that the reduced CDW order induces the increased bandwidth W and at the same time reduced U , which drives the Mott-CDW state into the critical regime of a correlated metallic state.

While the STM images we showed so far only deal with the lateral CDW ordering, we also notice that the vertical CDW stacking order has a crucial impact on this transition. Figure 4 shows that a relatively large domain within the metallic patch has extra but weak domain walls

inside (black arrows in Fig. 4a), which is assigned as the domain wall existing in the sublayer(s). The low bias images and the spectroscopy data indicate clearly that this domain harbors insulating subdomains as defined by the sublayer domain walls. One can straightforwardly deduce that these subdomains correspond to different interlayer stacking of the CDW; the interlayer CDW stacking order is lost by the formation of the irregular domain wall networks in each layer except for those metallic subdomains. This suggests that not only the intralayer but also interlayer CDW order has to be taken into account to explain the reduced electron correlation for the Mott transition. The importance of the interlayer CDW stacking order was recently discussed while the direct experimental information has been lacking [51].

The present case of $1T$ -TaS₂ is one of the very rare example of the nanoscale control over strongly correlated electronic states. We can find only one case for the nanoscale manipulation of a Mott insulator in GaTa₃Se₈ [32]. In this case, the strong electric-field-induced deformation of the lattice occurs and the transition is close to the avalanche dielectric breakdown [33]. In the present system, the transition is largely electronic and the resulting metallic state is a novel correlated state near the Mott criticality. The uniqueness of the present system lies on the intercoupled nature of the Mott state with the CDW order, which provides the extra tunability of the Mott state by a distinct order. The ultrafast switching capability of the present system [8, 15, 23] in combination with the nanoscale controllability is expected to provide a unprecedented novel device platform based on correlated electronic systems.

Methods

Preparation of single crystal 1T-TaS₂. The single crystals 1T-TaS₂ were grown by iodine vapor transport method in the evacuated quartz tube. Prior to growth of the sample, the powder 1T-TaS₂ was sintered for 48 hours at 750 °C. We repeated this process two times to get poly-crystals. In order to get high quality sample, the seeds were slowly transported by iodine at 900~970 °C for 2 weeks. The tube was rapidly cooled down to room temperature in the air due to the metastability of the 1T phase.

STM and STS measurements. The STM and STS measurements have been performed with a commercial STM (SPECS) in ultra high vacuum at $T = 4.3$ K. The STM tips were prepared by mechanically sharpened Pt-Ir wires. All of STM images are acquired with the constant current mode with bias voltage V applied to the sample with a fixed duration of $t = 100$ ms and a varying amplitude. When the positive V-pulses are applied to the sample, the feedback loop is opened with scanning condition ($V = -0.8 \sim -1.2$ eV and $I_t = 10 \sim 100$ pA). We can get the small texture CDW domain below $V_p \sim +2.0$ eV and a larger textured CDW phase with increasing amplitude. The dI/dV(eV) curves are recored using a lock-in technique with voltage modulation $V_m = 10$ mV and frequency $f = 1$ kHz.

Theoretical calculations. The CDW-Mott state in 1T-TaS₂ can be described by an effective one-band Hubbard model on the triangular lattice at half filling

$$H = -t \sum_{\langle ij \rangle \sigma} (c_{i\sigma}^\dagger c_{j\sigma} + H.c.) - \mu \sum_{i\sigma} c_{i\sigma}^\dagger c_{i\sigma} + U \sum_i n_{i\uparrow} n_{i\downarrow}, \quad (27.1)$$

where $c_{i,\sigma}$ is an electron annihilation operator with spin σ at site i , identified with each center of *David-star*. Hinted from the observation that the coherent peak emerges in the textured CDW state, we take the U(1) slave-rotor representation for possible spin-liquid physics at least in the intermediate temperature regime [34]. It is straightforward to perform the saddle-point analysis based on an ansatz for spin liquid physics [28], which leads us to confirm the existence of a metal-insulator transition from a spin-liquid-type Mott insulating state to a correlated metallic phase at critical value of U/t (see Supplementary information for details).

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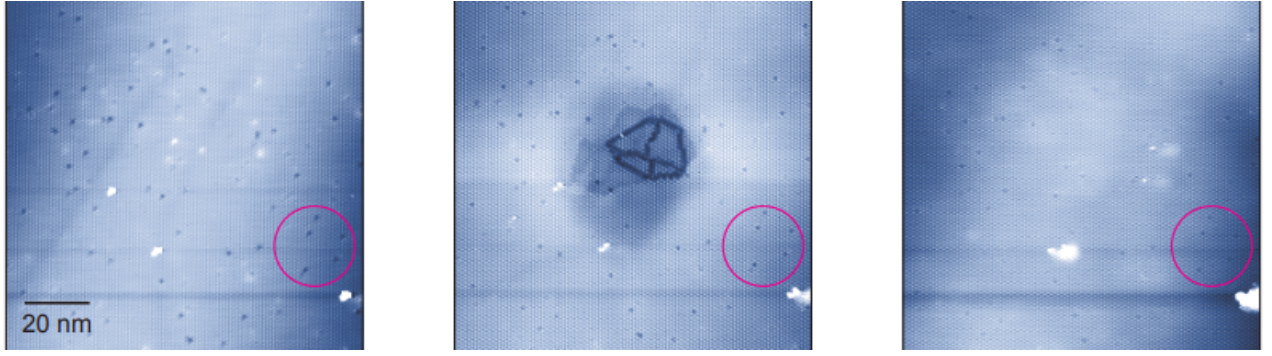


Figure S1: **Creation and annihilation of a small textured CDW Domain.** **a**, STM image ($I_t = 10$ pA, $V_S = -0.80$ V, $L^2 = 110 \times 110$ nm²) intrinsic several defects (a land mark indicated by a magenta circle) **b**, Creation of the textured CDW domain by applying V-pulse ($V_{pulse} = +2.0$ V and $t = 100$ ms). **c**, Annihilation of the metastable state by scanning. Although the tip condition was changed by applying V-pulse process, the quality of the STM images is enough to demonstrate the nanoscale manipulation.

27.0.1 SM. Creation and Annihilation of the Textured CDW Domain

In this section, we explain the details of the nanoscale manipulation in 1T-TaS₂. At first, we acquired STM image of the commensurate CDW domain with several intrinsic defects which can be a landmark (Fig. S1a). After applying a positive voltage pulse ($V_{pulse} \geq +2.0$ V and $t = 100$ ms) to the well ordered Mott-CDW state, the creation of the textured CDW patch is confirmed by acquiring STM images (Fig. S1b). The contrast of the textured domain is suppressed and the surface and subsurface domain walls are simultaneously generated. The minimum voltage required is about $+2.0$ V, where the smallest textured CDW patch as shown in Fig. S1a is created. The size of the patch increases as the pulse amplitude grows. No patch is formed with negative voltage pulses. The annihilation of the metastable phase with the domain walls, then, can be induced by applying another V-pulse near the textured domain or scanning over it repeatedly (Fig. S1c). The hidden states generated by macroscopic perturbations in 1T-TaS₂ have been known to be annihilated by the thermal annealing process ($T \sim 70$ K) due to its prominent stability [14].

27.0.2 SM. Dependence of the bandwidth on the CDW order

In order to investigate the relationship between the CDW order and the bandwidth of the Mott band of the CDW-Mott insulator 1T-TaS₂, we performed density-functional theory calculations that employ the generalized gradient approximation (GGA) [39] and the projector-augmented wave method [37], as implemented in VASP [38, 5]. Valence electron wavefunctions were expanded in a plane wave basis set with a cutoff energy of 259 eV. The k -point integration was performed using a uniform with a 4×4 mesh for the Brillouin zone of the $(\sqrt{13} \times \sqrt{13})$ cell with the *David-star* distortion (Fig. S2 a).

The star distortion makes the broad metallic band split into several subband manifolds with a narrow half-filled band at the Fermi level (Fig. S2 b). There are two important energy scales to characterize the electronic structure of the CDW state, the bandwidth (W) of the narrow band and the CDW gap (Δ_{CDW}). The latter defined as the energy gap between the Fermi level and the edge of the lower subband reflects the extent of CDW order. The dependence of the bandwidth on the CDW order was examined by calculating W and Δ_{CDW} as a function of the CDW order parameter, the size of the star distortion, using the linearly interpolated structures

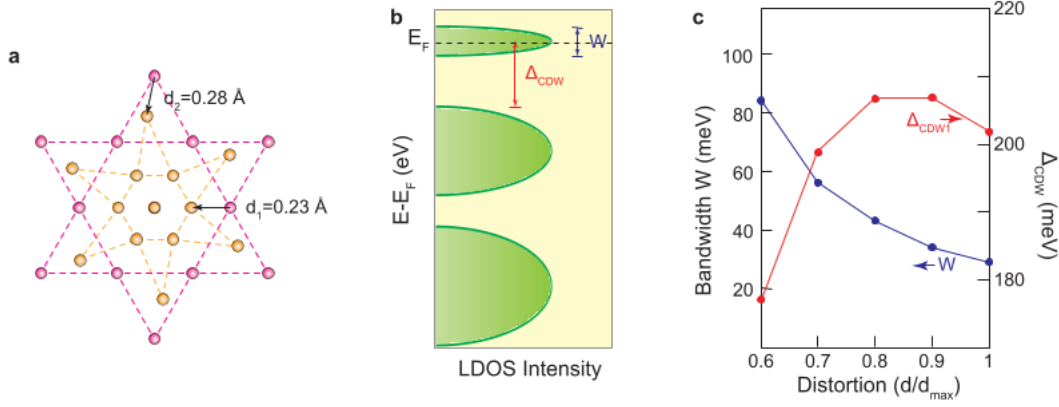


Figure S2: **Dependence of the narrow-band bandwidth on the CDW order** **a**, The atomic structure of the 1×1 triangular lattice (magenta dashed lines) and the *David-star* distortion (orange dashed lines). The atomic displacements are exaggerated. **b**, The schematic view of the CDW-induced band splitting. **c**, The evolution of the bandwidth and the CDW gap as a function of the degree of the star distortion. The atomic structures of intermediate distortions are taken by linearly interpolating the undistorted (1×1) and the fully relaxed $\sqrt{13} \times \sqrt{13}$ structure

of the undistorted (1×1) and the fully relaxed $\sqrt{13} \times \sqrt{13}$ structure (Fig. S2 c). At the full relaxation, W and Δ_{CDW} were calculated to be 30 meV and 202 meV, respectively. When the star distortion diminishes, the bandwidth increases, while the CDW gap decreases, establishing a clear inverse proportion between them, in consistent with the earlier expectations [13, 19]. The present result demonstrates that the CDW order can give us a extra controllability for the bandwidth-controlled metal-insulator transition in CDW-Mott insulator 1T-TaS₂.

27.0.3 SM. Caculation details for a metal-insulator transition in a spin-liquid-type Mott insulator

The correlations between unpaired electrons on the center of *David-star* seem to be responsible for the electrically controlled metal-insulator transition. It can be described by an effective one-band Hubbard model on the triangular lattice at half filling

$$H = -t \sum_{\langle ij \rangle, \sigma} (c_{i\sigma}^\dagger c_{j\sigma} + H.c.) - \mu \sum_{i, \sigma} c_{i\sigma}^\dagger c_{i\sigma} + U \sum_i n_{i\uparrow} n_{i\downarrow}. \quad (27.2)$$

$c_{i, \sigma}^\dagger$ ($c_{i, \sigma}$) is an electron creation (annihilation) operator with spin σ at site i . The site i corresponds to the center of *David star*. $n_{i, \sigma}$ is the number operator for spin σ at the site i . μ is an electron chemical potential, which fits the number of such unpaired electrons at half filling. U is the on-site Coulomb energy and t is the hopping integral between the nearest neighbors.

Resorting to the U(1) slave-rotor representation $c_{i\sigma} = e^{-i\theta_i} f_{i\sigma}$ for possible spin-liquid physics at least in the intermediate temperature regime [8], where bosonic field θ_i describes dynamics of collective charge fluctuations (sound modes) and $f_{i\sigma}$ expresses a fermionic field for spin degrees of freedom [9], we reconstruct an effective theory from the Hubbard model in terms of such

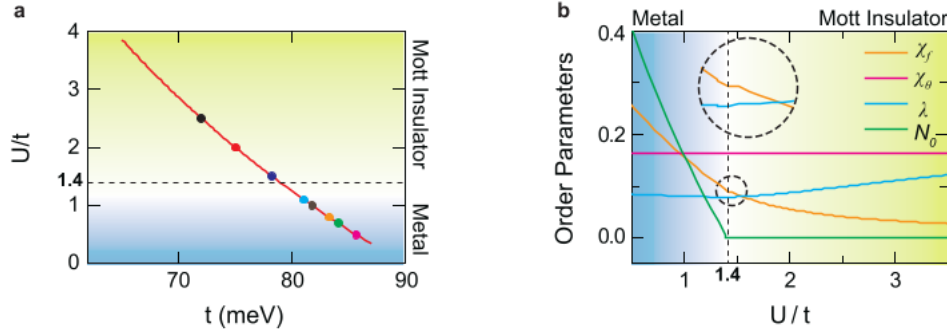


Figure S3: U/t controlled metal-insulator phase transition in spin-liquid description.

a, The phase diagram and the way to control U and t for spectral functions in Fig. 3f. Each spectral function was acquired at the colored dots. **b**, Using the parameters in Fig. S3a, the amplitude of order parameters $\chi_f, \chi_\theta, \lambda$, and N_0 are calculated self-consistently. These parameters show the Mott transition at $U/t \approx 1.4$. The circle-shaped inset shows a kink-like behavior, which is consistent with the usual phase transition nature in the spin-liquid description [28]. The lattice size is 30×30 and the temperature is set to be $T = 4.3$ K from the experimental condition.

bosonic and fermionic fields. As a result, it is given by

$$S_F = \int_0^\beta d\tau \left[\sum_{i,\sigma} f_{i\sigma}^\dagger (\partial_\tau - \mu) f_{i\sigma} - t\chi_f \sum_{\langle ij \rangle, \sigma} (f_{i\sigma}^\dagger f_{j\sigma} + H.c.) \right], \quad (27.3)$$

$$S_B = \int_0^\beta d\tau \left[\frac{1}{2U} \sum_i (\partial_\tau b_i^\dagger)(\partial_\tau b_i) - t\chi_\theta \sum_{\langle ij \rangle} (b_{i\sigma}^\dagger b_{j\sigma} + H.c.) + \lambda \sum_i (|b_i|^2 - 1) + 2L^2 z t \chi_f \chi_\theta \right], \quad (27.4)$$

where the conventional saddle-point approximation has been performed for a spin-liquid-type Mott insulating phase. Here, χ_f and χ_θ describes band renormalization for electrons and the width of incoherent bands, respectively. λ is a Lagrange multiplier field to control the spin-liquid to Fermi-liquid phase transition, regarded as the chemical potential of bosons. These equations are based on a nonlinear σ -model description, where the rotor variable $e^{-i\theta_i}$ is replaced with b_i and unimodular constraint $|b_i|^2 = 1$ is taken into account [9]. $z = 6$ is the nearest coordinate number of the triangular lattice. L^2 is the size of system.

Performing the Fourier transformation and the Gaussian integration for both bosons and fermions, we obtain the mean-field free energy

$$F_{MF} = F_F + F_B + L^2(2zt\chi_f\chi_\theta - \lambda), \quad (27.5)$$

$$F_F = -\frac{N_\sigma}{\beta} \sum_{\mathbf{k}} \ln [1 + e^{-\beta E_F(\mathbf{k})}], \quad (27.6)$$

$$F_B = \frac{1}{\beta} \sum_{\mathbf{k}} (\ln [1 - e^{-\beta E_B(\mathbf{k})}] + \ln [e^{\beta E_B(\mathbf{k})} - 1]), \quad (27.7)$$

where $E_F(\mathbf{k}) = t\chi_f\epsilon_{\mathbf{k}} - \mu$ is the dispersion of fermions and $E_B(\mathbf{k}) = \sqrt{2U(t\chi_\theta\epsilon_{\mathbf{k}} + \lambda)}$ is that of bosons. $N_\sigma = 2$ represents the spin degeneracy. $\epsilon_{\mathbf{k}}$ is the energy dispersion relation for electrons on the triangular lattice at $U = 0$ and $t = 1$.

Minimizing the effective free energy $F_{MF} = F_{MF}(\chi_f, \chi_\theta, \lambda)$ with respect to χ_f , χ_θ , and λ , we find a metal-insulator transition from a spin-liquid-type Mott insulator to a correlated metal

at $U/t \approx 1.4$ as shown in Fig. S3b. It is important to note that the U and t can be controlled by the strength of the commensurate CDW ordering as discussed in the section II.

Considering the U(1) slave-rotor decomposition representation, it is straightforward to find that the electron spectral function is given by the convolution integral between fermion and boson propagators,

$$G(\mathbf{k}, i\omega) = \frac{1}{\beta} \sum_{i\Omega} \int \frac{d^2\mathbf{q}}{(2\pi)^2} G_F(\mathbf{k} + \mathbf{q}, i\omega + i\Omega) G_B(\mathbf{q}, i\Omega), \quad (27.8)$$

where

$$G_F(\mathbf{k}, i\omega) = [i\omega + \mu - t\chi_f \epsilon_{\mathbf{k}}]^{-1}, \quad G_B(\mathbf{k}, i\Omega) = \left[\frac{\Omega^2}{2U} + t\chi_{\theta} \epsilon_{\mathbf{k}} + \lambda \right]^{-1} \quad (27.9)$$

are fermion and boson propagators, respectively. Then, the electron spectral function consists of coherent and incoherent parts, given by

$$A_{\text{incoherent}}(\omega, \mathbf{k} = \mathbf{k}_F) = \int \frac{d^2\mathbf{q}}{(2\pi)^2} \frac{U}{E_B} [\{n_F(E_F) + n_B(E_B)\} \delta(\omega - E_F + E_B) - \{n_F(E_F) + n_B(-E_B)\} \delta(\omega - E_F - E_B)], \quad (27.10)$$

$$A_{\text{coherent}}(\omega, \mathbf{k} = \mathbf{k}_F) = N_0 \delta(\omega) \quad (27.11)$$

at the Fermi energy. Here, $n_F(x)$ and $n_B(x)$ are Fermi-Dirac and Bose-Einstein distribution functions, respectively. $E_F = E_F(\mathbf{k} + \mathbf{q})$ and $E_B = E_B(\mathbf{q})$ are $\mathbf{q}$ -dependent dispersions at $\mathbf{k} = \mathbf{k}_F$. N_0 is the condensation amplitude of bosons, which determines the height of the coherent peak in the correlated metallic phase ($N_0 \neq 0$).

As shown in Fig. 3f, an important result of the spin-liquid approach is that the coherent peak in the electron spectral function increases gradually with the decreasing U/t within the correlated metallic regime. And the incoherent part constitutes the double peaks identified with Hubbard bands. They turn out not only to exist inside the Mott insulating state but also to persist rather deep inside the correlated metallic state.

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28 Imaging of electrically controlled van der Waals layer stacking in 1T-TaS $_2$ by Burri, Hua, Sanchez, Hu, Bell, Venturini, Huang, McConnell, Dizdarević, Mraz, Svetin, Lipovšek, Topič, Kazazis, Aeppli, Grolimund, Ekinci, Mihailovic, Gerber (2025)

Abstract

Van der Waals (vdW) materials exhibit a variety of states that can be switched with low power at low temperatures, offering a viable cryogenic “flash memory” required for the classical control electronics for solid-state quantum information processing. In 1T-TaS $_2$, a non-volatile metallic ‘hidden’ state can be induced from an insulating equilibrium charge-density wave ground state using either optical or electrical pulses. Given that conventional memristors form localized, filamentary channels which support the current, a key question for design concerns the geometry of the conduction region in highly energy-efficient 1T-TaS $_2$ devices. Here, we report *in operando* micro-beam X-ray diffraction, fluorescence, and concurrent transport measurements, allowing us to spatially image the non-thermal hidden state induced by electrical switching of 1T-TaS $_2$. Our results reveal a long-range ordered, non-filamentary switched state that extends well below the electrodes, implying that the self-organized, collective growth of the hidden phase is driven by a combination of charge flow and lattice strain. Our unique combination of techniques showcases the potential of non-destructive, three-dimensional X-ray imaging to study bulk switching properties in microscopic detail, namely electrical control of the vdW layer stacking.

28.1 Article

28.1.1 Introduction

Switching between low and high resistance states via electrical excitation has significant potential for analog and neuromorphic computing applications [1, 2, 3]. A key requirement for this is the ability to reversibly transition between two resistance states which can occur through mechanisms such as the formation of a conductive filament, ferroelectric and magnetic tunneling junctions, or phase transitions between crystalline and amorphous states [3, 4, 5, 6]. There is substantial research primarily focused on identifying new candidates for fast and energy-efficient memory devices, and also cryo-computing [7]. Van der Waals (vdW) materials, due to their layered structure, are well-suited not just to explore novel states and phase transitions [11, 12, 13, 14] but are potentially also useful for scalable electronic devices [7, 9, 10].

Among vdW materials, the transition metal dichalcogenide 1T-TaS $_2$ attracts considerable attention for its unique combination of correlated electron phenomena. These include various charge-density wave (CDW) states [27, 10], superconductivity under pressure or doping [9, 18], and a putative quantum spin liquid phase [4, 19]. At low temperatures it is believed to exhibit a Mott insulating state [21, 9], characterized by commensurate (C) CDW order formed by star-shaped polaron domains that tessellate the layers below 150 – 180 K [22, 21]. Moreover,

and of greatest interest to us here, it shows non-thermal, reversible switching to a metastable, metallic ‘hidden’ (H) CDW phase upon application of ultrashort optical or electrical pulses. The lifetime of this HCDW state is short at elevated temperatures and stable below ≈ 40 K [23, 24, 25, 26, 27].

The microscopic origin of the non-thermal switching of $1T$ -TaS₂ has been intensely studied but is not fully understood [23, 18, 41, 24, 30, 35, 32, 33]. It can be described in terms of a low-temperature free-energy landscape that features a global minimum (the Mott insulating equilibrium state) and multiple local minima separated by potential energy barriers [23, 24, 33, 32]. Excitation with a laser or current pulse can drive the system into these metastable states.

Optical switching of $1T$ -TaS₂ with femtosecond laser pulses, exciting electron and holes homogeneously, has been extensively studied with both quasi-static [30, 34, 35] and time-resolved [13, 23, 37, 38, 35, 39, 40, 41, 42] techniques. Surface-sensitive scanning tunneling microscopy (STM) shows formation of conducting domain walls [23, 30], while bulk-sensitive X-ray diffraction (XRD) reveals changes in the out-of-plane polaron stacking and a different in-plane commensurability of the HCDW state compared to the low- and room-temperature CDW states, confirming a non-thermal switching mechanism [35, 42].

In contrast, electrical switching has been less explored despite its promise for application in highly-efficient cryo-memory devices due to the compatibility with standard electronics. The electrically-induced hidden (e-HCDW) state has been studied using transport measurements [26, 25, 43, 44], STM [27, 41, 18], and angle-resolved photoemission spectroscopy [45], revealing macroscopic behavior similar to the optically-induced hidden (o-HCDW) state. Domain wall formation at the surface has also been observed with STM, but unlike the o-HCDW, it is understood that the e-HCDW state results from excitation due to charge carrier separation, leading to more inhomogeneous domain walls [27, 32]. Furthermore, in contrast to the o-HCDW state, the e-HCDW can be triggered with much longer pulses up to 100 ms [46], suggesting key differences in their switching mechanisms. As previously discussed [27, 32], the switching is non-thermal even for long current pulses.

It is unclear whether optical and electrical excitations lead to the same local free-energy minimum. If they do, can these two distinct perturbations—differing in pulse duration, electron-hole pairs accessed, and directionality—follow the same non-thermal pathway, or are there different mechanisms at play? Also, the lack of spatially-resolved studies on the e-HCDW leaves the question unanswered whether the switching is surface-localized or propagates through the bulk. Likewise, it is unknown if the e-HCDW spreads across the entire region in-between the electrodes or forms conducting filament channels. Finally, it is not established whether the principal actor of the switching is the electric field or the current. Resolving the spatial structure and population of the e-HCDW would provide insights into the switching mechanisms, and thereby contribute to designing devices with improved performance and scalability.

The required information can be obtained by mapping the bulk CDW states before and after switching. If the e-HCDW is structurally equivalent to the o-HCDW, then the known CDW diffraction peaks from photo-driven experiments [35] can be used as a fingerprint to identify the e-HCDW switching region. Here we report on *in situ* resistance measurements with micro-beam X-ray fluorescence (μ XRF) and diffraction (μ XRD) to spatially image a nano-fabricated $1T$ -TaS₂ device *in operando* (Fig. 28.1). Analysis of CDW Bragg peaks reveals the detailed three-dimensional (3D) spatial evolution of the material properties before and after electrical excitation.

28.1.2 Results

Figure 28.1b shows an optical image of the $1T$ -TaS₂ device, formed by a contacted flake, used to investigate the e-HCDW state (fabrication details in Methods). The distance between

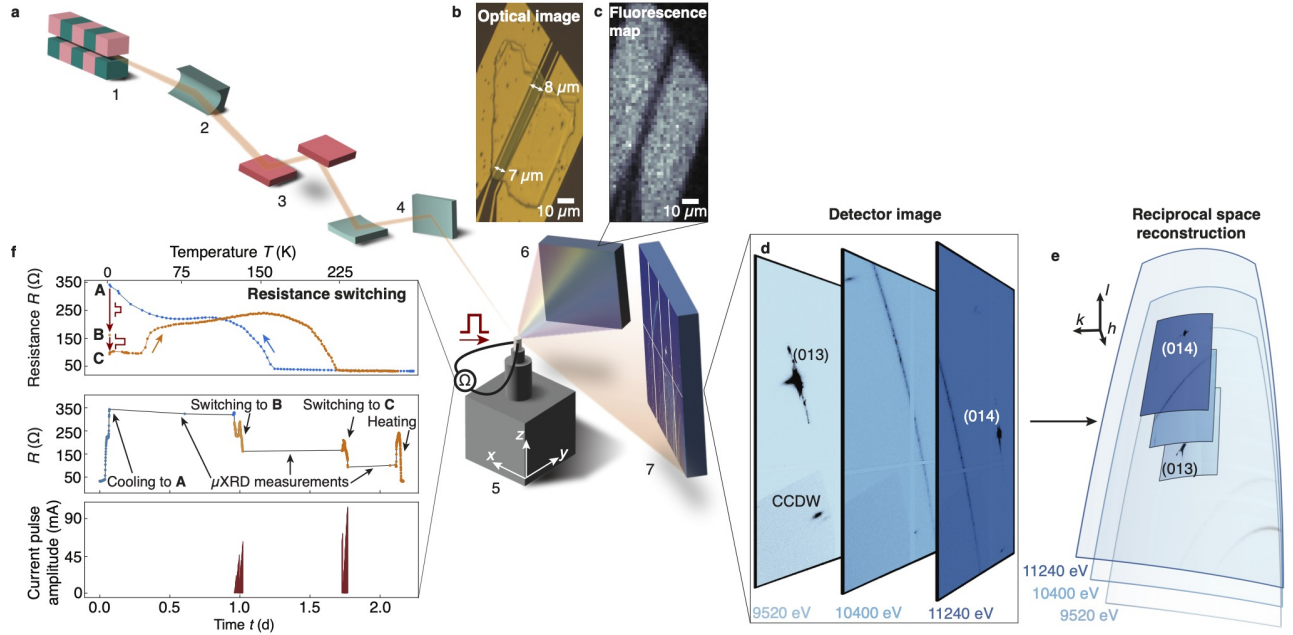


Figure 28.1: ***In operando* macro- and microscopic measurement of phase switching.** **a** Schematic of the synchrotron beamline including the undulator (1), a toroidal mirror (2), the monochromator (3) and Kirkpatrick-Baez focusing mirrors (4). The $1.5 \times 2.5 \mu\text{m}^2$ sized X-ray beam is directed at the 1T-TaS_2 device (5) in a ^4He cryostat that can be moved using translation stages. The device is electrically contacted, allowing for resistance measurements and application of current pulses. X-ray fluorescence (6) and diffraction (7) is recorded simultaneously on respective detectors. **b** Optical image of the 1T-TaS_2 device. **c** Au fluorescence map highlighting the electrodes. **d** Diffraction patterns measured at 6 K at selected X-ray energies with the lattice (013) and (014) Bragg reflections, as well as one CCDW peak. **e** Conversion of the 2D detector images taken at various X-ray energies to 3D (h, k, l) reciprocal space. **f** *In situ* resistance as a function of temperature and time with **A** the unswitched CCDW state, **B** and **C** the partially- and fully-switched HCDW states, respectively.

the electrodes was set to $\approx 8 \mu\text{m}$, considering the μm -sized X-ray spot and that the switching voltage scales with the distance between the electrodes [43]. There are two inert contacts between the outer electrodes that are not used for the resistance measurement. The device is located using μXRF (Fig. 28.1c) which is sensitive to even small traces of embedded elements [47, 48] (Supplementary Information). Before and after applying current pulses, μXRD and μXRF measurements are taken at room temperature and 6 K, as well as different energies spanning an extended portion of reciprocal space (Fig. 28.1d,e). Conversion to 3D reciprocal space allows us to identify the equilibrium and newly appearing signals, as well as to determine their position and peak shapes (Supplementary Information). Temperature-dependent resistance of the device is measured in a two-probe configuration (Fig. 28.1f). Upon cooling, the flake goes through a first-order phase transition, resulting in a step-like increase of the resistance at $\approx 150 \text{ K}$. We denote the unswitched low-temperature CCDW state with **A**. To induce the e-HCDW state, single square current pulses with a width of $100 \mu\text{s}$ are applied. The pulse amplitude is increased gradually until a resistance drop occurs. We denote the state **B** with 47% resistance compared to **A** as partially-switched, reached by applying a pulse amplitude of 63 mA. Increasing the pulse height to 105 mA induces another resistance drop to 27% of **A**, which we refer to as fully-switched **C**. Following the resistance upon heating, we observe the characteristic relaxation from the HCDW state to the equilibrium high-temperature states, as well as the first-order, hysteretic transition [24], confirming that the HCDW state is induced in

the device. As a function of time, the device resistance exhibits changes upon cooling, heating, and current pulse application, else it is stable over hours. During switching, we observe some resistance increase, likely due to a partial relaxation to the CCDW state, and then, as the current amplitude is further increased, a resistance drop indicating that the HCDW state is induced. We note that devices with an optimized design can be switched with a single current pulse [43, 44], whereas with our device design, optimized for *in situ* μ XRD measurements, multiple pulses with increasing amplitude have to be applied. During the μ XRD measurements at a constant temperature of 6 K the resistance remains stable. Importantly, the resistances measured at room temperature before and after the switching and μ XRD measurements are identical, which directly proves the non-destructive nature of our technique.

Several structural changes occur in the non-equilibrium o-HCDW state compared to the equilibrium CCDW order: (i) the CCDW and ‘dimer’ peaks vanish [35] (the latter are associated with inter-layer dimerization of the star-like domains), (ii) a new long-range order (at different positions in reciprocal space) appears as HCDW peaks [35, 30], and (iii) the out-of-plane lattice constant contracts [49] (observed as a shift of the lattice peaks in the out-of-plane direction). In the following, we show that these three characteristic features are also observed for the e-HCDW state. Here, we focus on the HCDW signal, whereas the vanishing dimer CCDW peaks and the out-of-plane lattice contraction are addressed in the Supplementary Information.

For each position on the device, we reconstruct the 3D reciprocal space and look for a decrease in intensity of the CCDW peak, as well as newly appearing signals hinting at the e-HCDW state: three 3D regions of interest (ROI) around the (013) lattice, as well as nearby CCDW and o-HCDW positions [35] are set, and the intensity within these ROIs is integrated. The shape of the flake can be clearly seen in the lattice peak maps (Fig. 28.2a,d,g), which remains intact throughout the switching process. However, a change occurs in the CDW structure of the flake: the CCDW peak map before switching (**A**, Fig. 28.2b) shows the same outline as the lattice peak; but Fig. 28.2e,h in the partially- and fully-switched states, **B** and **C**, respectively, reveal that the CCDW peak intensity in the bottom left part of the flake vanishes. Concurrently, an e-HCDW peak signal appears in the same region in-between the electrodes (Fig. 28.2f,i). That is, not the entire flake switches from the CCDW to the HCDW order, but rather a conducting channel appears between the electrodes on one edge of the flake, while the rest of the device remains in the equilibrium state.

Having identified the spatial region of the flake that switches to the HCDW state, we examine the momentum-space structure and real-space distribution of the CDW states. The CCDW signal in Fig. 28.3a features the characteristic elongation parallel to the out-of-plane l direction due to partial disorder, and the reciprocal space position is close to the previously reported values [33, 51, 35] (Tab. 17). Figures 28.3b-d are from the fully-switched state **C**, deduced from different regions on the flake and revealing that CCDW order gradually gives way to the e-HCDW state as the switching channel is approached. The reciprocal space position of the e-HCDW peak in-between the electrodes is also found to be consistent with the o-HCDW signal in the literature [35] (Tab. 17). Therefore, we conclude that the optically- and electrically-driven HCDW order are equivalent not only from an electronic but also a 3D structural point of view. In turn, this also implies control of the switching into the same local minimum of the free-energy landscape regardless of the excitation method.

Next, we use the intensity shift from the CCDW to the HCDW peak to assess the switching depth. We take the ratio of the HCDW and the total (HCDW + CCDW) signals as a proxy for the volume fraction of the switched layers. Since the Pd/Au electrodes are on top of the flake—thus, the highest current density is there—we also assume that the switching starts from the top. Figure 28.4 shows the respective 3D tomographic representation of the device. Clearly, the switching is not restricted to the surface but penetrates deep into the bulk of the 500-nm-thick flake. This observation is in agreement with previous reports on the importance of the

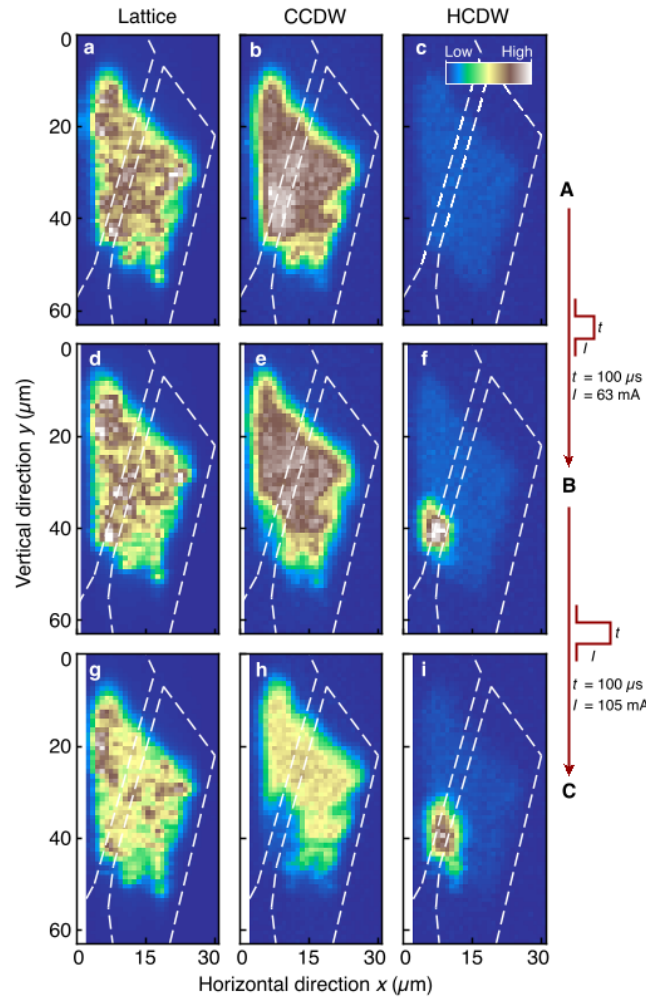


Figure 28.2: **Electrically-induced non-thermal phase switching.** **a-c** Spatially-resolved intensity at the reciprocal space positions of the (013) lattice reflection, as well as a nearby CCDW and HCDW peak in the unswitched state **A**. The lattice and CCDW peaks are observed across the whole flake, whereas no HCDW signal is found. **d-f** and **g-i** show the respective peak intensities in the partially- **B** and fully-switched state **C**. The CCDW signal is suppressed in the lower left corner of the flake where the HCDW signal emerges. Color scales show a minimal intensity of 0 counts and maxima of $2.5 \cdot 10^3$ (lattice), $1.3 \cdot 10^3$ (CCDW) and $8.0 \cdot 10^2$ (HCDW) for an integration time of 100 ms. Dashed lines indicate the position of the electrodes.

out-of-plane layer reconfiguration in the HCDW state [41, 35, 42]. We take cuts parallel and perpendicular to the electrode gap to further characterize the bulk material switching: The HCDW region extends in volume going from the partially- **B** to the fully-switched state **C**. Parallel to the gap the cut reveals that the switching starts at the edge of the flake that is the shortest path to ground. Moreover, from the cut perpendicular to the gap we see that the electrons flowing from the $-$ to the $+$ electrode do not symmetrically switch the intergap space. In addition, a fraction of $\approx 10\%$ remains unswitched between the electrodes. Though using XRD, we cannot extract information down to the single layer and consequently the remaining unswitched intergap layers are within the error of our technique. We also observe sizeable HCDW order induced under the electrodes that is not directly the shortest path to ground, hinting that not only the out-of-plane layer reordering [41, 35, 42] but also strain and the out-of-plane conductivity [46, 52] play an important role in the switching process.

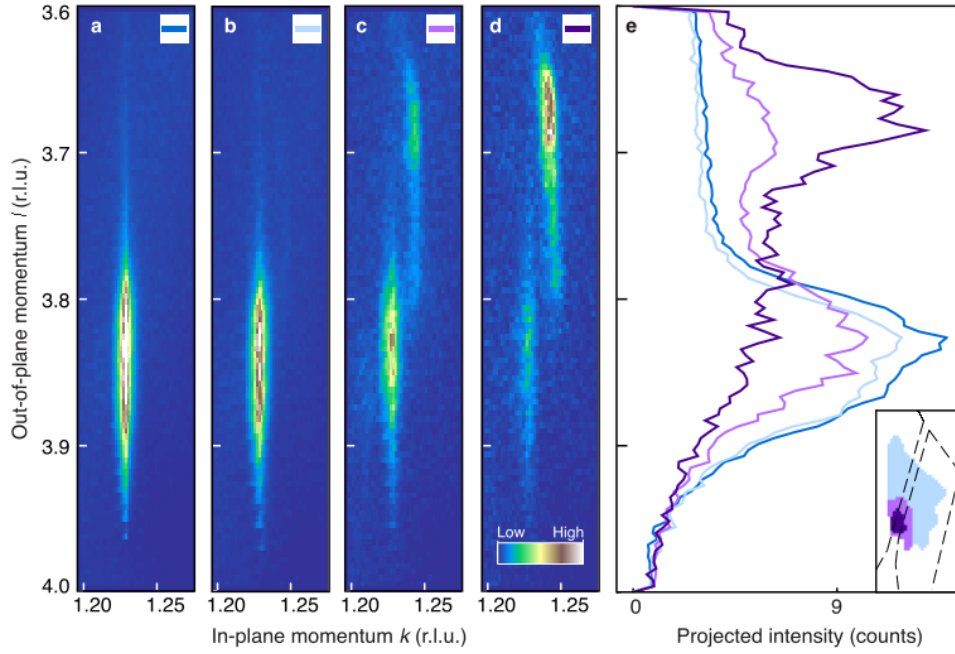


Figure 28.3: **Momentum- and real-space structure of the CDW states.** **a** 2D (k , l) projection in reciprocal lattice units (r.l.u.) of the CCDW peak in the unswitched state **A** (dark blue), obtained by integrating the intensity along the in-plane h direction and normalizing per pixels. **b** Measurement of the fully-switched state **C** in the light blue region (inset of **e**), showing a CCDW and only a very faint HCDW signal. **c,d** Respective projection measured in the light and dark purple regions (inset of **e**), close to and in the vicinity of the electrode gap, respectively. Fewer pixels in those regions result in poorer statistics of the projections. **e** Out-of-plane projection of the data shown in **a-d**. Dashed lines on the spatial map in the inset indicate the location of the electrodes.

28.1.3 Discussion

We non-destructively acquire *in operando* “tomograms” of cryo-memory device switching, addressing a long-standing challenge for the engineering of phase-change memory devices [3, 53]. Our approach allows us to identify the switched HCDW state along one edge of the flake and extending under the electrodes into the bulk of the material. This hints at charge injection as the initiator of the switching. The appearance of a current-induced conducting boundary channel at the flake edge / electrode interface aligns also with previous findings [54].

Finite element method simulations (Supplementary Information) indicate that the geometry of the device dictates the switching channel’s location: The switching occurs where the electrode gap is narrowest, providing the shortest path to ground and resulting in the highest current density during pulse application. Once the channel has formed, the current primarily flows through it, and the switched volume only extends when the current is further increased, *i.e.*, from state **B** to **C** (Fig. 28.4). The Au electrodes ensure high conductivity along the flake, rendering a conductivity gradient unlikely [55]. The switching channel also does not seem to form along defects or impurities, as its size ($\approx 20 \times 20 \mu\text{m}^2$) exceeds that of defects or domains [56, 30]. Moreover, the lattice peak maps in Fig. 28.2a,d,g confirm that the flake remains intact during the switching process, ruling out structural fracture as the root cause.

The switching region can also be located by mapping the vanishing dimer peak (Supplementary Information), associated with the breaking of the pairwise alignment of vdW layers [35]. The nature of the equilibrium CCDW state—whether it is a Mott or a band insulator—remains controversial and is found to be tied to the out-of-plane restacking [42]. Here, we confirm control and local modification of the out-of-plane stacking via current pulses.

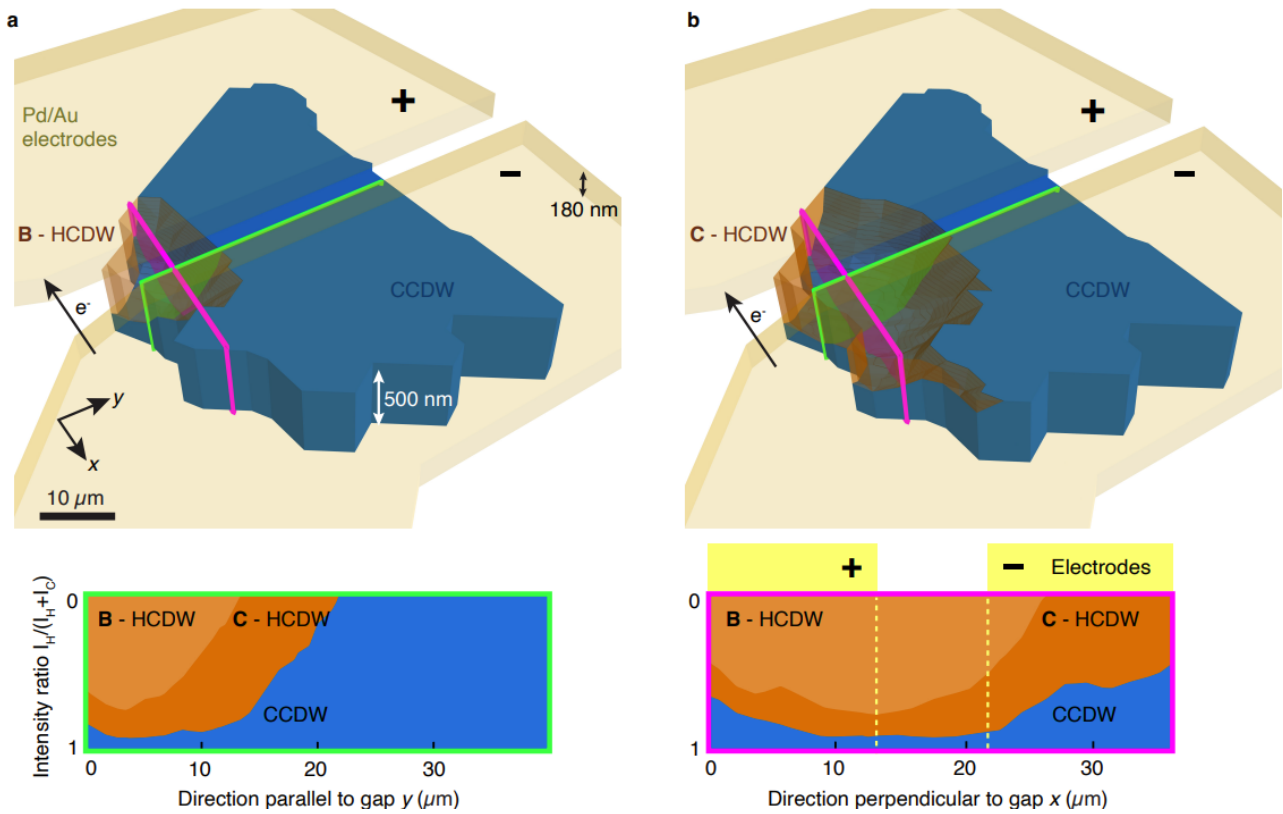


Figure 28.4: **Bulk electrical switching.** 3D tomographic representation of the device in **a** the partially- **B** and **b** fully-switched state **C**. The vertical dimension represents the normalized switching depth, defined by the ratio of the HCDW signal and the total (CCDW + HCDW) intensity. 180-nm-thick Pd/Au electrodes (yellow) are on top of the 500-nm thick 1T-TaS₂ flake, where the CCDW region and the HCDW switching channel are depicted in blue and orange, respectively. Width and depth are not to scale. The arrow indicates the electron (e^-) flow upon application of the current pulse. Cuts through the flake parallel (green) and perpendicular (pink) to the electrode gap are shown on the bottom left and right, respectively. Going from **B** to **C**, the in-gap HCDW order extends both laterally towards the $-$ electrode and in volume.

In- and out-of-plane strain between the flake and the substrate or electrodes may not only influence the stability of the HCDW state [57, 24] but also the switching region's location. Studies on other phase-change materials show that local strain inhomogeneities can arise upon electrical triggering [58]. We also observe an out-of-plane lattice contraction localized exclusively in the intergap space of our 1T-TaS₂ device when a current pulse is applied (Supplementary Information). This creates local strain between the switched and unswitched areas. Thus, we identify strain propagation via the CDW domains as an essential factor contributing to the localized and bulk-nature of the switching, in close analogy to what occurs for ferroelectric devices [59]. Since strain is a long-range effect, it may also explain why the switching extends beneath the electrodes—an aspect not captured by the strain-free simulations.

Interestingly, the original CCDW intensity is higher in the region where the switching channel forms. Observed only for the CCDW but not the lattice peak (Fig. 28.2a,b), this indicates that structural differences, such as variations in flake thickness, are not responsible but rather that switching is potentially promoted by a particularly coherent (well-ordered) CDW state. Our results, therefore, underscore the importance of resolving electronic heterogeneities and looking into the role they play in the non-thermal switching process of 1T-TaS₂.

Our 3D reconstruction of the phase change suggests optimized device designs using narrow

flakes with electrodes positioned along the edges. Ultimately, we envision separate electrode pairs that allow for multiple switched regions and controlled cross talk between them, eventually enabling highly-efficient and fast logic operations.

Studying bulk switching using XRD with nano/micro-beams offers many opportunities. Direct imaging of filamentary paths arising from strain or different structural reconfiguration can also be applied to other memristive materials. So far these have mostly been investigated in thin films without contacts [60], in-plane with transmission electron microscopy, or indirectly and destructively using conductive atomic force microtomography [61, 62, 63, 64]. Our non-destructive, 3D, *in operando* approach represents a significant advance over these technologies, providing microscopic detail of the switching mechanism, thereby advancing the design of scalable next-generation memory technologies.

28.1.4 Methods

Device preparation. 1T-TaS₂ single-crystals were synthesized using chemical vapor transport with iodine as the transport agent leading to consistent crystal quality [4]. Flakes were mechanically exfoliated from bulk crystals using GelPak and excess flakes removed using Scotch tape such that a large, single flake could be deposited onto an oxidized Si wafer (oxide thickness: 280 nm) with predefined Ti/Au alignment markers. The electrodes were written on the flake using electron beam lithography, followed by physical vapor deposition of 20 nm Pd and 160 nm Au. The investigated flake has lateral dimensions of about $50 \times 50 \mu\text{m}^2$ and a thickness of 500 nm. The in-plane crystal orientation of the device was characterized at the Material Science beamline of Swiss Light Source synchrotron [65], and it was then glued onto a Cu sample holder using GE varnish.

Transport measurements and sample cooling. The device was mounted in a CryoVac ⁴He cryostat with Kapton windows for the incident and scattered X-rays. The resistance was measured in a two-probe configuration on the flake, and converted to four-probes on the sample holder such that only the resistance of the Pd/Au electrodes on the flake is measured in series with the flake. The electrical setup consisted of a Keithley 6221 pulsed current source and a Keithley 2182 nano-voltmeter connected in delta mode. For electrical switching single, square-wave pulses were applied using the current source. The sample temperature was monitored using a Cernox thermometer mounted on the sample holder about 2 cm from the device. A specific cooling procedure ensured that the first-order phase transition to the CCDW state was crossed in a controlled fashion. The following ramp rates were used: 300 to 250 K: 5 K/min, 250 to 200 K: 2 K/min, 200 to 100 K: 1 K/min, and 100 to 6 K: 5 K/min.

X-ray diffraction and fluorescence. Spatially-resolved X-ray scattering was performed at the microXAS beamline of the Swiss Light Source [66], allowing for simultaneous *in situ* resistance measurements, as well as μXRD and μXRF imaging. The incidence angle of the X-rays with respect to the device was fixed to $\approx 25^\circ$, resulting in a beam spot size $\approx 1.5 \times 2.5 \mu\text{m}^2$ (v $\times$ h) using Kirkpatrick-Baez focusing mirrors. The nominal X-ray flux was adjusted to about 10^9 photons/s. Considering that the X-rays were passing through about 10 cm air before impinging on the sample, the effective incident flux on the sample was about 15 % and 10 % lower at 9.1 and 12.0 keV, respectively. As the cryostat was mounted on translation stages without rotational degree of freedom, to take μXRD spatial maps we scanned through reciprocal space by changing the incoming X-rays energy between 9.1 and 12.0 keV using the undulator and monochromator. The diffraction and fluorescence signals were recorded by Eiger X 4M and VIAMP-KC detectors, respectively. To locate the device the μXRF signal at the Au (11.9 keV) and Ta (9.88 keV) *L*-edges was used (Supplementary Information).

Peak	Literature	Experiment	Exp. uncertainty
Lattice	(0, 1, 3)	(0.00, 1.00, 3.00)	$(3.7e^{-4}, 3.7e^{-5}, 3.6e^{-3})$
CCDW	(0.08, 1.23, 3.80)	(0.08, 1.23, 3.83)	$(1.0e^{-3}, 7.7e^{-4}, 3.4e^{-2})$
HCDW	(0.07, 1.24, 3.67)	(0.07, 1.24, 3.68)	$(3.5e^{-4}, 5.8e^{-4}, 4.2e^{-2})$

Table 17: **Peak positions from electrically- and optically-switched experiments.** Reciprocal space coordinates (h, k, l) in r.l.u. of the measured structural (013), CCDW and e-HCDW peaks, as well as the respective literature values for the CCDW [51] and the o-HCDW [35] signals. The experimental position and uncertainty are determined from fitting Lorentzian peak shapes after the reciprocal space reconstruction.

28.2 SM

28.2.1 Fluorescence

X-ray fluorescence of Ta and Au was used to locate the device and set the range of the spatially-resolved scans. The signal was captured by VIAMP-KC detectors. Even small traces of elements such as Cu from the sample holder, Ti from the binary markers on the substrate, and Ni traces under the electrodes were detected (Fig. 28.5). Fluorescence data were fitted using the PyMCA libraries [67].

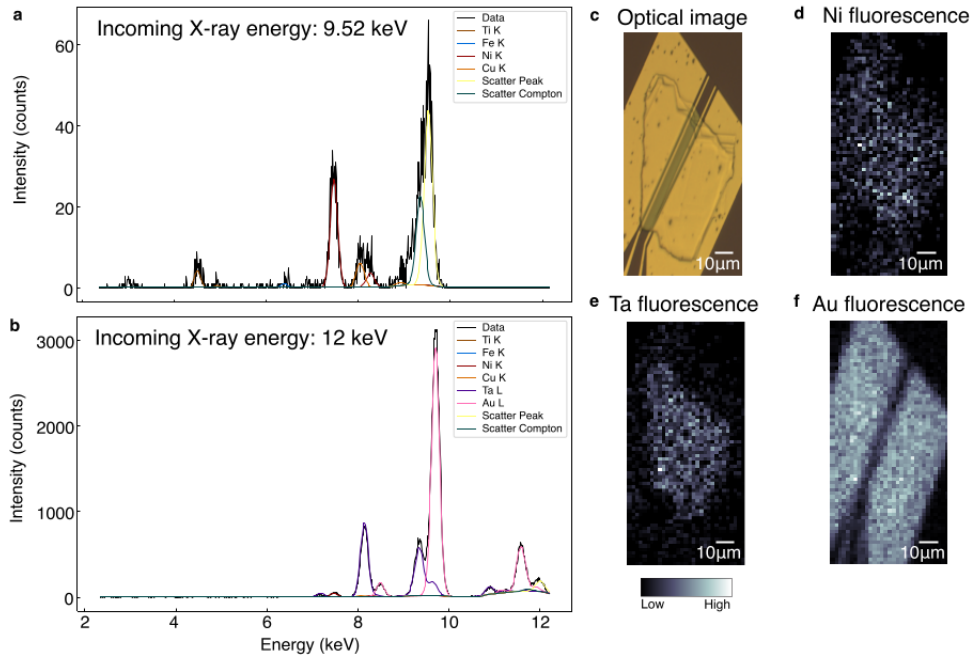


Figure 28.5: **Elements in the 1T-TaS₂ device detected by X-ray fluorescence.** **a** Total fluorescence intensity measured using an incoming X-ray energy of 9.52 keV, below the Ta L -edge [68]. Peak fitting traces elements such as Ti, Fe, Ni and Cu on the device and sample holder (via the respective K -edges), as well as elastic and Compton scattering. **b** Respective fluorescence signal measured at 12 keV, above the Ta and Au L -edge [68], where in addition to the elements observed in **a**, also Ta and Au are detected. **c** Optical image of the device. **d** Ni signal mapped spatially across the device showing traces along the electrodes and the flake. **e,f** The Ta and Au signals outline the flake and electrodes, respectively. The minimal intensity in **d-f** is 0 counts, and the maximal intensity is 6.7 counts (Ni), 9.6 counts (Ta), and 67 counts (Au), measured using an integration time of 100 ms.

28.2.2 X-ray diffraction data processing

Experimental geometry constraint and reciprocal space reconstruction

In the following, we describe how we assigned pixels on the detector at each X-ray energy (x_d, y_d, E) to reciprocal space coordinates (h, k, l) .

The known parameters in this experiment are the energy of the X-rays, the orientation of the detector which was perpendicular to the X-ray beam and further detector specifications of the Eiger X 4M detector. In addition, we know the optimal pixel and energy of scattering reflections of three accessible lattice peaks (004), (013), (014) and four commensurate CCDW peaks on the detector and also their theoretical (h, k, l) parameters [51], leading to seven known quantities. The measured peak positions were determined by fitting a Lorentzian to the projected intensities. The CCDW peaks are elongated along the out-of-plane direction, therefore only the in-plane (h, k) dimensions were fitted. The unknown parameters in this setup were the relative position of the detector with respect to the sample (x, y, z) which was roughly measured and used as an initial guess, the sample orientation parameterized with angles (α, ϕ, χ) and the lattice constants of the flake (a, b, c) . If we parametrize the Eiger X 4M orientation with Cartesian coordinates (x, y, z) where (x, y) point along the x, y pixel directions and z perpendicular to the detector surface, the flake orientation can be expressed in this coordinate system using angles (α, ϕ, χ) . α denotes the angle between the surface normal of the detector and the surface normal of the flake, ϕ is the azimuthal angle and χ the tilt angle. Since there were only seven measured parameters (three lattice and four CCDW reflections), we took the in-plane lattice parameters $a = b = 3.32 \text{ \AA}$ as known [69] and only the out-of-plane lattice parameter c as unknown.

As a next step, a cost function was defined that includes all known and unknown parameters, and with which the full experimental geometry was described as

$$F(\vec{x}, \vec{y}) = \sum_{i=1}^7 \left| \vec{Q}_i(\vec{x}, \vec{y}) - \vec{Q}_i^{\text{theory}} \right|^2, \quad (28.1)$$

where $\vec{x}$ are the unknown parameters, $\vec{y}$ are the known parameters and the two-norm is used.

With this function, the reciprocal space coordinates of our measured peaks was compared to the theoretically known position [51, 35]. The cost function was minimized with respect to $\vec{x}$ using a standard minimization algorithm from the SciPy optimization python library [70] which finds the experimental conditions $(\alpha, \phi, \chi, x, y, z, c) = (25.61^\circ, -86.42^\circ, 0.57^\circ, -0.14 \text{ m}, -0.06 \text{ m}, 0.0 \text{ m}, 0.6 \text{ nm})$ of the unknown parameters that matches the experimental results. The resulting error table is shown in Tab. 18 with small errors, meaning that there is good agreement between the measured peaks and the known structure of the material.

Once this experimental geometry was calculated, the real space position with respect to the sample of all pixels on the detector were defined. The reciprocal space coordinates (h, k, l) were assigned to the pixels on the detector at every X-ray energy using the Laue equation. We note that the pixel size of the Eiger X 4M detector is $75 \times 75 \mu\text{m}^2$ whereas the lateral size of the flake was about $50 \times 50 \mu\text{m}^2$. Hence, any movement of the diffraction pattern due to rastering over the sample was still within 1 pixel of the detector and can be neglected.

The conversion from (x_d, y_d, E) to (h, k, l) leads to a curved surface in reciprocal space which was probed by the flat 2D detector in real space. Putting all the curved surfaces of the measured energies together, allowed us to reconstruct the 3D shape of the lattice, CCDW, HCDW and dimer peaks. Figure 28.6 shows this 3D reciprocal space representation measured in the fully-switched state **C**. This is a volumetric plot using the intensities of the measured peaks, giving an overview over the peak shapes and position. Importantly, this is not a spatially-resolved

Peak	Literature (r.l.u)	Experiment (r.l.u)	Two-norm error (pixels)
(013) CCDW1	(0.08, 1.23, 2.80)	(0.08, 1.23, 2.86)	1.5
(013) CCDW2	(−0.08, 0.77, 3.20)	(−0.08, 0.77, 3.14)	0.7
(014) CCDW1	(0.08, 1.23, 3.80)	(0.07, 1.24, 3.68)	1.2
(014) CCDW2	(−0.08, 0.77, 4.20)	(−0.08, 0.77, 4.16)	0.7
(013) lattice	(0, 1, 3)	(0.0, 1.0, 3.0)	3.5
(004) lattice	(0, 0, 4)	(0.0, 0.0, 4.0)	5.0
(014) lattice	(0, 1, 4)	(0.0, 1.0, 4.0)	2.3

Table 18: **Error table of the measured peaks.** Lattice and nearby CCDW peaks detected in the experiment are listed with their index from the literature [51, 35], the calculated (h , k , l) positions determined from the experimental geometry and the error from the peak fits. The latter is given in pixel and calculated by taking the norm of the absolute error divided by the reciprocal space pixel resolution of 1.03×10^{-3} r.l.u.

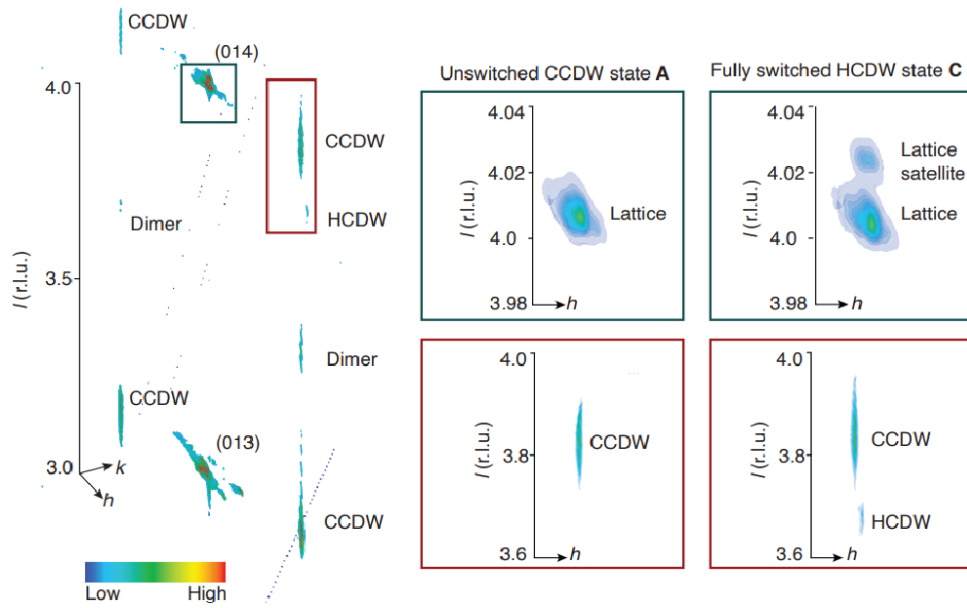


Figure 28.6: **3D reciprocal space reconstruction of the fully-switched state.** Shown on the left is the reconstruction of the fully-switched state **C** summed from all pixels on the flake (no spatial resolution), including the (013) and (014) lattice peaks, two CCDW peaks near each of them, a HCDW peak near the (014) peak and dimer peaks. This is a volumetric plot from the intensities of the peaks showing the general shape of the different peaks. The reconstruction is done for the measured energies between 9.2 and 12 keV, which is why only certain peaks are observed. The blue pixel lines are due to dead pixels of the detector. On the right are extracts around the (014) lattice peak and a corresponding CCDW peak, showing the appearance of the HCDW peak and also a new lattice satellite when comparing the unswitched **A** and the fully-switched state **C**.

3D reciprocal image, it is the reconstruction coming from the sum of all pixels measured at the different energies, therefore we observe all peaks in the same plot. Next to the overview plot are extracts of reciprocal space around the lattice and CCDW peak in the unswitched **A** and in the fully-switched state **C**. We see that in the fully-switched state a HCDW peak appeared below the CCDW peak, as well as an additional lattice satellite (Sect. 28.2.5). For the spatially-resolved intensity maps of the device, we used such 3D reconstruction of every pixel. The peak positions were determined from the 3D reconstruction by summing along two reciprocal space directions to obtain a 1D intensity plot along the remaining reciprocal space direction and fitting a Lorentzian function to the peak.

Gold ring correction

We observed five ring-like features in the raw diffraction patterns (Fig. 28.7a). After the detector position with respect to the sample was determined, the 2θ angle of these rings, *i.e.* the radius r , at a certain energy of the incoming X-rays was determined using Bragg's law

$$\sin(2\theta) = \frac{n\lambda}{2d} = \frac{\lambda}{2k}, \quad \tan(\theta) = \frac{r}{d}, \quad (28.2)$$

where λ is the wavelength of the incoming X-rays, d the spacing between the crystal planes, n an integer for the diffraction order and k the wavenumber. Comparison with literature showed that the radii of the rings matches Au with Miller indices (111), (200), (220), (311) and (222) [71] (Fig. 28.7c). The electrodes are made from amorphous gold, therefore we observe these rings when spatially scanning over the device. Taking a region of interest (ROI) with radius $r \in [r_{\text{ring}} - 0.0018, r_{\text{ring}} + 0.0018]$ (in m) corresponding to the thickness of the gold rings, allowed us to collect and sum up the intensity of all detector pixels within this ROI. We did this procedure for every pixel (x_d and y_d) on the sample which gave us spatially-resolved intensity maps outlining the electrodes of the device. We used these electrode images for aligning the spatial scans at the different X-ray energies.

After confirming that no peak of interest cut through the gold rings, we replaced them for the 3D reciprocal space reconstruction by an average background (Fig. 28.7b). This was simply done for better visibility of the peak shapes in the reconstruction, but did not affect the reconstruction itself.

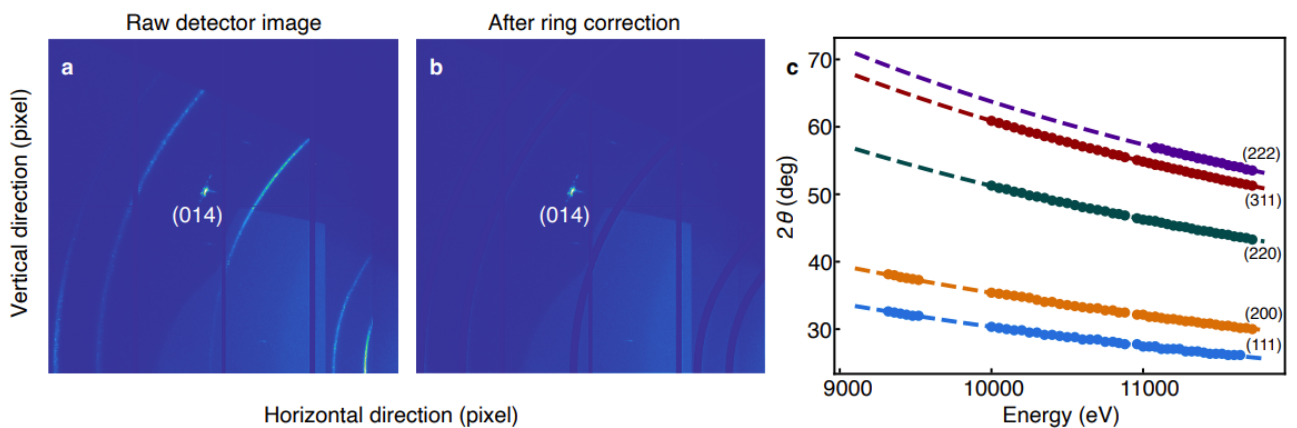


Figure 28.7: **Gold ring correction.** **a** Exemplary raw detector image taken at 11.12 keV and showing five rings coming from the Au electrode material as well as the (014) lattice peak of the 1T-TaS₂ flake. **b** The same detector image after fitting the gold rings and replacing them with an average background. **c** Fitting of the five gold rings observed in the experiment (data points), corresponding to the (111), (200), (220), (311) and (222) Au reflections from the literature [71] (dashed lines).

Spatially-resolved maps

In the following, we describe how we obtain the spatially-resolved intensity maps, as well as the spatially-resolved projections in reciprocal space. For each state of the device, *i.e.* the room-temperature, as well as the unswitched **A**, partially- **B** and fully-switched states **C** at the base temperature of 6 K, we measured spatial maps at different energies. As a next step, we performed a spatial jitter correction. That is, we spatially aligned the scans at different energies and for the different states. We did this by choosing a gold ring which shows clear outlines of the electrodes in the spatial maps. For each state, we first chose one reference spatial map I_{ref} measured at a certain X-ray energy. We then aligned all other spatial maps measured at different energies to this reference map. Due to the finite scan range, we confined a possible shift in the x and y spatial directions to $\delta x \in [-10, 10]$ and $\delta y \in [-20, 20]$ (in pixel) and found $(\delta x, \delta y)$ such that

$$F(\delta x, \delta y) = \sum_{i,j} [I_{ref}(x_i, y_j) - I(x_i + \delta x, y_j + \delta y)]^2, \quad (28.3)$$

summing over the pixel indices i, j , was minimized. The result shows in general good alignment within ± 1 pixel. But there were a few scans at certain energies which still had to be manually tweaked to improve the alignment.

After having the scans at different energies for every state spatially aligned and a 3D reciprocal space reconstruction for each pixel performed, we defined 3D ROIs in reciprocal space around the peaks of interest. Since the CCDW and dimer peaks are elongated along l , as has been reported before [35], we took cylindrical ROIs around these peaks. For the lattice and HCDW peaks which are better defined along the out-of-plane direction, we took spherical ROIs. We computed the signal within these ROIs by summing up the intensities. For every spatial map at every energy, we set a spatial $1.5 \times 1.5 \mu\text{m}^2$ (room temperature) and $1 \times 1 \mu\text{m}^2$ (6 K) grid according to the minimal step size of the scan. Then, we assigned intensity values to the grid by considering that if the closest scan to a respective grid pixel is > 2 pixel, we set it to zero and otherwise we consider the data within the predefined ROI in reciprocal space. For the spatially-resolved intensity maps, such as in Fig. 2 of the main text, the intensity in the spatial pixels was therefore the sum of the intensities within the ROI. We note that with a minimal step size in the x and y direction of $1.5 \mu\text{m}$ at room temperature and $1 \mu\text{m}$ at the base temperature, we were in fact oversampling given the X-ray spot size of $1.5 \times 2.5 \mu\text{m}^2$ ($v \times h$).

After identifying the region which switched to the HCDW state from the spatial maps, we could separate the device into different spatial regions to extract the spatially-resolved 2D reciprocal space projections (Fig. 3 of the main text) and calculate the ratio of the HCDW and the CCDW peak intensity. The spatial region near the intergap space (light purple) corresponds to a intensity ratio 0.5 and that region in the switching channel (dark purple) corresponds to a ratio of 5. Then, we summed up the 3D reciprocal space reconstructions of the pixels within these regions. For the projected maps, such as Fig. 3 of the main text, we set a grid in reciprocal space and interpolate. From this, we obtain the 2D projections by summing along one reciprocal space axis and dividing by the number of pixels in the spatial regions.

28.2.3 Room-temperature spatial maps

At the beginning of the experiments, the device was mounted at room temperature and spatial scans at different X-ray energies were measured to check the alignment, as well as to record the lattice and NCCDW signals. We took spatially-resolved scans at a few energies, corresponding to only selected cuts through reciprocal space. Hence, we only observed a few peaks with reduced statistics, compared to the low-temperature measurements. This resulted in a less accurate 3D reconstruction. Nevertheless, we took 3D ROIs around the (013) lattice

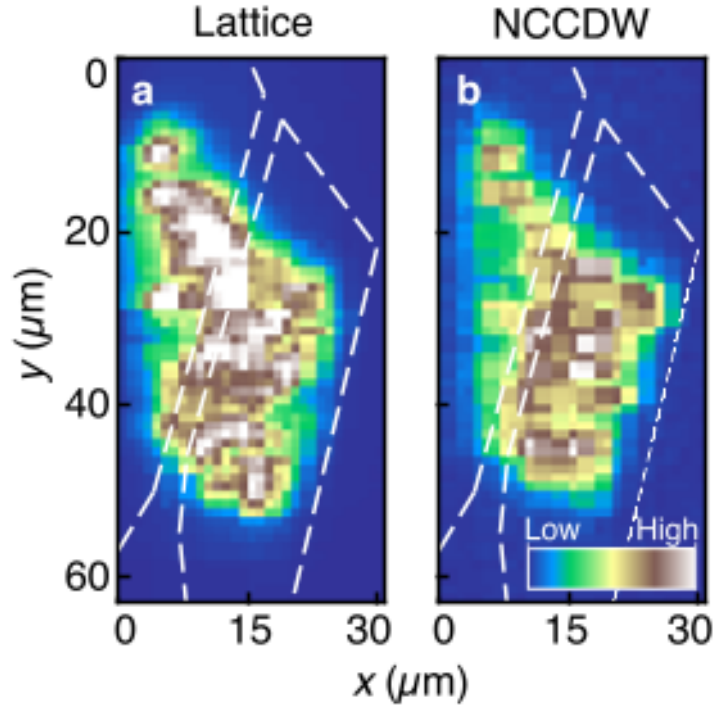


Figure 28.8: **Room-temperature spatially-resolved maps.** **a**, **b** show the (013) lattice and NCCDW peak intensities, respectively. The minimal intensity is 0 counts and the maxima are $6.0 \cdot 10^4$ counts (013) and $1.0 \cdot 10^3$ counts (NCCDW) for an integration time of 100 ms. Dashed lines outline the electrodes. The step size was $1.5 \mu\text{m}$.

peak and a respective NCCDW peak and plotted the corresponding spatial intensity map which both reproduce the general shape of the flake (Fig. 28.8).

28.2.4 Dimers and phase switching

As discussed in [35, 31], dimer peaks associated with a doubling of the real-space unit cell in the out-of-plane direction were observed in the CCDW state and vanish upon switching to the o-HCDW state [35]. We also observed dimer peaks in our measurements (Fig. 28.6) and took 3D ROIs around those in reciprocal space. We recorded only a few energy scans cutting through the dimer peaks, meaning that the statistics was reduced compared to other peaks. Figure 28.9 shows the spatially-resolved intensity maps of the CCDW and dimer peak in the unswitched **A**, the partially- **B** and the fully-switched state **C**. We see that both peak intensities vanish in the bottom left part of the flake in the fully-switched state. Hence, we observe the same vanishing dimer peaks in the e-HCDW state in the intergap space as reported for the o-HCDW state, meaning for both there is also collapse of dimerization. Indirectly, observed as a local doubling of the out-of-plane dispersion, this has also been reported in a recent μARPES study [45]. As addressed in the main text, we observed that the intensity of the CCDW and dimer peaks in the unswitched state was the highest in the bottom left part of the flake that switches to the HCDW state. This supports the notion that the location of the switching channel may not only be dictated by the geometry of the device, but also the most homogeneous (dimerized) CDW order.

28.2.5 Switching-induced out-of-plane lattice contraction

As reported before for the o-HCDW state [49], we also observed a change in the out-of-plane lattice constant in the e-HCDW state. Figure 28.10 shows the 1D projection onto the

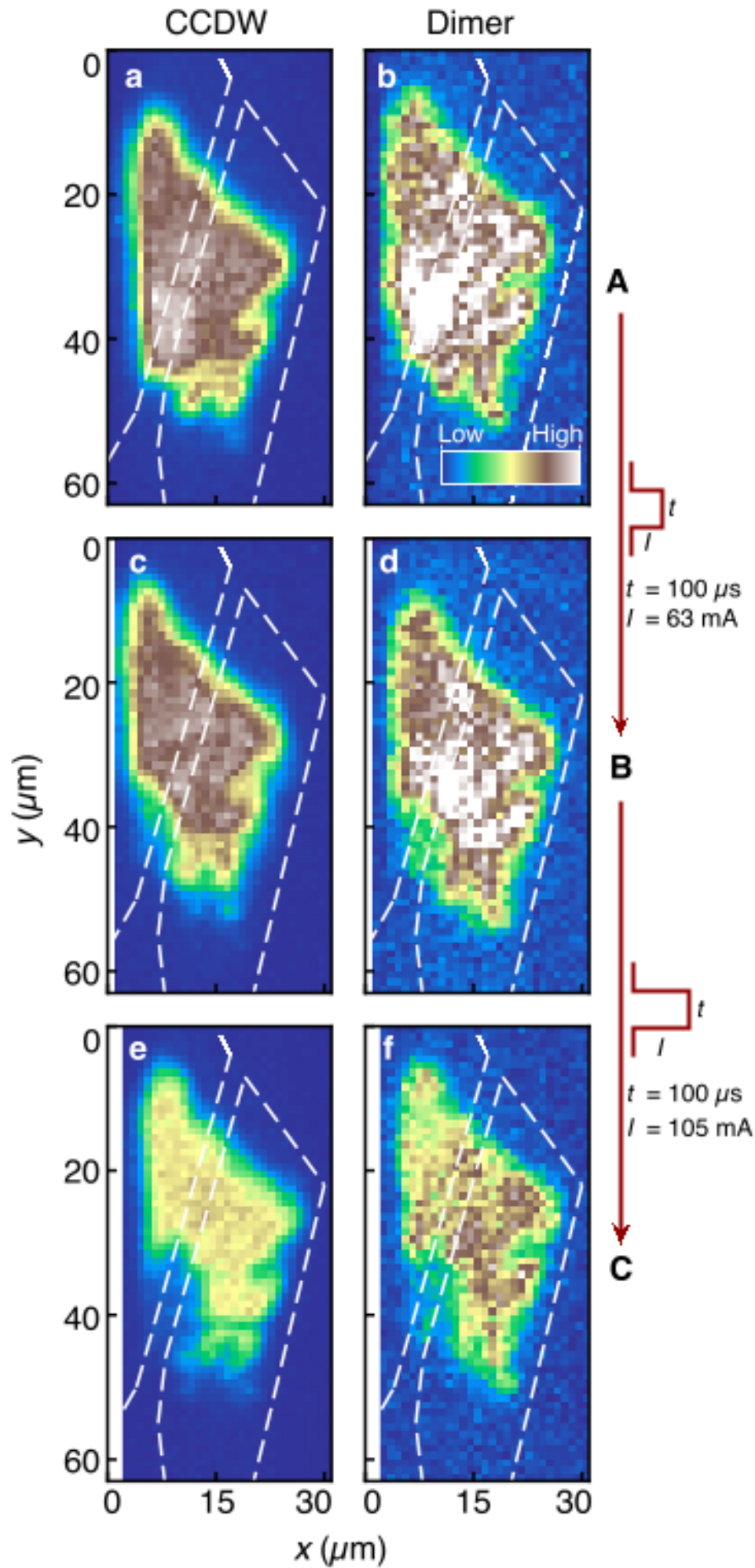


Figure 28.9: Vanishing dimers in the switching channel. a,b Spatially-resolved intensity

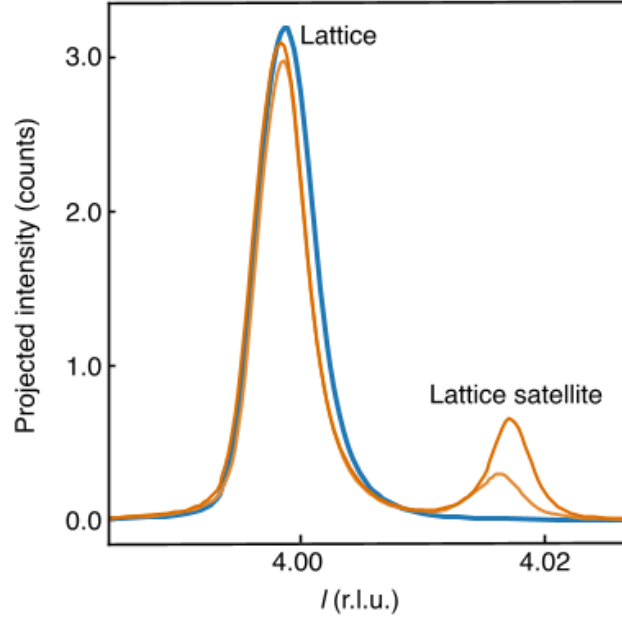


Figure 28.10: **Out-of-plane lattice contraction.** Out-of-plane projection of the (004) lattice peak in the unswitched (**A**, blue), the partially- (**B**, light orange) and the fully-switched state (**C**, dark orange). This measurement integrates over the entire flake. Upon switching intensity shifts from the (004) peak to the satellite at higher l values, corresponding to an out-of-plane lattice contraction of 0.5 %.

out-of-plane reciprocal space coordinate l of the (004) lattice peak. The signal was measured on the entire flake (no spatial resolution) in the unswitched **A**, the partially- **B** and the fully-switched state **C**. The high intensity peak is the (004) lattice peak reflection. We note that because this measurement is not spatially-resolved, intensity (from the unswitched portions of the flake) still shows up there even in the **C** state. Clearly, in the **B** and **C** states a satellite lattice peak emerges from the HCDW state in the switching channel. Thus, we observed that for the e-HCDW state the out-of-plane lattice peak position shifts to a higher reciprocal space value, meaning that the lattice contracts by 0.5 %. The out-of-plane lattice constant difference between the switched and unswitched region leads to strain along the border which we speculate facilitates the switching in-plane but also in volume. Similarly, the c lattice constant contracts between the NCCDW and CCDW states [73, 74, 75, 31].

We set two ROIs around the lattice signals in reciprocal space: $l \in (3.99, 4.01)$ and $(4.015, 4.035)$ r.l.u. for the main and satellite peak, respectively, to obtain spatial maps by summing up the intensity within these ROIs (Fig. 28.11). Also here we observe that the HCDW state switching channel appeared at the bottom left corner of the flake. Thus, not only the electronic CDW structure is modified in the e-HCDW state but also the out-of-plane lattice contracts in the non-volatile switching channel of the device. In the following, we show the agreement of the HCDW state switching channel observed from the out-of-plane lattice contraction and the HCDW peak.

As done for Fig. 3 of the main text, we define different spatial regions of the device: outside of the switching channel (light blue), near the switching channel (light purple) and in-between the electrodes (dark purple). We then map out the 2D reciprocal space projections of the (004) lattice peak (Fig. 28.12). Unlike the CCDW peak which shows a characteristic elongation, the lattice peak is sharp also in the out-of-plane direction. The correlation of the ratio of the projected out-of-plane lattice intensities of the main and satellite signal, $I_{\text{satellite}}/I_{\text{main}}$, and that of the HCDW and CCDW peak intensity, $I_{\text{HCDW}}/I_{\text{CCDW}}$, is shown in Fig. 28.13a. Figure 28.13b compares the contours of the switching region based on the ratio of the lattice signals, and the

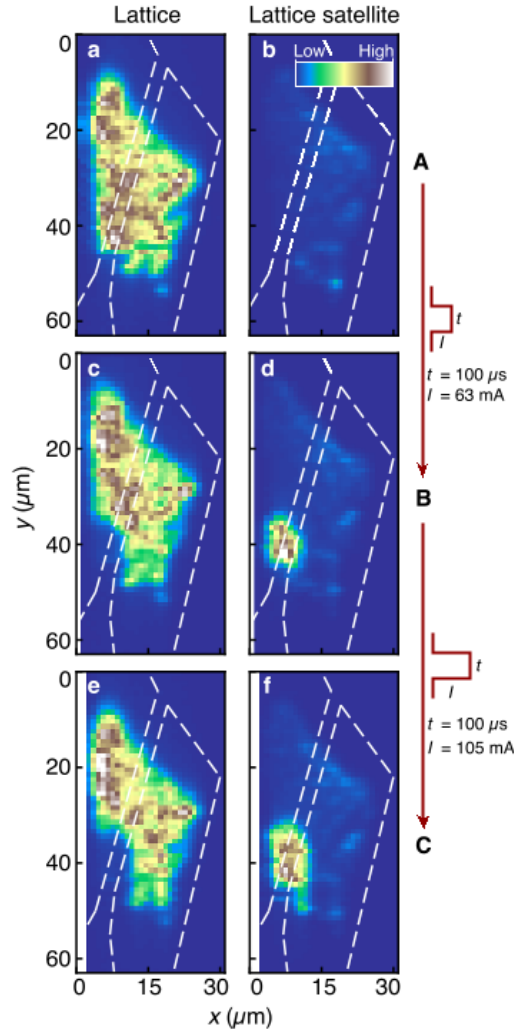


Figure 28.11: **Spatially-resolved out-of-plane lattice contraction.** **a,b** Intensity map at the (004) lattice peak and satellite position in the unswitched state **A**, respectively. **c,d** and **e,f** show the respective maps in the partially- **B** and fully-switched state **C**, respectively. As for the CCDW and HCDW signal, the main lattice peak vanishes in the bottom left part of the flake and the satellite lattice peak is observed instead, showing that the switching channel can also be observed via the out-of-plane lattice contraction. Color scales show a minimal intensity of 0 counts and maxima of $1.0 \cdot 10^3$ counts for an integration time of 100 ms for both columns. Dashed lines outline the electrodes. The step size was 1 μm .

HCDW/CCDW peaks, revealing that the two are also spatially correlated. Thus, also the lattice peak contraction can be used as a fingerprint to locate the HCDW switching.

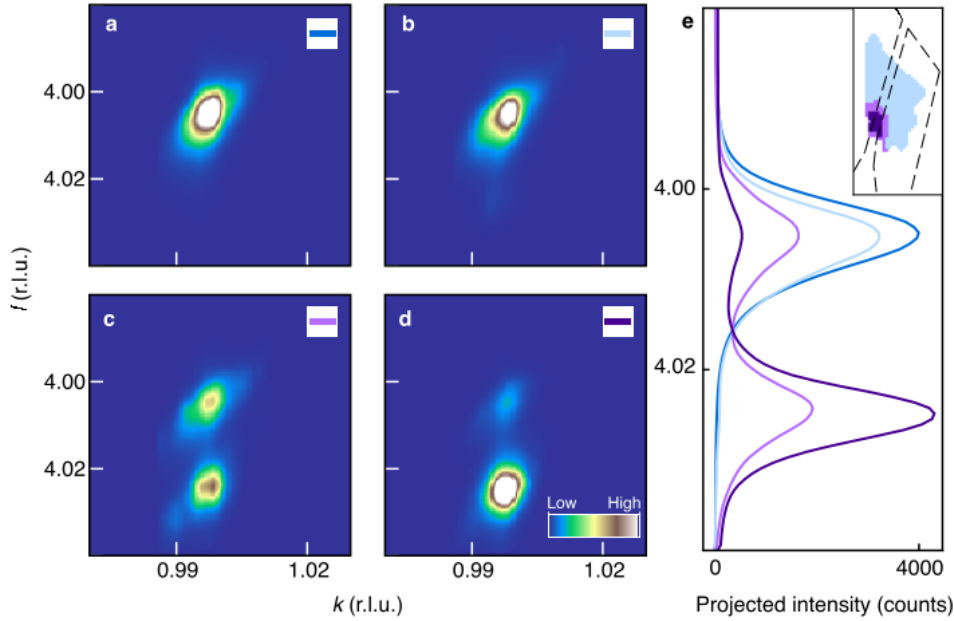


Figure 28.12: **Momentum- and real-space structure of the lattice contraction.** **a** 2D (k , l) reciprocal space projection of the lattice peak in the unswitched state (**A**, dark blue). **b-d** Respective measurement in the fully-switched state **C** in the light blue, as well as light and dark purple region (inset of **e**), respectively. The 2D projected intensities have been normalized by the size of the respective spatial region. **e** Out-of-plane projection of the data shown in **a-d**. The Inset shows the color-coded regions on the flake. Dashed lines in the inset outline the electrodes.

28.2.6 Finite element method simulations

Numerical simulations were performed using the COMSOL Multiphysics software, which uses the finite element method to solve partial differential equations governing heat conduction in solid materials and devices:

$$\rho C_p \frac{\partial T}{\partial t} - \nabla \cdot (k \nabla T) = Q_e, \quad (28.4)$$

$$Q_e = \sigma |\nabla V|^2, \quad (28.5)$$

where T is the temperature, V the volume and Q_e the heat source term. The density of the material ρ , heat capacity C_p [76], as well as the k thermal [77] and σ electrical conductivity of all materials in the device were taken from literature or experiments [23, 32]. The thermal model was coupled to the electromagnetic one which provided Q_e in the differential equations by calculating the resistive losses in the device, *i.e.* Joule heating.

The structure and dimensions of the simulated device is shown in Fig. 28.14a. The geometry of the Au contacts and the 1T-TaS₂ crystal flake was realistically replicated both in shape and size, including irregularities such as the narrower spacing at one (left) side of the structure and the two additional disconnected contact fingers in the middle. Excitation of the device was applied via the two outer contacts by assuming 100 μ s square wave current pulses

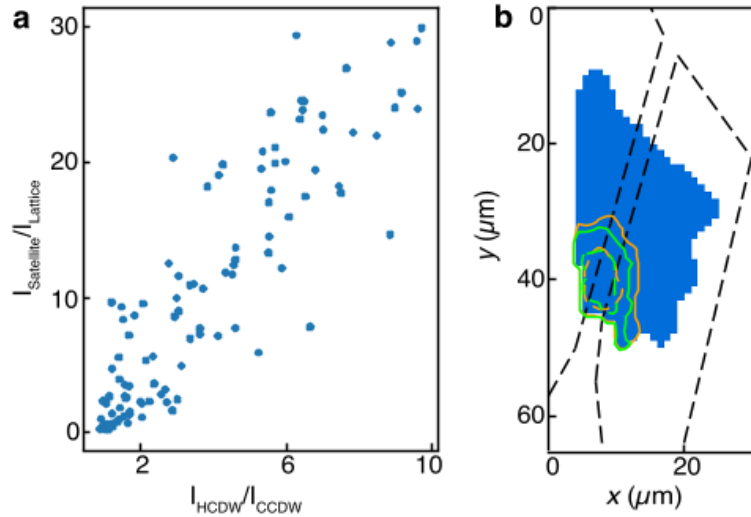


Figure 28.13: **Correlation between lattice contraction and HCDW peak appearance.** **a** Linear correlation among the ratio of the out-of-plane lattice signals and the HCDW/CCDW peak intensity. **b** The blue region indicates the shape of the flake. The spatial switching region as identified by the lattice contraction and HCDW appearance is indicated in orange and green, respectively. Dashed lines outline the electrodes.

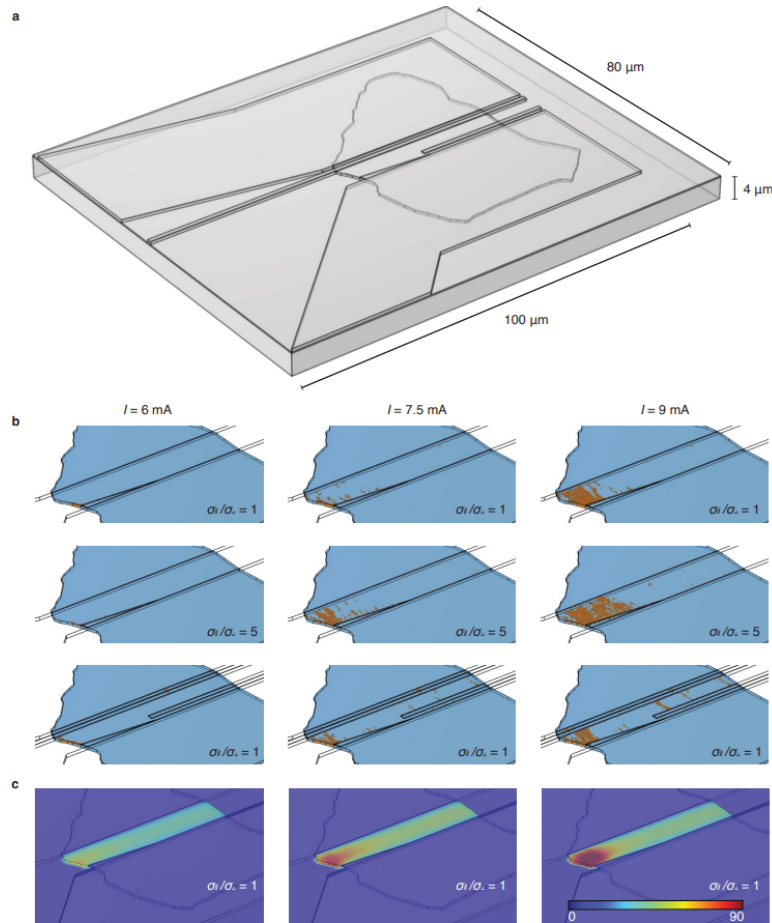


Figure 28.14: **Finite element method simulations.** **a** Schematic of the device considered for the simulation. **b** Switching volume (orange) under different current excitation levels (columns), as well as assuming different material isotropy (top and middle row) and inclusion of a more detailed electrode geometry (bottom row). **c** Device heating upon switching for top row in **b** (color scale in Kelvin).

of amplitudes between 0 and 10 mA. At the beginning of each simulation, the device was fully in the unswitched state **A** at 4 K temperature. After applying the excitation, switching of the elements from **A** to the fully-switched state **C** was handled by a simplified model which predicts formation of the HCDW state domain wall network under the influence of a sufficiently large charge carrier injection. Thus, in the present simulations the state of each element was switched once the current density of the element reached a predefined current density threshold of $5 \times 10^8 \text{ A/m}^2$, calibrated by the experiment. Figure 28.14b shows the switched material (orange) for different magnitudes of current excitation. All cases identify the preferential area of device switching at the left side of the device, which is influenced primarily by the narrower spacing between the contacts. With increasing current amplitude, the area gradually expands along the intergap space. Furthermore, we observe that the penetration depth of the switching is determined by the level of anisotropy of 1T-TaS₂. In the isotropic case (Fig. 28.14b, top row), the switched volume propagates throughout the entire thickness of the crystal flake, whereas it remains closer to the surface when assuming an out/in-plane conductivity anisotropy of 1:5 (Fig. 28.14b, middle row). A final set of simulations (Fig. 28.14b, bottom row), we tested also the influence of the disconnected contact fingers. While they do affect the quantitative extent of the switched volume, the additional conductive paths they provide qualitatively agree with the simulations in the top row of Fig. 28.14b.

Contrary to the experiment these simulations do not reproduce the widening of the switched volume laterally and beneath the contacts. We speculate that this effect in the experiment is driven by propagation of local strain between the switched and unswitched area—a feature presently not included in the numerical simulations. We also observe that compared to the experiment, the device switches fully at a lower current amplitude (between 10 to 20 mA). We attribute this to slight discrepancies between the assumed and effective material parameters. Finally, in Fig. 28.14c, device heating due to the current excitation is also demonstrated for the isotropic situation without influence of the disconnected middle contacts (Fig. 28.14b, top row). The uneven heating upon current pulse application localized to the left side of the device is also in agreement with the preferential path of the current flow across the 1T-TaS₂ flake.

29 A time-domain phase diagram of metastable states in a charge ordered quantum material by Ravnik, Diego, Gerasimenko, Vaskivskiy, Vaskivskiy, Mertelj, Vodeb, Mihailovic

Abstract

Metastable self-organized electronic states in quantum materials are of fundamental importance, displaying emergent dynamical properties that may be used in new generations of sensors and memory devices.

Such states are typically formed through phase transitions under non-equilibrium conditions and the final state is reached through processes that span a large range of timescales.

By using time-resolved optical techniques and femtosecond-pulse-excited scanning tunneling microscopy (STM), the evolution of the metastable states in the quasi-twodimensional dichalcogenide 1T – TaS₂ is mapped out on a temporal phase diagram using the photon density and temperature as control parameters on timescales ranging from 10^{-12} to 10^3 s.

The introduction of a time-domain axis in the phase diagram enables us to follow the evolution of metastable emergent states created by different phase transition mechanisms on different timescales, thus enabling comparison with theoretical predictions of the

phase diagram and opening the way to understanding of the complex ordering processes in metastable materials. (I have no idea what is meant here?)

Short optical or electrical pulses can create non-equilibrium conditions that lead to electronic self-organization in quantum materials which can be usefully applied in various devices ^{1–9}. Recent rapid progress in the time-domain investigations of non-equilibrium phase transitions has led to the observation of a variety of emergent transient and metastable states in complex quantum materials, including organic electronic crystals ¹⁰, oxides ^{11,12}, dichalcogenides ¹³, and fullerene superconductors ¹⁴. Self-organized non-equilibrium matter that emerges after pulsed laser excitation evolves in a sequence of processes that eventually cause it to reach the ground state. However, sometimes new emergent metastable states may be created during the relaxation process which are not present in the equilibrium phase diagram ¹³.

The formation of such metastable states can occur by different mechanisms: in addition to first or second order transitions characterized along the Ehrenfest scheme, topological and jamming transitions may occur under non-equilibrium conditions -leading to fundamentally different dynamical ordering phenomena and diverse spatial orders. For example, domain structures can emerge through the Kibble-Zurek ^{15,16} mechanism in second-order transitions or transient mesoscopic phase separation in first-order transitions. To obtain broader understanding of the dynamics of mesoscopic emergent phenomena that accompany such phase transitions the boundaries between metastable phases need to be determined on different timescales.

Presenting phase diagrams of temporally-evolving systems is a significant challenge. Most experimental techniques that can give sufficiently detailed microscopic and mesoscopic structure, such as electron and scanning probe microscopies, work well only on timescales $10^{-3} \sim 10^3$ s. On the other hand, the investigation of ultrashort timescale phenomena that occur in phase transition require stroboscopic repetitive scanning, which requires that the system dynamics is periodic, i.e. the transition outcome should be the same each time, so that it can be probed many times at the same moment in its cycle, and the signal can be averaged over many cycles. This has significant limitations, such as the requirement that all phenomena need to fully relax between measurements. The outcomes of singular ultrafast events, such as ultrafast phase transitions caused by a single laser shot that lead to metastable states which are of particular recent interest here, are an even greater challenge. Single shot techniques are limited by balancing signal to-noise and damage by the probe unless the metastable state lifetime is sufficiently long, so that each outcome can be examined by STM or AFM for example.

Yet, as we show here, using a combination of multi-pulse femtosecond time-resolved coherent phonon spectroscopy in combination with STM, a temporal phase diagram may be pieced together when the lifetime of the states can be tuned by temperature. The different phases that appear in the experiment on different timescales can then be compared with the results of a theoretical charged-lattice-gas model calculation of equilibrium and metastable photoinduced phases.

The studied material is a prototypical quasi-2D dichalcogenide $1T$ - TaS_2 , which was shown recently to display multiple metastable electronic and structural ordering phenomena. Its' phase diagram includes different structural polytypes ($1T$ - TaS_2 , $2H$ - TaS_2 etc) ¹⁷, different configurational charge-ordered states ^{13,18–21}, superconductivity ²² and a quantum spin liquid candidate state ²³. The $1T$ polytype is metallic above 550 K. In the range $350 \sim 550$ K it displays an incommensurate (IC) charge density wave (CDW), which undergoes a transition to a nearly-commensurate (NC) phase below ~ 350 K. Below 180 K, the material becomes insulating and fully commensurate (C), discussed either in terms of a CCDW, a polaronic Wigner crystal ^{24–26} or a Mott state ²². Upon heating, the material goes through a triclinic domain state in the range $220 \sim 280$ K, whereupon it reverts to the NC state. Among the many different equilibrium orders, the material also exhibits long-lived metastable states. Of particular interest are (i) the non-equilibrium topological transition to a 'hidden' (H) metallic

state with chiral domain structures¹⁹, and (ii) the jamming transition to an amorphous (A) state with hyperuniform electronic order¹⁸, both of which can be reached by photoexcitation.

The non-equilibrium phases in $1T - \text{TaS}_2$ were previously investigated by optical pump-probe techniques²⁷, transport measurements^{1,3,4,28}, time-resolved X-ray diffraction^{29–31}, and timeresolved electron diffraction (TrED)^{32–35}, sketching the timeline of the transient phenomena. After the creation of $e - h$ pairs by the incident laser photons (in $< 1\text{fs}$), melting of the Mott state takes place within $\sim 50\text{fs}$, while the periodic lattice modulation melts on the timescale of the collective mode $1/2$ -period ($\sim 200\text{fs}$)³⁶. The transition to the H state was observed by coherent phonon measurements to take place in 450fs ²⁷. TrED measurements³² revealed a number of transient phases on the picosecond timescale dependent on photon density, with a semi-continuous rotation of the CDW ordering wavevector with respect to the crystal axes as a function of laser fluence. The ordering wavevector angles observed in TrED are consistent with the angles obtained from the Fourier transformed STM images¹⁹ and with recent static X-ray measurements of the H state³⁷. X-ray diffraction showed electronic domain fusion dynamics associated with the formation of the IC phase, described in terms of coherent domain formation on the picosecond timescale³⁵ followed by diffusive processes on a timescale of $\sim 100\text{ps}$ ³¹.

Importantly for this study, the lifetime of the hidden (H) state is temperature-dependent, ranging from an extrapolated $\gg 10^{10}\text{ s}$ at 4 K to $< 10^{-4}\text{ s}$ at 150 K , which allows us to tune its relaxation time², facilitating stroboscopic measurements. The A phase was suggested to be stable to temperatures above 200 K ¹⁸ but the temperature-dependence of its lifetime is not known.

29.0.1 Results

To map out the temporal phase diagram we link STM images of different phases with the femtosecond optical spectroscopy results. First, we identify which long-lived nonequilibrium phases we can reach with different photoexcitation densities. To this end, we conduct STM experiments at low temperatures (4 K), where all of the previously known photoinduced phases can be considered stable, and we can distinguish them by their distinct spatial electronic ordering. Next, we link the latter to specific coherent phonon spectral features measured with the low-fluence two-pulse transient reflectivity spectroscopy. With the phonon fingerprints of the various states ascertained, we present three pulse technique measurements designed to track the non-equilibrium phonon evolution on short timescales.

STM experiments. We use an ultrahigh vacuum (UHV) low temperature STM (LT Nanoprobe, ScientaOmicron) with optical access (Figure 1a). The $1T - \text{TaS}_2$ samples are excited with an external laser. Since the STM scans cover a very small ($30 \times 30\text{ nm}^2$) area of the elliptical Gaussian laser spot ($\sim 100 \times 150\mu\text{ m}^2$ at FWHM) we can investigate the effect of different laser fluences simply by choosing an appropriate area of the STM scan with respect to the center of the Gaussian beam. The excitation is done with a laser pulse with the peak fluence of 12 mJ/cm^2 , which gives us a possibility to perform STM measurements over a wide range of fluences $F = 0 \sim 12\text{ mJ/cm}^2$ (Figure 1a). Typical experiments are done with a single laser pulse photoexcitation, but multiple pulse excitations were also performed to understand the effects of heating the sample. The outcome of different 1 and 10^6 shot experiments are shown in Figures 1c and 1d, where the colors of triangles represent the different observed states (Figures 1e – j). In both cases, the system returns to the original (C) state after photoexcitation (Figure 1e, blue in 1c and 1d) in the region where the fluence $F < 1.5\text{ mJ/cm}^2$. Above $\sim 1.5\text{ mJ/cm}^2$ the characteristic H state domain mosaics¹⁹ consistently appear (Figure 1f, yellow in 1c and 1d), independent on the number of the excitation pulses. Increasing the fluence beyond $\sim 3.5\text{ mJ/cm}^2$ patches of the amorphous A

state with a characteristic hyperuniform electronic structure¹⁸ start to appear within the H-state areas (Figure 1g, pink in 1c and 1d). These appear very inconsistently, and independent of the number of excitation pulses. At even higher fluences, we observe irreversible structural changes (ISC) that cannot be annealed by heating the sample (black). These include single layer polytype transformations from 1T to 1H (Figure 1h), which appear as triangular patches of various sizes without charge ordering above 70 K¹⁷. Another form of ISC is the layer peeloff and the creation of 1D nanotube-like objects (Figure 1i). Eventually melting/ablation of the material is observed and an uneven surface is created with nano-scale modulations (Figure 1j) or craters a few microns in diameter (Figure 1b). Large regions of ISC sometimes appear in single pulse experiments, but are more common with pulse-train excitation (Figure 1d) (Figure 1c shows an example of a single pulse excitation, where ISC did not appear, however this is not always the case), implying that the accumulated heating of multiple pulses enhances the formation of ISC. The ISC areas are surrounded and sometimes intermixed either by H or A state on micrometer scale regions. We further note that for high fluences $> 3\text{mJ}/\text{cm}^2$ the transition outcome is not perfectly reproducible on different areas of the sample. We attribute this to uneven thermal coupling between the sample and the substrate, possible imperfections of the layer stacking, or strains caused during cleaving.

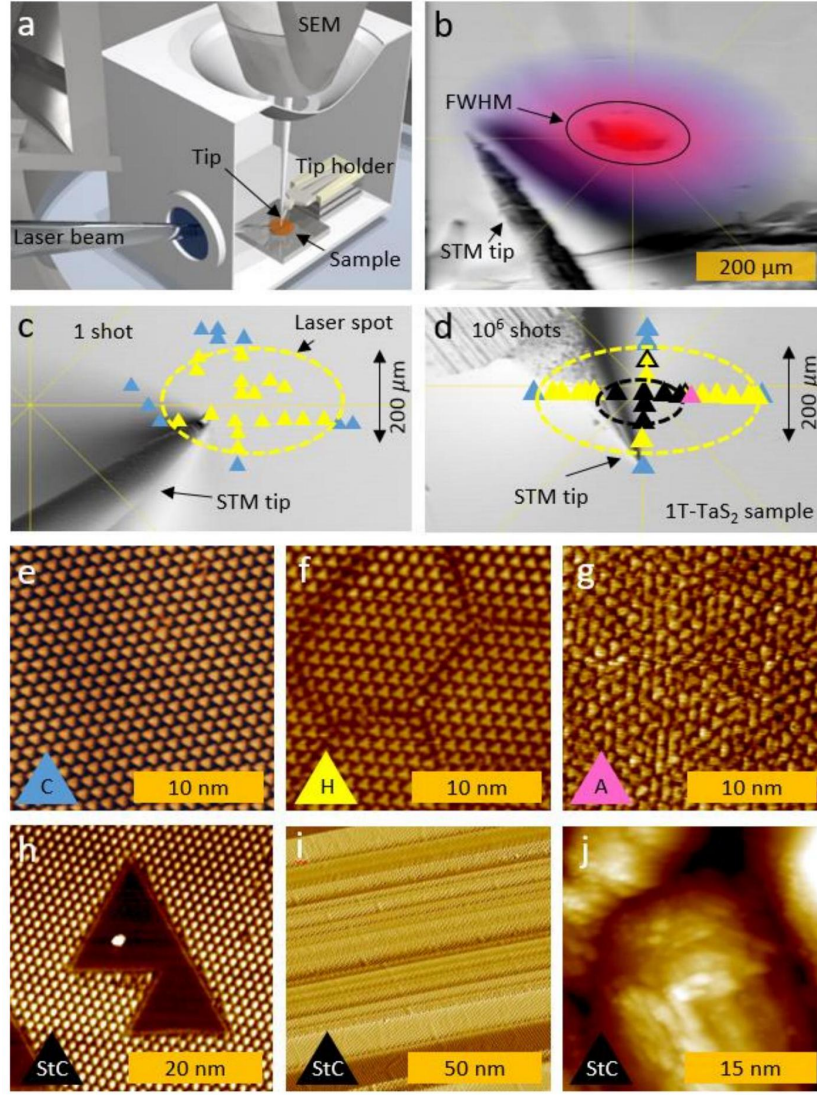


Figure 1. The STM experiment. a) A scheme of the optically excited STM setup. b) SEM image of an area exposed to 22 mJ/cm^2 peak fluence showing damage at the center of the laser spot, which was initially used to define the beam position. The local fluence decreases as we move away from the center of the beam (from red to blue as marked on the image). c) and d) SEM images of the sample with the marked state profile (color code from Figure 1 e-j)) after excitation with a single shot and multiple shots respectively. e)-j) STM images of various states achieved by photoexcitation at 5 K . e) ground C state, with a commensurate CDW and a perfect triangular lattice of polarons (bright spots), f) H state with CDW and domains of ordered polarons, g) A state with hyperuniform polaronic order, h) polytype transformation (at 77 K), where dark regions represent the 1 H polytype monolayer which has no charge modulation at this temperature ¹⁰ i) 1D surface ripples and j) sample melting.

Femtosecond laser spectroscopy. Having established the boundaries of the phase diagram on the STM timescale of $\sim 10^3 \text{ s}$, we use femtosecond spectroscopy with three different pulse sequences (Figure 2a) to investigate the trajectory of the system on the timescale down to 10^{-13} s via coherent phonons: (i) A single "Driving" (D) pulse causes the change of state, followed by a standard stroboscopic two-pulse Pump (P) - probe (p) experiment, in which the timescale is defined by the total time of the measurement (~ 10 minutes). The weaklyperturbative P – p protocol allows us to extract the near-equilibrium phonon fingerprints of the metastable

phases on the same timescales and temperatures as in the STM experiments, thus matching the signatures obtained by the two techniques. (ii) A repetitive three-pulse D – P – p sequence gives access to the picosecond timescale. Here, each scan of the P – p experiment is taken with a small (ps) fixed delay between the D and P pulses. This is applicable for mapping the H state at temperatures where its lifetime is shorter than the repetition time (1 ms using a 1 kHz laser system) and thus the sample fully relaxes before the next D – P – p sequence arrives. (iii) The D-P-p technique, with the changed order of the pulses. Here the P-p pulses come a few tens of ps before the D pulse, which effectively produces ~ 1 ms D-P delay (defined by the repetition rate). This way, we are able to establish whether the sample has relaxed between the pulses or in the case that it has not relaxed, we are able to see which state was present after 1 ms. To ascertain that no permanent change has occurred in the sample in the case when it does not completely relax in 1 ms, we turn off the D pulse and re-measure the reflectivity transient using only the weakly perturbative P – p sequence.

The C and H states can be distinguished by the frequency of the collective amplitude mode (AM)¹³. While the AM frequencies in both states are temperature dependent, the AM frequency of the H state is about 0.1 THz lower than the AM frequency of the C state at any given temperature²⁷, thus making the two states easy to distinguish. The T and NC states show a characteristic double peak in the phonon spectrum with lower amplitude and about 0.1 THz lower frequency than the H state at any temperature and can thus also be clearly differentiated²⁷. In Figure 2a and b we show the transient reflectivity oscillations and the respective Fourier spectra for C, H and T states. A detailed analysis of the C, H, NC and T state AM peak frequencies and line shapes with multi phonon fits and their temperature dependences are given in Reference 27.

The data for different D pulse fluences $F = 0.2 \sim 10$ mJ/cm² were taken at 80, 100, 140, 160 and 200 K. In Figure 2c and d we show the transient reflectivity oscillations and the respective Fourier spectrum at 160 K at different D fluences after 30 picoseconds and after a millisecond after switching to the metastable state.

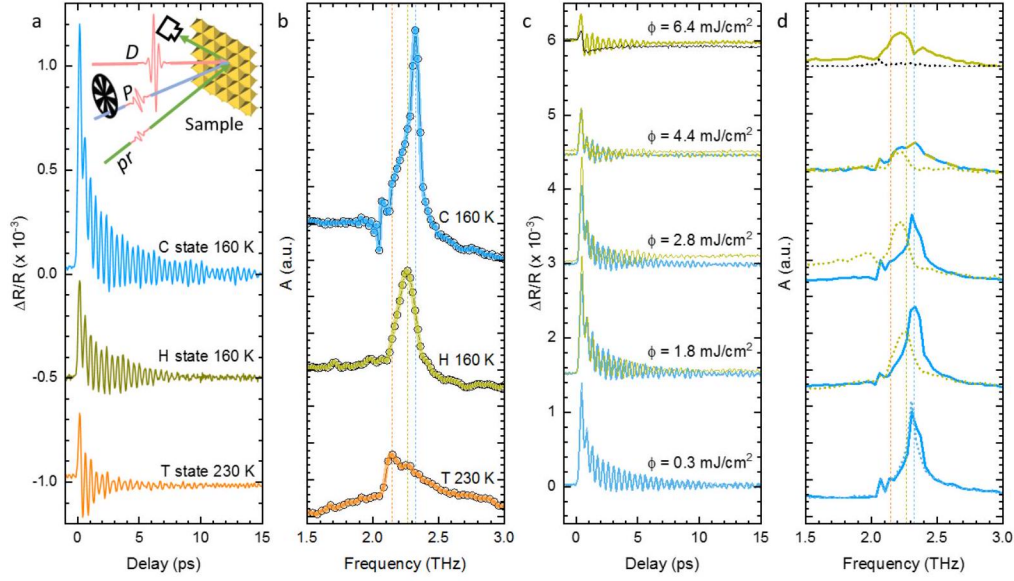


Figure 2. a) and b) The transient reflectivity oscillations and their Fourier spectra for C, H and T state, measured with three-pulse (C and H states) and two-pulse (T state) technique. The inset in a) shows the schematic of the setup. The vertical dashed lines in b) mark the peaks and are also shown in d) for comparison. c) Three-pulse D-P-Pr transient reflectivity measurements for different fluences at 30 ps (bold lines) and 1 ms (thin lines) showing different transition outcomes at 160 K, d) their respective Fourier transforms. The bold and dotted spectra correspond to the measurements at 30 – ps and 1 – ms, respectively.

Following the difference between the AM peaks in the C and H state, the C/H boundary on the low-fluence side can be defined with a high degree of certainty. The photoinduced H state at fluences slightly above 1 mJ/cm² forms already on the picosecond timescale and relaxes at this temperature within the ~ 1 ms time between the pulses. The same was observed at 100 K and 140 K. At 80 K, the H state does not completely relax between the successive pulses, which is in agreement with the STM data at 77 K.

On the high-fluence side, the boundary of the H state cannot be as clearly ascertained. With increasing fluence, we see lowering of the AM peak intensity, broadening of the peak and a further shift to lower frequencies. In this regime, we cannot easily recognize a unique fingerprint of any of the known states. To ascertain the presence of the A state, we compare the spectra of pristine and exposed samples 1 ms after photoexcitation at high temperatures, where the contribution of H phase is absent due to its short lifetime. We see that for fluences above ~ 3 mJ/cm² the sample does not relax completely to the C state in 1 ms, which is expected for the A state, but may also appear when other unidentified long-lived disordered phases or phase separation are present. As observed by STM for $F < 7$ mJ/cm², such transient states with no characteristic oscillation fingerprint eventually evolve into either the H or the A state. Since (i) multiple pulse experiments in STM show little or no difference from single pulse experiments (with fluences below the damage threshold) and (ii) repetitive single-shot measurements in the same spot in STM show different electronic ordering pattern of the H and A states after each pulse, we conclude that the final photoinduced states are 'reconfigured' by each pulse and independent of the initial electronic order.

For $F > 7$ mJ/cm², the AM peak intensity decreases even further, indicating the appearance of ISC. The irreversibility of the excitation process was tested by turning off the D pulse and measuring a control P – p transient from the same spot. At fluences up to 7 mJ/cm², the signal mostly recovers. With increasing the fluence beyond 7 mJ/cm², the signal recovers only

partially, while finally, at fluences above 10 mJ/cm^2 , the sample suffers enough damage to completely suppress the signal, which is consistent with the STM scans.

The time-domain phase diagram with a compilation of the transition outcomes for different F and T is shown in Figure 3, combining STM (triangles) and transient reflectivity data (squares). The time-axis signifies the time after the photoexcitation pulse (Figure 3a) grouping the data into three timescales: ultrashort ($< 10^{-10} \text{ s}$), intermediate (10^{-3} s) and long (10^3 s). The F axis is converted into the photon density taking a penetration depth of 30 nm at 800 nm

(Figure 3b). The color shade (blue, yellow, pink, black) represent different states as shown in Figure 1e)-j). White represents unidentified transient states, or an inhomogeneous mixture of states, which cannot be separated spectroscopically.

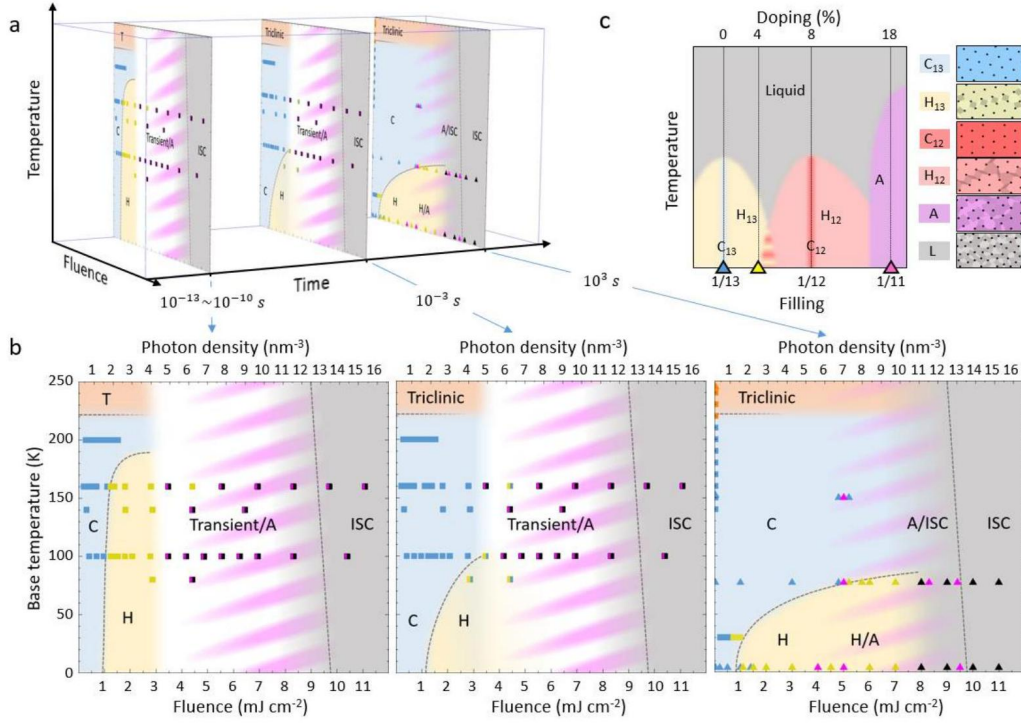


Figure 3. The time-domain phase diagram. a) Schematic timeline of the phase diagram evolution b) Detailed phase diagrams on the three timescales, as indicated. Triangles represent the STM data and squares represent the transient reflectivity data (color code from Figure 1 e) – j), and white represents the unresolved transient states). Note the significant shift of the long-time H state stability at high temperatures to higher fluences. c) The equilibrium phase diagram obtained from simulations²⁴. The C phase ($1/13$ filling-blue), the H phase (around $1/13$ filling-yellow) and the A phase ($\sim 1/11$ filling-violet) are all observed experimentally. The predicted phases at and around $1/12$ filling (red) are not observed in any of the experiments. The triangles and the dashed lines show at which filling values we observe the various states by STM.

We see that the H state has a nearly temperature-independent threshold fluence and is stable at low temperature in agreement with Ref. 3. When the measurement timescale is longer than the relaxation time, the H state disappears, thus the C/H boundary moves to lower temperature with time. The phase boundary of the C state observed by TRED³² agrees remarkably well with the present measurements on short timescale. Also, the suppression of the CDW diffraction peaks is in agreement with the decrease of the AM peak intensity in the transient optical spectroscopy data reported here^{27,32}. Finally, we note that the H

state boundaries on long timescales are also consistent with the recent XRD measurements³⁷. Comparing the appearance of the H state on short and long timescales we see that the H state immediately appears at low fluences, but it takes much longer to stabilize at higher fluences. On the other hand, on the long timescale at 77 K the H state is only visible at fluences above $\sim 5 \text{ mJ/cm}^2$, but is absent at lower fluences, even though it was observed there on a short timescale. This implies that the relaxation first happens on the outskirts of the beam, where the excitation fluence is lower.

To obtain insight into the origin of different phases we compare the observed experimental phases on the STM timescale with the equilibrium configurational states obtained from theoretical treatment. The model considers the ordering of electrons subject to screened Coulomb interaction on a triangular atomic lattice, and was previously successfully applied to describe both irregular domain patterns^{24,25} and hyperuniform polaron orders^{18,24} in the H and A states, respectively. It's predictions can be compared with the experiment by assuming a correspondence between the photoexcited carrier density (which is proportional to incident photon density) and electron filling. The model defines the filling of the system as the number of electrons at the Fermi level divided by the number of atoms²⁴. In 1T-TaS₂ with one electron per Ta atom, a $\sqrt{13} \times \sqrt{13}$ reconstruction of the CCDW state gaps 12 out of 13 electrons, resulting in 1/13 filling by the remaining electron^{38,39}. Doping is defined as a change of the filling with respect to 1/13. Experimentally, the filling is obtained by counting the number of polarons per unit area in an STM image (1 polaron equals 1 electron)^{18,24}.

Monte-Carlo simulations using this model give a theoretical phase diagram (Figure 3c) that is consistent with the experimentally observed C (1/13 filling) and H states at $\sim 4\%$ nominal doping^{24,25}, observed at the experimental photodoping of 0.09 photons/unit cell. Remarkably, they also predict the A state towards 1/11 filling (at $\gtrsim 15\%$ nominal doping, observed at a threshold of ~ 0.3 photons/unit cell)^{18,24}. Simulations also predict the existence of a uniform ordered state with 1/12 filling and close to 1/12 domain states around it, but these states are not observed experimentally. Possibly, the 1/12 superlattice is less stable and may only exist as a transient phase, but so far it has not been observed. In spite of the crudeness of the simple model, which correctly predicts the observed metastable charge configurations, we cannot expect it to predict their stability, for which one needs to consider additional effects, such as long-range order and topological defects created in the transition¹⁹. Larger density of such defects created by higher fluences may be the cause of the higher long-term stability of the metastable H phase at higher fluences, which was observed at 77 K. The amorphous state on the other hand is stabilized by the constraints imposed by jamming, which is an entirely different stabilization mechanism¹⁸.

We conclude that by a carefully chosen combination of techniques, phase-diagram 'snapshots' can be obtained during the relaxation trajectory of a non-equilibrium system. Comparison of the experimental phase diagram with the theory under the assumption that photoexcitation is equivalent to doping confirms that three out of four phases can be reached with photoexcitation fluence as the only control parameter. While the transition outcome reproducibility is excellent on the low-fluence side (up to $\sim 3 \text{ mJ/cm}^2$), various factors that are not under direct control contribute to variable transition outcomes on the high fluence side. This has important implications for the stability and potential device reliability. The understanding of the time-evolution of different nonequilibrium states revealed by temporal phase diagrams opens the way to the development of new functionalities in metastable quantum materials based on configurational electron ordering.

29.0.2 Methods

Sample preparation. 1T – TaS₂ crystals were grown by chemical transport method with iodine as a transport agent. The samples have average dimensions of $2 \times 2 \times 0.1$ mm. For optical measurements, the samples were glued to a copper plate with thermally conductive vacuum glue and cleaved just before inserting into the cryostat. For STM measurements, the samples were glued to the holder with a UHV compatible silver paste and inserted into the machine. The samples were cleaved inside the UHV chamber to prevent surface contamination.

STM experiments. We use a low temperature STM (LT Nanoprobe, ScientaOmicron) with optical access. For the photoexcitation of the samples, we use a 100kHz, 800 nm laser system, with 50 fs pulses. The number of shots was selected using an acousto-optic modulator. The laser pulses are guided into the STM chamber using an automatic stabilizing system with the positioning precision of $< 5 \mu\text{m}$. The laser beam profile was carefully determined externally with a CCD camera. A scanning electron microscope mounted above the STM allowed for precise tip positioning. The center position of the laser beam was determined from the perimeter defined by the border between the equilibrium and switched states.

Femtosecond spectroscopy. For the optical experiments, we use a 1kHz, 800 nm laser system with 50 fs pulses. The sample is held in a vacuum cryostat with optical access. As an addition to the standard pump (P) and probe (p) pulses, we use the third driving (D) pulse to drive the sample out of equilibrium. We varied the fluence of the D pulse from 0.2 mJ cm^{-2} to 10 mJ cm^{-2} . The fluences of the P and Pr pulses were always below 0.1 mJ cm^{-2} to ensure minimal disturbance. We use a mechanical chopper to modulate the P pulse, while the D and p pulses are unmodulated. This makes the D pulse »invisible« in the repetitive measurement with the lock-in technique and we only observe its effect on the sample.

Theoretical model. The model is based on the charged lattice gas (CLG) Hamiltonian $H = \sum_{i,j} V(i,j)n_i n_j$ where n_i is the occupational number of a polaron at site i with values either 0 or 1 and $V(i,j) = V_0 \exp(-r_{ij}/r_s)/r_{ij}$ is the Yukawa potential that describes the screening. $V_0 = e^2/\epsilon_0 a$ in CGS units and $r_{ij} = |r_i - r_j|$, where r_i is the dimensionless position of the i th polaron and r_s is the dimensionless screening radius. The value 1 for both $|r_i|$ and r_s corresponds to one lattice constant a . ϵ_0 is the static dielectric constant of the material. Polarons can only occupy the sites of the underlying triangular lattice with the lattice constant a and the ratio of polarons in the system divided by the number of lattice sites is expressed as the filling f . The Monte-Carlo method used to simulate the model was described previously²⁴.

We studied the phase diagram of such a system at fixed values of f and r_s . The CLG interpretation of polarons assumes a system of interacting phonons and repulsive electrons that is canonically transformed into a system of interacting small polarons in the strong electron-phonon coupling limit. We neglect spin effects, assume a screened Coulomb interaction, and assume that the hopping of polarons $\tilde{t} \ll V_0$, which is justified by the static nature of observed charges.

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29.0.3 Details of STM experiments

29.0.4 Hidden state

The threshold fluence for switching to the hidden state as seen with the STM appears to change with the temperature (Figure S1). At 4 K the average threshold fluence for observing the H state is 1.5 mJ/cm², while at 77 K we only observe the H state where the fluence is larger than 5.7 mJ/cm² (the observed area of the H state on the sample is smaller for the same laser beam). This is due to the faster relaxation of the H state at higher temperatures, which happens on the outskirts of the beam and prevents us from observing the whole switched area of H state with the relatively slow STM device. The observation could as well imply a higher switching threshold at higher temperatures, but the transient reflectivity measurements do not support this claim. Another important observation is that the observed switching fluence stays independent from the number of the incident pulses, both at 77 K and at 4 K. A very slight decrease in the threshold fluence (increase of the switched area) at 4 K with increasing the number of pulses is most likely the consequence of the spatial drift of the beam during long exposures. We conclude that the laser induced accumulated heating and nonequilibrium photoexcitations are well-separated effects.

29.0.5 Amorphous state

The amorphous state does not appear consistently across all experiments. In some cases, it is observed in patches within a larger area of the H state, while in other cases it is mixed with ISC areas. At 4 K the amorphous state was found both surrounded by H state and mixed with ISC, while when excited at 77 K it was only found mixed with ISC. On heating the A state from 4 K above 77 K, it was found surrounded by the C state when not mixed by ISC. In contrast with the electric switching¹, we have not found a way to controllably use optics to reproducibly switch the sample to the A state. However, we have found the boundary conditions at which the A state is likely to appear in optical experiments.

29.0.6 Irreversible structural changes

We observe no correlation between the sample temperature and the area of the induced ISC at the sample temperatures of 4 and 77 K (Figure S2). However, the area of ISC increases with the number of laser pulses, implying that at large fluences the accumulated heating plays a more critical role as opposed to low fluences. In most cases the threshold fluence to induce ISC is between 7 and 10 mJ/cm². This is particularly important for the polytype transformations², which were never observed in a single shot experiment, as they are a consequence of heating the sample, rather than an ultrafast electronic process. The same experimental conditions (power, exposure time and temperature) that lead to the polytype transformation in one case can create a large visible hole in the sample in another case. Single shot experiments can also have different ISC outcomes. When switching the sample with a single shot at two well-separated positions on the same crystal, we did not observe any ISC in one case, while in the other case we were able to see ISC in the form of melted sample in the middle. In both experiments the peak fluence exceeded 10 mJ/cm² and the sample was held at 4 K. This clearly suggests that the

outcomes at high fluences are strongly dependent on local properties of the sample, which are responsible for uneven sample cooling. The heat transfer is determined by the quality of the thermal coupling between the top layer(s) and the bulk sample and/or the sample holder. This varies with the amount of glue, the thickness of the sample and the interlayer structure, which are not very well controlled experimental variables.

29.0.7 Boundaries between the photoinduced states

While the H state is usually found in large homogeneous patches ($> 1\mu\text{ m}^2$), the A state and ISC more likely appear in smaller patches intermixed with other states. The boundaries between the states are usually gradual. As an example, a transition between an H area and a completely melted sample area generally includes a few intermediate areas. First, transiting from the pure H state, we see the H state gets mixed with A state areas or covered with lots of small ($< 5\text{ nm}$) material deposits when moving towards the higher fluence region. Further, the ratio of the H area and the melted parts changes and larger melted parts start appearing more frequently (Figure S3b and c) until the H parts completely disappear in favor of the melted region. Similar kind of transitions are observed in all cases, many times including spots where more than two states are intermixed (Figure S3a).

As a contrast to Figure 1h in the main text, we show Figure S3d, where most of the area is transformed to 1 H polytype with only small triangles of 1 T.

29.0.8 Transient reflectivity measurements of switching

Transient reflectivity at 100 and 160 K

The first set of D-P-p measurements was done at 100 K, with the D-P delays of 400ps, 30ps, -3 ps and -30 ps and with the fluences ranging from 0.4 mJ cm^{-2} to 10 mJ/cm^2 (Figure S4). In case where the D pulse arrives before the P – p sequence, we performed two separate sets of measurements, for the D-P delay of 30 ps and 400 ps. This way make sure that the observed state is not changing on the timescale of the measured P – p trace (30 ps). Since the excited states at $t_{D-P} = 30\text{ps}$ and $t_{D-P} = 400\text{ps}$ show the same characteristics, we conclude that they are stable on the 10 – 100ps timescale and further consider only the measurements at $t_{D-P} = 30\text{ ps}$.

One can notice the generally decreasing amplitude of the oscillations when increasing the D pulse fluence. Comparing the measurements of the millisecond state to picosecond state, we can see that the oscillation amplitude is at all fluences at least partly restored, suggesting that some sort of relaxation takes place even at the highest fluences. At fluences higher than 10 mJ/cm^2 a visible damage (a hole) was created and we were unable to perform any further measurements on that part of the sample. From the measurements, where the D pulse hits the sample during the P – Pr sequence ($t_{D-P} = -3\text{ps}$) we see that above a certain threshold fluence the slow transient reflectivity component (neglecting the oscillatory part) changes to another value. This is associated with the switching to the H state and was described in details previously³.

To more accurately determine the states, we did fast Fourier transforms (FFT) of the data for the millisecond and picosecond states (at $t_{D-P} = -30\text{ps}$ (corresponding to the relaxed state after 1 ms) and 30 ps, respectively), which are shown in Figure S 5. The maximum of the amplitude mode (AM) peak in the millisecond state stays approximately constant for the fluences of up to 3 mJ/cm^2 , and corresponds to the C state. Above that fluence the peak becomes broader and weaker, suggesting a change which does not relax back to the initial state within 1 ms. The data for the picosecond state shows a similar change above 3 mJ cm^{-2} as for the millisecond state, but the peaks are even more suppressed than for the millisecond

state. The most important thing we see in the picosecond state is that at the fluences above 1 mJ cm^{-2} the AM peak shifts to lower frequencies, indicating the switching to the H state.

An equivalent set of measurements was done also at 160 K . The data shows the same characteristics as at 100 K .

Transient reflectivity at 200 K

At 200 K, $1T - \text{TaS}_2$ can be found in two different thermodynamically stable states, namely the C and NC state, depending on how the sample reached this temperature. Upon cooling it undergoes a phase transition from the NC to C state at 180 K , thus it is in the NC state at 200 K . Upon heating it stays in the C state until 220 K before reaching the triclinic state, thus it is in the C state at 200 K . By performing the experiment at 200 K we check if the switching to the H state can be distinguished from the effects of the accumulated heating of the sample to the triclinic or NC state by the train of D pulses. If the main mechanism is indeed heating, the sample should stay in the NC/triclinic state also after cooling and would not relax back to the

C state at this temperature. In this case we would observe the characteristic oscillations of the triclinic or NC state when photoexciting the sample. Another thing that we could expect if heating was the transition mechanism, would be a decrease of the threshold fluence at higher temperatures. The highest measured fluences (up to 1.5 mJ/cm^2) are comparable or higher than the switching fluences observed at lower temperatures, but no change in the transient reflectivity is observed (Figure S 6). We conclude that switching to the H state is a different process than supercooling a thermodynamically stable state.

Transient reflectivity at 80 K

We performed two-pulse and three-pulse measurements at 80 K , with two different D pulse fluences, in the range where we expected the switching to the H state to occur (2.86 mJ/cm^2) and at a bit higher value (4.41 mJ/cm^2), shown in Figure S7. At this temperature, the relaxation time of the H state should be comparable to the time between the laser pulses ⁴ and thus a two pulse measurement of the C state was also made for the comparison. By exciting the sample with a 2.86 mJ/cm^2 laser pulse, the AM peak moves to a lower frequency with respect to the AM peak in the C state, consistently with observations at other temperatures.

When observing the millisecond state, the AM peak seems to be combination of both C and H AM peaks, suggesting that the sample is only partially relaxed. This is consistent with the STM measurements at 77 K , where the sample partially relaxes. By increasing the fluence to 4.41 mJ/cm^2 , we observe that the oscillations in the picosecond state have smaller amplitude consistently with the measurements at higher temperature.

Theoretical phase diagram

The parameter range of the filling f , relevant for comparison with the experiment is from $1/14$ to $1/11$, where all the experimentally observed states lie (Figure 3c). The model predicts a polaronic crystalline state (commensurate state) at $f = 1/12, 1/13$. Only $1/13$ is observed experimentally and it corresponds to the thermodynamically stable C state. Upon increasing the value of f from $1/13$, a domain state (experimentally observed H state) emerges, where domains of the $1/13$ lattice are separated by domain walls. Further increasing of f introduces $1/12$ lattice domains into the domain structure, which are not observed experimentally. The $1/13$ domains disappear at some point and only $1/12$ domains are left. When $f = 1/12$ is reached, polarons assume a perfect lattice pattern. Increasing f from $1/12$, a domain state with $1/12$ lattice domains separated by domain walls reemerges, which eventually disappears and we are left with an amorphous state consisting of mixed striped states ⁵. In the experiment, the only values of f observed are $1/13$ in the commensurate state, $\sim 1/12.6$ in the hidden state and $\sim 1/11$ in the amorphous state. To map the model to the experiment, we count the number of polarons per unit area in STM images. We assume the zero doping at the filling level of $1/13$,

which corresponds to the equilibrium C state. The deviations from the equilibrium state are linked to photodoping of the system which changes the value of f . The absence of observation of all the possible fillings between the values $1/12.6$ and $1/11$, which includes the $1/12$ lattice as well as the mixture of $1/12$ and $1/13$ lattices is most likely due to various effects, which are not included in the model. The model neglects Fermi surface nesting, electron-phonon coupling, overlapping polaron deformations and itinerant carriers, which are all a part of the complex nature of $1T - \text{TaS}_2$. As an example, Fermi surface nesting is the dominant factor in determining the high temperature incommensurate charge density wave state ⁶ and could as such significantly influence the outcome of the model. On the other hand, our correlated polaronic approach is valid to a certain degree due to its ability to predict the many different states, which could arise in other similar systems ⁵.

29.0.9 References

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29.0.10 Supplementary Figures

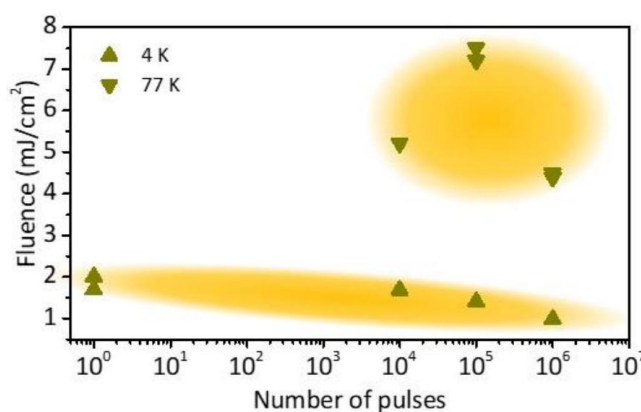


Figure S1. Threshold fluence for switching to the hidden state with respect to the number of shots. The upward and downward facing triangles show measurements at 4 K and 77 K respectively. The threshold fluence is lower at 4 K in all cases, which we attribute to the faster relaxation at 77 K. The yellow ellipses serve only as a guide to the eye.

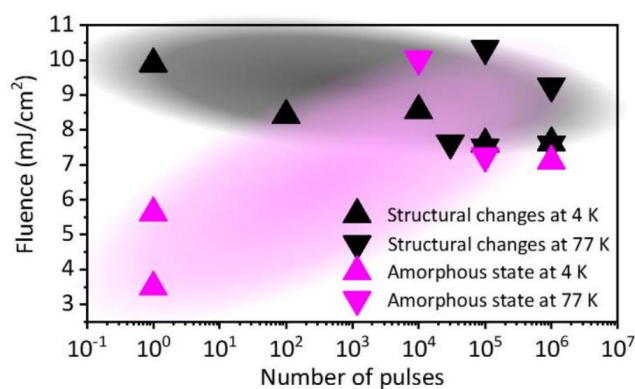


Figure S2. The observed threshold fluences for switching to the amorphous state (pink) and to induce structural changes (black) with respect to the number of shots. The upward and downward facing triangles show measurements at 4 K and 77 K respectively. The black and pink ellipses serve only as a guide to the eye.

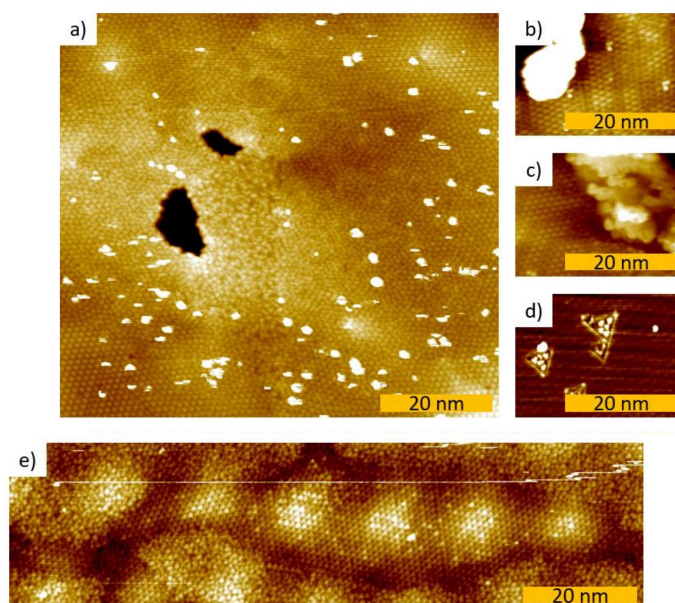


Figure S3. STM images of areas with more than one state present. a) Mixture of H and A state with ISC in form of material deposits and holes, b) and c) H state with large material deposits, d) 1H polytype area with small triangles of 1T polytype. e) a large A area encapsulating a small H area.

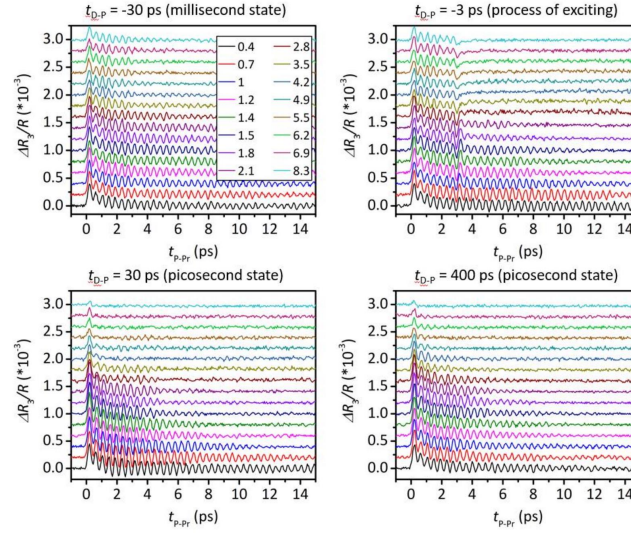


Figure S4. Three pulse transient reflectivity data at various D pulse fluences at $T = 160$ K.

The measurements at $t_{D-P} = -30$ ps show the sample in a 1 ms state, the measurements at $t_{D-P} = -3$ ps show the arrival of D pulse during the P – Pr sequence and measurements at $t_{D-P} = 30$ ps and $t_{D-P} = 400$ ps show excited sample. We see that the latter two sets show identical behavior. The numbers in the legend represent fluences in mJ/cm^2 .

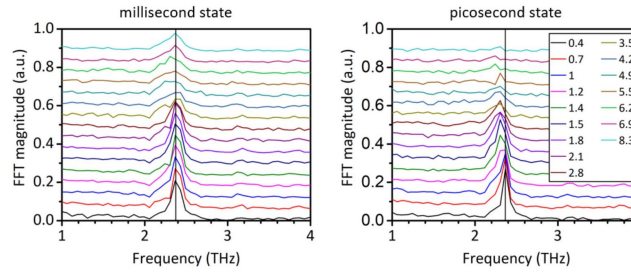


Figure S5. AM spectra of the data from Figure S4. The data of the millisecond state shows

complete relaxation to C state up to the fluence of about $3 \text{ mJ}/\text{cm}^2$ and an obvious suppression of the AM peak at higher fluences. The data on the picosecond state shows switching to the H state at the fluence above $1 \text{ mJ}/\text{cm}^2$ and a lowering of the peak at fluences above $3 \text{ mJ}/\text{cm}^2$. The numbers in the legend represent fluences in mJ/cm^2 .

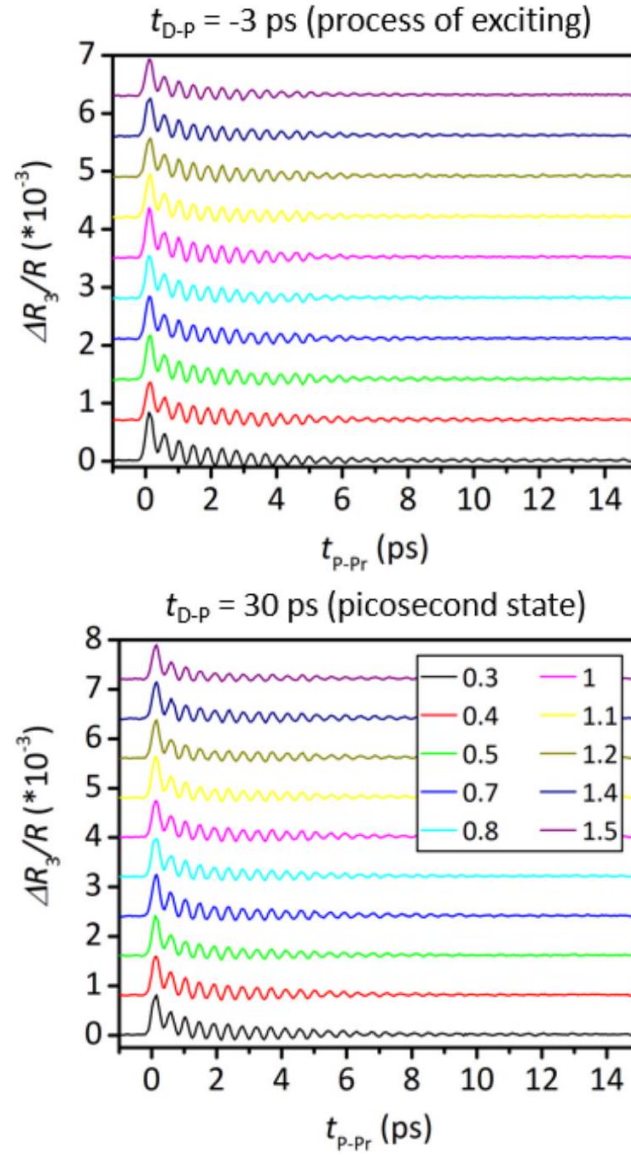


Figure S6. Three pulse transient reflectivity for various D pulse fluences at $T = 200$ K. The graphs show the measurements where the D pulse excites the sample during the P – p measurement ($t_{D-P} = -3\text{ps}$) and 400 ps before the measurement. The numbers in the legend represent fluences in mJ/cm^2 .

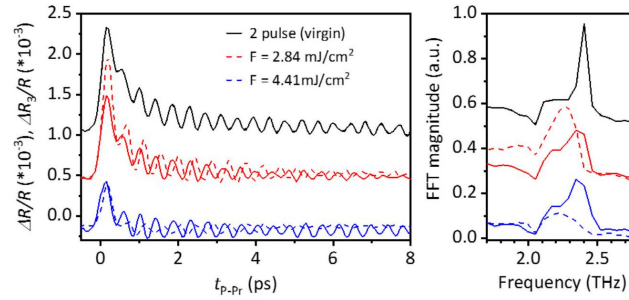


Figure S7. Two and three pulse pump probe measurements at 80 K (left) and their respective FFTs (right). The fluence of the D pulse was set to 0 mJ/cm² for the two pulse measurement (black) and 2.84 mJ/cm² (red) and 4.41 mJ/cm² (blue) in three pulse experiments. In the three pulse experiments the dashed and full lines represent the picosecond and millisecond states, respectively. We see that the sample does not relax from H state completely in 1 ms at 80 K. The amplitude of oscillations in the picosecond state significantly drops when the fluence is increased.

30 Electronic Dislocation Dynamics in Metastable Wigner Crystal States by Kranjec, Karpov, Vaskivskyi, Vodeb, Gerasimenko, Mihailovic

Abstract

Metastable states appear in many areas of physics as a result of symmetry-breaking phase transitions (examples?) .

An important challenge is to understand the microscopic mechanisms which lead to the formation of the energy barrier separating a metastable state from the ground state.

In this paper, we describe an experimental example of the hidden metastable domain state in 1T-TaS₂, created by photoexcitation or carrier injection.

The system is an example of a charge density wave superlattice in the Wigner crystal limit (how is it?) displaying discommensurations (how is it?) and domain formation when additional charge is injected either through contacts or by photoexcitation.

The domain walls and their crossings in particular display interesting, topologically entangled structures, which have a crucial role in the metastability of the system.

We model the properties of experimentally observed thermally activated dynamics of topologically protected defects-dislocations-whose annihilation dynamics can be observed experimentally by scanning tunnelling microscopy as emergent phenomena described by a doped Wigner crystal.

The different dynamics of trivial and non-trivial topological defects are quite striking.

Trivial defects appear to annihilate quite rapidly at low temperatures on the timescale of the experiments, while non-trivial defects annihilate rarely, if at all. (why is it so? basically, it is the main statement of the abstract)

30.0.1 1. Introduction

Metallic transition metal dichalcogenides (TMDs) commonly display commensurate charge-ordering at low temperatures. While some materials have received particularly detailed attention with a focus on specific features, the generic features, and the origin of broken translational symmetry, in particular, cannot be easily described in terms of traditional concepts, such as Fermi surface nesting, exciton condensation phenomena or peculiarities of the electron-phonon

interaction occurring in specific systems. On the other hand, a lattice Wigner crystal description appears to offer a common conceptual starting point for discussion not only of the ground-state ordering, but also metastable states in the system. The justification for the lattice Wigner crystal comes from the ratio of the kinetic energy T in relation to the Coulomb energy V , expressed in terms of the Wigner-Seitz radius r_s , that defines the crossover from Fermi-liquid behaviour to a lattice Wigner crystal state with dominant Coulomb interactions. The ratio of Coulomb energy to kinetic energy defines $r_s = \frac{V}{T} = e^2 m^* / (\hbar^2 n^{1/2})$, where n is the electron density, e is the elementary charge, and m^* is the effective mass of electron [1]. r_s is strongly dependent on the electron density n . In the prototypical dichalcogenide charge-density-wave (CDW) system-1 T – TaS₂, for example-the electron density n is small (one electron per 13 unit cells). Due to strong coupling to the lattice [2], polaronic effects renormalize the electronic bands, which become narrow, resulting in an increase in effective mass [3], which leads to an $r_s = 70 \sim 100$ and carrier localization in the lattice Wigner-crystal limit. There are two consequences: the first is the introduction of Mott physics [4,5], where the ordering dynamics are dominated by the Coulomb interaction, and the second is instability towards domain formation upon external perturbation or doping that takes place in the form of a symmetry-breaking transition.

The domains in such electronic crystals display very rich physics [6-9]. For example, the structure of domains created by laser excitation displays intertwined orders and intricate chiral ordering [9]. The structure of domain walls (DWs) themselves has been addressed on different levels [10-13]. In the context of Wigner crystal domains, Karpov and Brazovskii [10] introduced fractional charges associated with different mutual domain configurations. On a microscopic level, domain walls were analysed with scanning tunnelling microscopy in combination with density-functional-theory calculations [10-13], revealing the electronic structure within DWs. However, such modelling cannot be used to understand domain formation kinetics, the origins of metastability [14], or the dynamics of domain relaxation, governed by spatial topological constraints; nor can it be used to predict the generic formation of commensurate and domain structures across the entire series of metallic TMDs. The first step toward understanding such phenomena is the experimental characterization of the topology of the domain structure.

Here, we present an experimental analysis of the domain wall junctions, analysing the vertex structure in terms of 2D classical edge dislocations. Real-time measurements of domain relaxation using scanning tunnelling microscopy show the possibility of measuring dislocation annihilation dynamics.

30.0.2 2. Experimental Results

At low temperature (< 140 K), the unperturbed ground state in 1 T – TaS₂ is an electronic superlattice with a filling of $1/13$ with respect to the atomic triangular lattice, which is commonly referred to as the commensurate charge-density-wave (CCDW or C-state). The superlattice vector is given by $\mathbf{A} = 3\mathbf{a} + \mathbf{b}$, where $\mathbf{a}$ and $\mathbf{b}$ are the fundamental crystal lattice vectors (Figure 1a), the stars signify the polaronic distortions around extra electron charge on the Ta atom at the centre of each star-of-David hexagram. Domains are ubiquitously observed when a charge is injected by a large STM tip current pulse [6], an electrical pulse through contacts of a device [8], or by photoexcitation (photodoping), where the effect was originally discovered [14]. The resulting 'hidden' (H) domain state is metastable and has a lifetime that is sufficiently long that its domain structure can be investigated in detail at low temperatures [15].

In the present work, we excite in situ cleaved single crystals of 1 T – TaS₂ at 4.2 K with a voltage pulse from the tungsten tip of an STM. The area around the location of the voltage

pulse is first probed to determine where the hidden state borders the surrounding CCDW. When an appropriate area is found, we let the STM scanning run until at least several frames are acquired and a substantial relaxation is observed. Typical domain-forming pulse parameters are $V = 4$ V, pulse duration 1 ms and tunnel junction resistance $1\text{G}\Omega$.

To study the topological properties of the domain network, we need to accurately determine domains' phase shifts, fitting them on the underlying atomic lattice. To this end, we employ a simulated annealing Monte Carlo (MC) algorithm: first, we determine the most probable values of phase shifts for each neighbouring pair of domains, which we then globally optimize for the whole domain network. Such a local procedure supplemented by global "sewing" helps us to determine the domains' phases, even for big STM images which exhibit non-uniform values of the underlying lattice constant or lattice rotation angle.

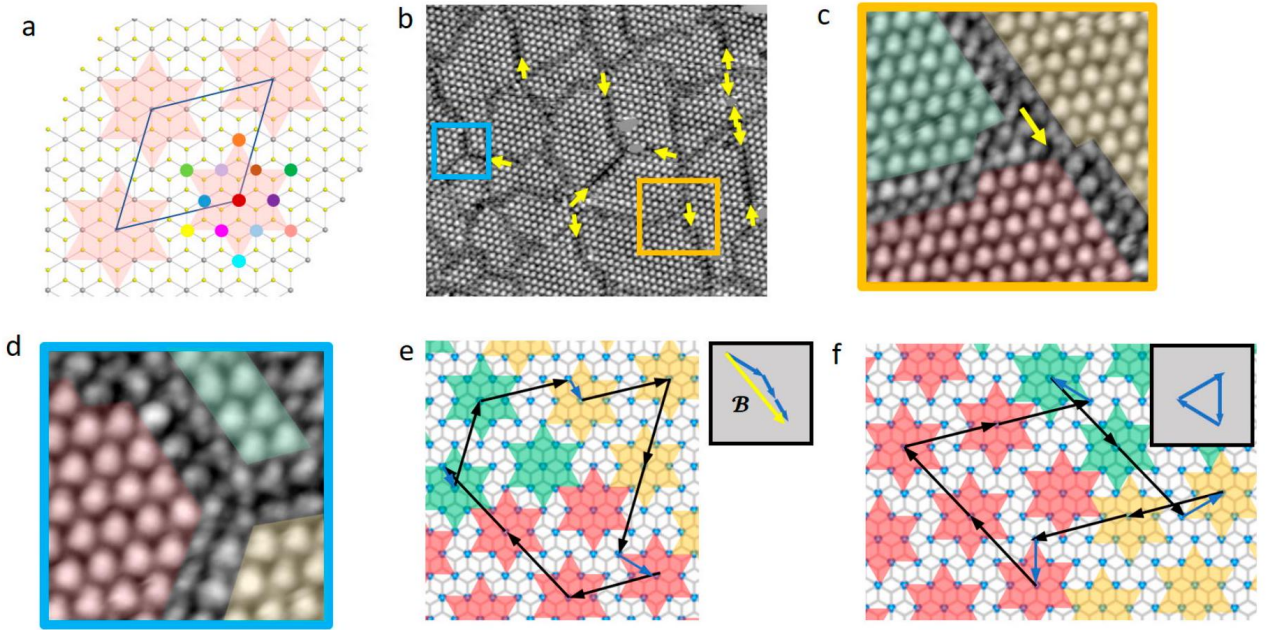


Figure 1. (a) Schematic representation of the commensurate superlattice showing twelve possible interdomain phase shifts with the corresponding colour coding. The parallelogram shows the CDW superlattice unit cell. (b) STM image ($V = -800\text{mV}$) of a part of the domain state with a relatively high density of dislocations. Yellow arrows indicate non-zero Burgers vectors at the vertices. (c) Zoom-in of the orange square on (b), rotated to align the underlying atomic lattice with the horizontal axis. Colour shading indicates different domains. A yellow arrow represents the Burgers vector. (d) Same as in (c) for a trivial vertex marked with the blue square in (b). (e) A schematic representation of the 3-vertex in (c). Blue circles are tantalum atoms; star of David overlays represent polarons using the same colour scheme as (c). Black arrows are CDW superlattice vectors indicating the Burgers circuit around the vertex. Blue vectors are relative shifts of domains upon crossing a domain wall. The inset shows that the relative shifts add up to a CDW superlattice vector, the Burgers vector of the vertex. (f) Same as in (e) for the trivial vertex. The inset of image 9 (f) shows that relative shift vectors add up to zero. Note that all domain wall types are the most common ones observed as reported previously in Ref. [13].

Using the above procedure, we analyse a large area domain structure formed by STM tip current injection shown in Figure 1b. The domain walls cross, typically forming three or four-pronged vertices. The vertices may be trivial, or non-trivial, according to whether a Burger's

vector construction around the vertex is zero ($\mathcal{B} = 0$), or non-zero ($\mathcal{B} \neq 0$), to which we refer as trivial (t) and non-trivial (nt) vertices, respectively. In Figure 1b, vertices are labelled according to whether the Burger's vector construction is t (no arrow), or nt (the yellow arrow shows $\mathcal{B}$). Figure 1c,d show examples of nt and a t vertices, respectively. The corresponding Burgers circuit construction in each case is shown in Figure 1e,f. The construction is always made, along with the shortest possible interdomain shifts upon crossing a domain wall, which is either of the nearest-neighbour types, with length a , or the next nearest-neighbour type with length $\sqrt{3}a$ (Figure 1e,f). We emphasize that the Burgers vector construction does not depend on the detailed structure of the vertex or the presence of extrinsic defects in its vicinity.

A relaxation sequence of the H state induced by a voltage pulse from the STM tip is shown in Figure 2. The domain area is entirely surrounded by the C-state (red overlay). The panels a – b6 show a gradual diminishing of the H -state and expansion of the C -state in discrete steps. Each frame was analysed by the MC-simulated annealing algorithm to determine the presence of dislocations at vertices. The vertices are labelled according to how many domains are adjacent to the vertex, which is the first number, and whether they are trivial (t) or non-trivial (nt). The arrows next to non-trivial vertices indicate their Burgers vector, yellow for $4nt$ and white for $3nt$. Panels b1-b6, with overlaid Burgers vectors, display the dislocation dynamics. We observe a constant number of dislocations in the domain reconfiguration process until the last frame, where two dislocations with opposite Burgers vectors annihilate. The latter two are marked by blue circles on image b5 prior to annihilation. Movement of some dislocations is also observed (which we attribute to a combination of climb and glide-see Figure 3).

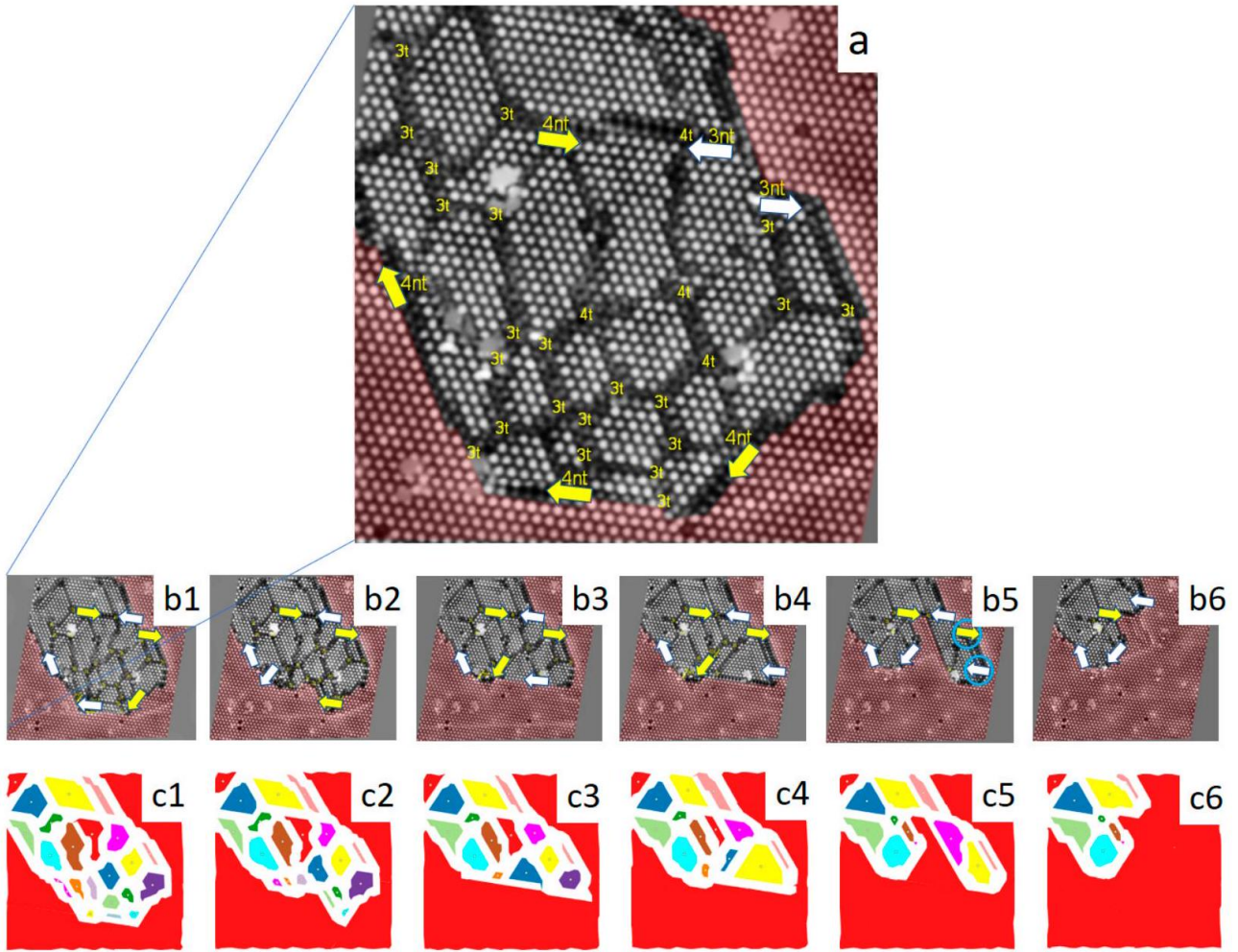


Figure 2. Relaxation sequence of the hidden state induced by a voltage pulse from the STM tip. (a,b) Analysed STM sequence of the relaxation of a patch of hidden state surrounded by the CCDW. Vertices are marked by yellow markings, with the number representing the number of domains that meet at a vertex and the letters "t" and "nt" stand for trivial and non-trivial, respectively ($3nt$ = non-trivial 3-vertex). The yellow arrow next to non-trivial vertices indicate their Burgers vector. Red shading indicates the surrounding CCDW and the domain, which is not shifted with respect to the CCDW. Blue circles in frames 4- and 5-mark pairs of dislocations that annihilate in the next frame. (c) Colour maps of domains for each frame in (a,b) as a result of the Monte Carlo algorithm. Colours correspond to relative domain shifts according to Figure 1d, with the origin (red) chosen as the CCDW. The colour of lines connecting centres of domains represents the quality of recognition of the MC algorithm. Green edges correspond to the best reliability, orange to lesser, red even less and black poor recognition. The vast majority of lines in all frames are green indicating reliable interdomain shift recognition. White lines in the CCDW are used to cut it into smaller pieces for better algorithm recognition.

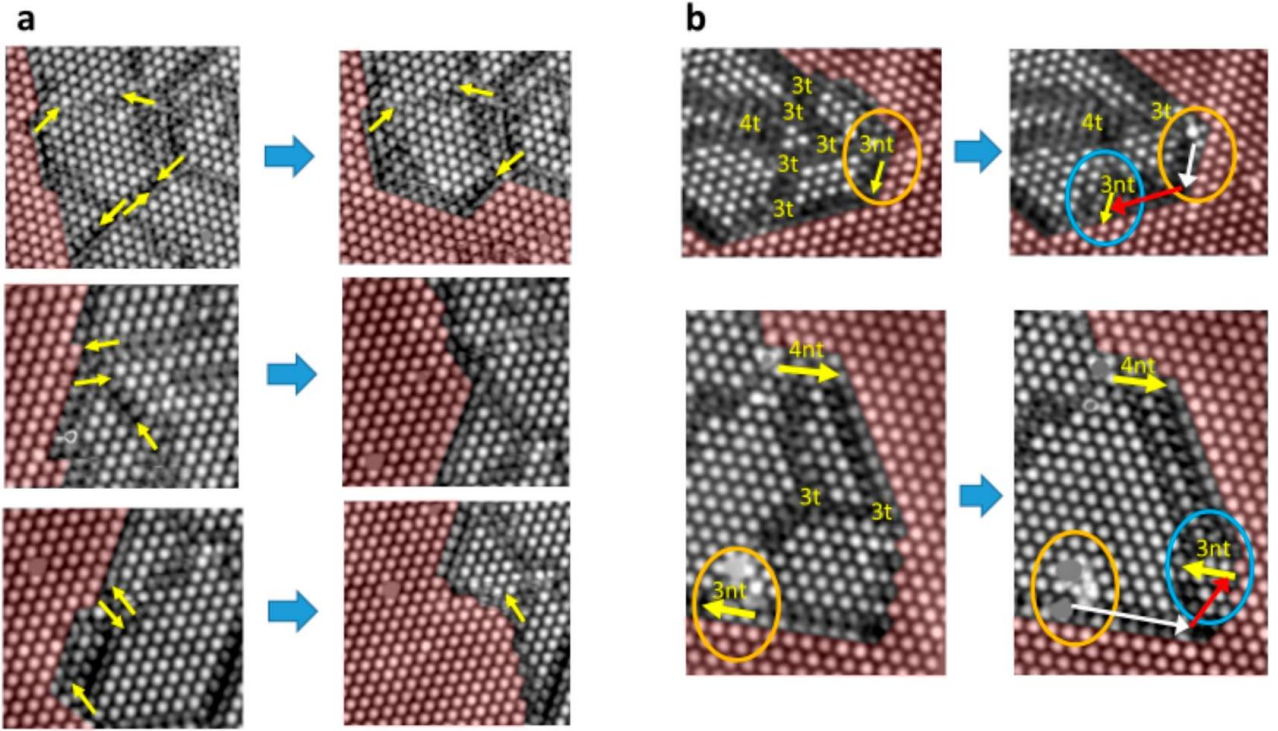


Figure 3. (a) Relaxation events involving annihilation of non-trivial defects. The Burger's vectors are indicated by the yellow arrows; (b) two examples of glide and climb motion of 3 nt dislocations. The red overlay represents the bordering CCDW.

The panels c1 – c6 show the same time evolution with colour maps for domains generated by the MC algorithm. The colouring of domains is according to their shift with respect to the original reference domain (which is chosen to be the C-state) following the colouring scheme of Figure 1a. We note that the colouring of domains remains consistent throughout the relaxation in the sense that domains do not change the CDW phase until they disappear. This is to be expected, since it is energetically costly to change the phase shift of a whole domain. They do, however, change their shape and size during relaxation.

Annihilation, glide and climb. Figure 3a shows three examples of dislocation pair annihilation in subsequent frames. In the middle panel, three dislocations disappear; in the last panel, two dislocations annihilate, and one is displaced. Yellow arrows are Burgers vectors, red shading indicates the surrounding CCDW. Figure 3b shows two examples of dislocation (3nt vertex) displacements, which we can attribute to a combination of glide and climb motion, as indicated by the different-coloured arrows (glide: white, climb: red). Glide motion involves motion along the direction of $\mathcal{B}$, while climb involves motion at an angle of either 60° or 120° to $\mathcal{B}$.

Annihilation dynamics. By examining STM frames in sequence, we can obtain an idea of the different rates of dislocation annihilation. While the amount of data is limited by the small number of frames and the slow relaxation rate, we can clearly distinguish different relaxation rates for different types of vertices. Figure 4 shows a count of the number of t and nt vertices for three- and four-pronged vertices on the full STM sequence of images shown in Figure 2. The three-pronged t vertices appear to show relaxation on the timescale of tens of minutes. In contrast, the four-pronged vertices show much slower dynamics. This is possibly due to the fact that most $3t$ vertices are located closer to the border with the CCDW, or simply due to the fact that they have more phase constraints and are therefore more energetically costly to relax. The nt defects show very little dynamics on this timescale. The number of dislocations

is constant until the last frame (when two dislocations annihilate) and so they form a sort of stable backbone of the domain wall network. It is clear from the examination of the STM images that t and nt vertices are inextricably entangled with each other in the sense that vertex ($3nt$) and anti-vertex ($\overline{3nt}$) pairs are not adjacent to each other, but there may be other vertices geometrically constraining their annihilation. It is quite likely that some defects have their anti-defects outside the image area, and the present experiments are limited in this way. Nevertheless, the general trend is clear. We also note that the fraction of nt vertices increases during relaxation, making the hidden state more topologically protected. This could have implications for data retention in memory-device applications.

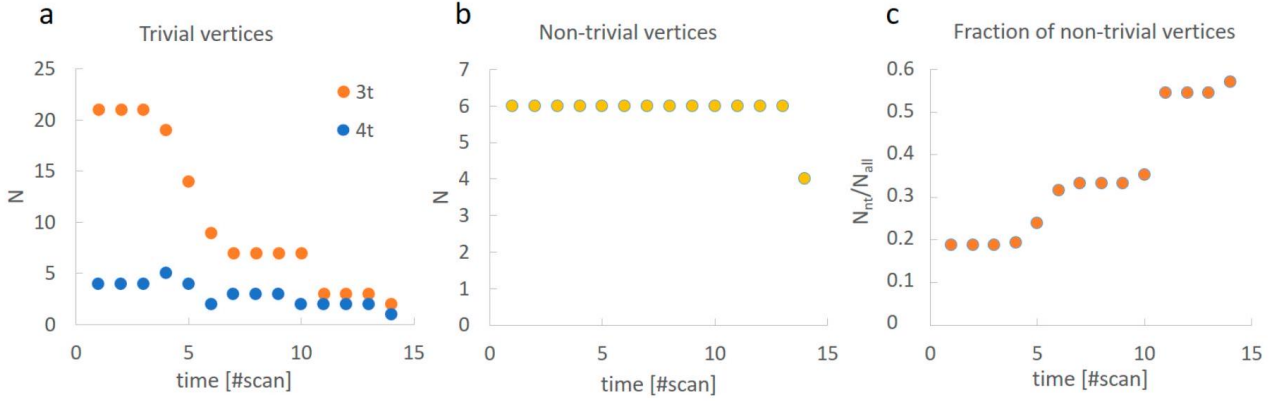


Figure 4. Temporal dynamics of (a) trivial (t) and (b) non-trivial (nt) vertex relaxation, respectively in consecutive STM scans. Each scan takes around 20 min. (Note the different scales.) (c) The number of nt vertices as a fraction of the total number of vertices.

30.0.3 3. Domain Textures as an Emergent Phenomenon

To understand the formation of domains, one may approach it from different directions [9-14,16,17]. A generally applicable theory with useful predictive value considers the domain structure as an emergent property, as a response of the polaronic Wigner crystal to doping [10,14,16]. The model Hamiltonian is given by [16]:

$$H = \sum_{i,j} V_{i,j} n_i n_j \quad (1)$$

where $n_i = 0$ or 1 is the occupation number of a polaron on the site i , and

$$V(i, j) = V_0 \exp(-r_{ij}/r_s) / r_{ij} \quad (2)$$

is the Yukawa screening potential, where $V_0 = e^2/\epsilon_0 a$ in CGS units and $r_{ij} = |r_i - r_j|$, where r_i is the dimensionless position of the i -th polaron, and r_s is the dimensionless screening radius. ϵ_0 is the dielectric constant of the material. The use of the model for quasi2D transition metal dichalcogenides has been justified previously, and has predicted the existence of electronic superlattices at magic-filling fractions and domains or amorphous electronic structures in between. Details of the calculation can be found in Ref. [16].

One possible way to represent the topological defects in the data is by using WignerSeitz cell (or sometimes called Voronoi) constructions around each polaron. Figure 5b shows such a construction for the large area experimental STM image with a large density of dislocations in Figure 5a. As before, the domains are first put to the underlying lattice with the MC simulated annealing process. Hexagons are coloured blue, while pentagons and heptagons are coloured orange and green, respectively. We see that nt vertices indicated by the arrows (which have

non-zero $\mathcal{B}$) are associated with heptagon-pentagon pairs. These are topologically equivalent to dislocations on a hexagonal lattice. The Wigner-Seitz cell representation is thus a useful abstraction for the rather complicated domain structure observed in STM experiments.

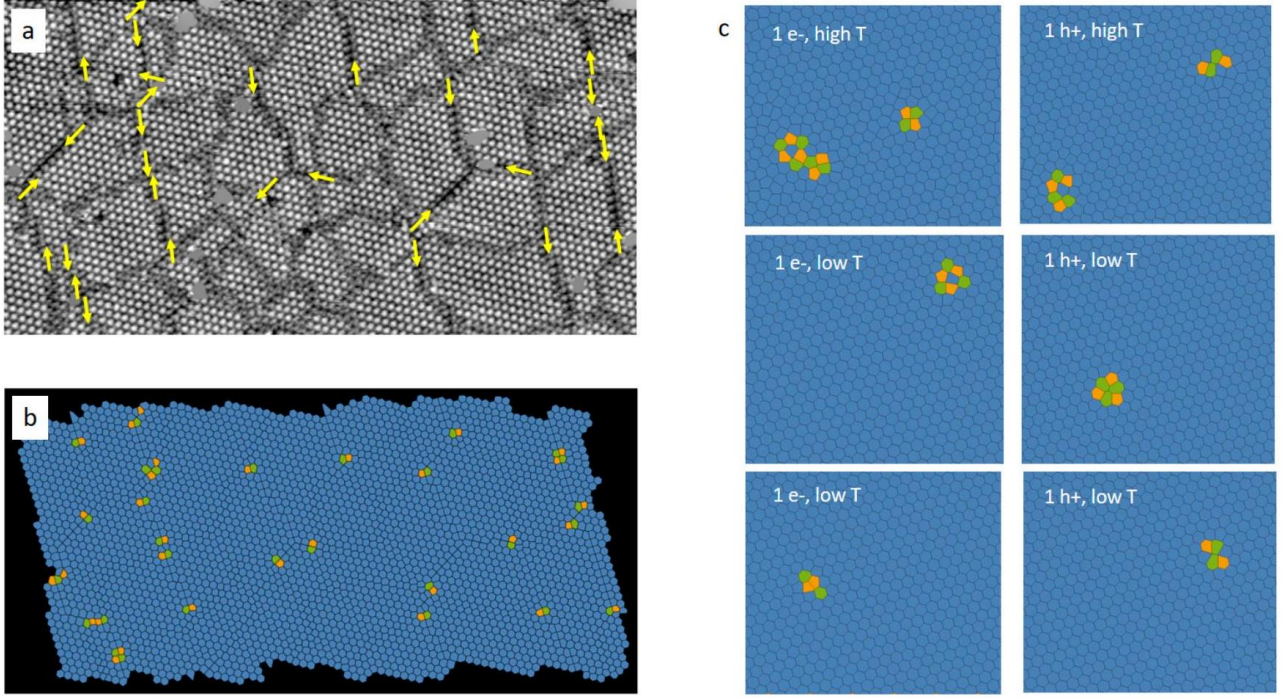


Figure 5. Comparison of an experimental image with the MC lattice gas model. (a) An STM image with a relatively high density of dislocations. Yellow arrows are Burgers vectors. (b) Wigner-Seitz cell diagram of the MC lattice fit to the image in (a). (c) Wigner-Seitz cells of the MC lattice gas model simulation after adding an electron (e^-), or a hole (h^+) to the lattice at different effective temperatures. Colour code: hexagons (blue), pentagons (orange), and heptagons (green).

The results of the calculation for lightly doped (adding 1 electron or 1 hole) Wigner crystal with a magic filling fraction of $1/13$ are shown in Figure 5c in the form of a WignerSeitz cell plot. We see that doping creates topological defects in the form of pentagonheptagon pairs, irrespective of the temperature. At higher temperatures, additional defects are visible due to $e - h$ pair excitations appearing as fluctuations in the number density. Comparing the predictions of this classical polaronic lattice gas model (Figure 5c) with the experiment in Figure 5b, we see that the model predicts the formation of the same kind of defects associated with doping. In both cases, we can see paired dislocations. The difference is in the presence of single heptagon-pentagon pairs in the experimental image, while in the model they are all paired or clustered. The comparison strongly suggests that the vertices are associated with an extra trapped charge.

Our simulations also show that the number of defects increases as we increase doping in the system and when doping is zero, no defects are remaining. Therefore, from the point of view of our polaronic Wigner crystal approach, the domain formation mechanism is the following. Photoexcitation or charge injection introduces additional charges in the system. Karpov and Brazovskii [10] have already shown that a domain wall is energetically more favourable than a hole or interstitial charge; therefore, a network of domain walls forms. The number of topologically protected defects is governed by the doping level and this number does not change if the doping level remains the same. Trivial defects, however, can relax and disappear. Experimen-

tally, it was noted before [16] that the doping level differs in the ground state and metastable state, which suggests that extra charges responsible for topologically protected defects also eventually leak back into the Fermi sea below the Fermi level.

30.0.4 4. Discussion

'Standard' theory of domain walls in CDW systems considers the energy of DW formation and energy of DW crossings (DWCs), which are of opposite signs, such that the two form a metastable minimum in the free energy of the system [14,18-21]. The minimum corresponds to a particular, topologically protected domain state, in the sense that the minimum is determined by specific details of the material and is immune to external single-particle perturbations. However, this does not include the additional complication of real-space pinning defects, nor is it immune to strain, for example [15]. In the same sense, the domain size is controlled by carrier injection [14,22,23]. The self-organized intrinsic formation of topological defects at DW crossings observed above is not included in the theory, yet it is likely to have a significant effect on the system stability, and hence the free-energy potential landscape. The dynamics of dislocations in particular are governed by annihilation dynamics, the bottleneck being matched defect pair annihilation. In 2D, conventional Kosterlitz-Thouless (K-T) theory, the dynamics are discussed in terms of edge dislocations, which are created and annihilated in pairs. At high density, the dislocations destroy long-range order, resulting in a hexatic phase. When the dislocations dissociate into five- and seven-fold disclinations, an additional isotropic phase may appear. The two-step melting of such a phase is described in terms of the Kosterlitz-Thouless-Halperin-Nelson-Young (KTHNY) theory with two consecutive K-T transitions. These theories do not consider the dynamics of the dislocations, which can be quite intricate.

The dynamics of classical lattice dislocations under stress is governed by a PeachKoehler (P-K) force between dislocations described in terms of their Burger's vector and the stress tensor, with additional terms arising from pinning by extrinsic defects, temperature-driven lattice fluctuations, local (Peierls-Nabarro) strains, etc. [24,25]. Simulations of the dynamics in classical 2D systems typically reveal aggregation of dislocations in the form of clusters, and at the edges.

In the case of an electronic crystal on a hexagonal lattice, the structure of non-trivial defects is formally equivalent to lattice dislocations, but the microscopic structural details, on which the dynamics will depend, are quite specific. The experimental data above show the structure of trivial and non-trivial vertex dynamics and are presented formally in terms of dislocation dynamics. Aggregation of dislocations at the edges or in the centre of the domain structures is not observed on the timescale of the STM experiments, suggesting that annihilation is faster than the P-K dynamics at 4 K. More importantly, the dynamics is governed by the entanglement of defect pairs, which prevents direct annihilation of defect-anti-defect pairs through a simple glide or climb motion, but requires 'circumnavigation' and annihilation in a particular sequence. The fact that the domains are created spontaneously, from initial fluctuation-nucleation after a quench suggests some degree of randomness in the initial distribution of defects. However, domain-wall repulsion and the energy gained by crossings at vertices act to form a more uniform, long-ranged order in the domain structure. The latter process is hindered by topological constraints at the vertices.

We note that the present analysis is limited to the temporal and spatial window of the STM experiments. Dynamics on other timescales cannot be excluded, but currently, there are no other methods to observe the defect dynamics. In spite of experimental limitations, the dynamics of the observed difference in nt and t dynamics are quite significant, indicating that the forces between nt and t are quite different. An additional complication arises from the fact that nt and t vertices are intertwined, which brings a complex topology to the problem.

On a phenomenological level, the relaxation was previously described in terms of the Ostwald ripening process, with double exponential relaxation, but the approach is not very insightful in explaining the magnitude of the energy barrier E_B for relaxation to the ground state [15]. However, the strong observed sensitivity of E_B to external strain suggests that a general P-K approach is reasonable.

A suitable framework for describing the quantum nature of such a system may be provided by fractions, excitations within a tensorial field theory that are dual to classical elasticity theory used in the present analysis [26], but such treatment is beyond the scope of this paper.

Given that the detailed construction of DWCs is likely to play an important role in the overall relaxation process of the electronic Wigner crystal, one may comment on the prospect of dealing with the dynamics of such a system on the microscopic level (e.g., density functional theory) used recently to describe the static structure of single DWs. Such modelling may be useful in determining the relative energy stability of different DWs and eventually DWCs. The transitions between states on the resulting energy landscape may form the basis of more material-specific relaxation dynamics.

30.0.5 5. Conclusions

The difference in t and nt dynamics is striking and proves that the topological protection of nt vertices plays a crucial role in the stability of the domain state. We conclude by commenting on the fact that at low temperatures, the dynamics are limited by macroscopic quantum tunnelling between different, but energetically near-degenerate domain configurations that were shown, in recent experiments, to be finite [27].

30.0.6 References

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Part VIII

Applications and Potential Applications: Main Articles

31 A charge-density-wave oscillator based on an integrated tantalum disulfide-boron nitride- graphene device operating at room temperature by Liu, Debnath, Pope, Salguero, Lake, Balandin (2016)

Abstract

(well-known CDW) The charge-density-wave (CDW) phase is a macroscopic quantum state consisting of a periodic modulation of the electronic charge density accompanied by a periodic distortion of the atomic lattice in quasi-1D or layered 2D metallic crystals ^{1–4}.

(materials for CDW, different T_c) Several layered transition metal dichalcogenides, including 1T-TaS₂, 1T-TaS₂ and 1T-TiSe₂ exhibit unusually high transition temperatures to different CDW symmetry-reducing phases ^{1,5,6}.

(there are many factors for T_c) These transitions can be affected by the environmental conditions, film thickness and applied electric bias ¹.

(it was unknown what to do with them at room T and what if we put different substrates) However, device applications of these intriguing systems at room temperature or their integration with other 2D materials have not been explored.

(we'll show current switching, their main discovery) Here, we demonstrate room-temperature current switching driven by a voltage-controlled phase transition between CDW states in films of 1T-TaS₂ less than 10 nm thick.

(350K, IC-NC ph change, hysteresis) We exploit the transition between the nearly commensurate and the incommensurate CDW phases, which has a transition temperature of 350 K and gives an abrupt change in current accompanied by hysteresis.

(it is possible to voltage control of the circuit) An integrated graphene transistor (graphene transistor (G-FET) will be explained later) provides a voltage-tunable, matched, low-resistance load enabling precise voltage control of the circuit.

(protection from oxidation) The 1T-TaS₂ film is capped(=covered) with hexagonal boron nitride to provide protection from oxidation.

(we can create a voltage-controlled oscillator and it can be somewhere useful) The integration of these three disparate 2D materials(b-BN, graphene, TaS₂) in a way that exploits the unique properties of each yields a simple, miniaturized, voltage-controlled oscillator suitable for a variety of practical applications.

31.1 Article

Article

(phases of TaS₂) The 1T polytype of TaS₂ undergoes the transition from a normal metallic phase to an incommensurate CDW (IC-CDW) phase at 545 K, to a nearly commensurate CDW (NC-CDW) phase at 350 K and, finally, to a commensurate CDW (C-CDW) phase at 180 K (refs 7-11).

(PLD, change of bands) Each phase transition is accompanied by a lattice reconstruction, which results in strong modifications to the material's electrical properties.

(at low T, there is a Mott insulating state) In 1T- TaS₂, the C-CDW phase drives a Mott-Hubbard metal-to-insulator transition (MIT) that results in a Mott insulating state.

(diff. factors influence ph tr-s) Intercalation and doping, the ambient pressure, the thickness of the quasi-2D films, optical excitation and the applied electric source-drain and gate bias can modify the transitions to different CDW phases ^{7–16}.

(thick film -> no NCCDW-CCDW transition) For example, when the thickness of the 1T- TaS₂ film is <10 nm, the C-CDW-NC-CDW transition at 180 K disappears, whereas the NC-CDW-IC-CDW transition at 350 K persists ¹⁰.

(intro to source-drain voltage factor) A source-drain voltage can trigger the phase transition.

(bigger applied fields -> bigger conductivity) In the case of 1 T – TaS₂ the electrical conductivity abruptly increases when the applied electric field exceeds 20kVcm⁻¹, which is attributed to the insulator-to-metal transition (IMT) ¹⁴.

(decrease appl field (=voltage) -> transition back) A reverse MIT is revealed when the voltage is swept back(back to 0) ¹⁴.

(MIT, IMT (which are at 350K) have not been observed before room T.) Despite great recent interest in the CDW properties of quasi-2D transition metal dichalcogenides ^{10–12,14,17}, neither the IMT nor the MIT induced by an electric field have been observed above room temperature. (they haven't been observed not because of T, but because of inability to cross the border of ph tr by electric field)

(why if ph tr is at 350K, then we can still have it at room Ts? because we are using some voltage which does this job. explanation should be below)

(no devices were at room T) Correspondingly, no devices that use CDW transitions as the basis of their operation have been demonstrated at or near room temperature.

(we'll show you a device at room T) In this work, we show that an abrupt change in the electrical conductivity and hysteresis observed at the IMT and MIT transitions associated with the transition between the NC-CDW and IC-CDW phases in a quasi-2D 1T- TaS₂ channel can be used to construct an oscillator that operates at room temperature and up to 320 K.

(substrate (h-BN) makes TaS2 robust) A second quasi-2D material, hexagonal boron nitride (h-BN), provides environmental protection against oxidation and preserves the CDW phase.

(graphene gives the transistor, controls voltage somehow) A third integrated 2D material, graphene, provides a transistor with a current density and load resistance that closely match(physically touches) to TaS₂, allowing precise voltage control of the oscillator frequency.

(maybe such oscillator will be cheap to create) The voltage-controlled oscillator (VCO) demonstrated here does not require a complicated biasing circuit and could lead to inexpensive technologies for communication systems and other applications.

(chemical vapour was used for preparation) High-quality 1 T – TaS₂ crystals were prepared by the chemical vapour transport method (see Methods).

(exfoliated thin films) The prototype devices were fabricated with exfoliated thin films.

(again about h-BN) To protect the exfoliated 1T- TaS₂ from oxidation we used an h-BN capping layer positioned on top of the CDW channel ^{18,19}.

(material, contacts to it) The fabricated devices consisted of 1T- TaS₂ channels(channel=part of the device) with depth in the range of 6-9 nm and Pd/Au (15/60 nm) contacts.

(image of the device) An optical image of a typical device is shown in an inset in Fig. 1b (see also Supplementary Figs 1-6).

(Figure 1a: I – V curve) Figure 1a shows the current-voltage (I – V) characteristics of such TaS₂ – BN devices in the temperature range from 78 to 395 K, which includes the 1T- TaS₂ phase transition from the NC-CDW to IC-CDW states.

(above 320K there is a jump in I in $I - V$ curve) Below 320 K, we observe a prominent abrupt current jump as the voltage exceeds a certain value, denoted here as V_H .

(jump = threshold switching) This behaviour is also referred to as threshold switching between the low and high conductivity states.

(fall in I when we sweep back) When the voltage is swept back to zero, a reverse threshold switch occurs at a lower voltage V_L that corresponds to a smaller critical electric field.

(it is a hysteresis) The difference between these two voltages forms a hysteresis window.

(more is in SM) Details extracted from Fig. 1a are shown in Supplementary Fig. 4.

(repetition of the range where there are jumps) It is important to note that the threshold switching effect in our device exists throughout the temperature range from 78 to 320 K.

(ph tr is after 350K and little jump) As the temperature is increased to 345 K, slightly below the transition from NC-CDW to IC-CDW at 350 K, threshold switching becomes weak (inset, Fig. 1a).

(then ICCDW phase and no jump) Increasing the temperature above 350 K results in the disappearance of threshold switching and the I-V characteristics become linear as the 2D 1T-TaS₂ channel enters the IC-CDW phase.

(Fig. 1b: we fix V , use $R = V/I$ to get this plot for different T , we always have same small voltage) Figure 1b presents the temperature-dependent resistance measured with a small voltage (20 mV).

(R decreases until ph tr) The resistance decreases as temperature increases until the NC-CDW-IC-CDW transition point near 350 K is reached, where the resistance drops abruptly.

($R \approx \text{const}$ after ph tr) After the transition the resistance becomes almost constant with temperature.

(little hysteresis in R) In the cooling cycle, the resistance jump occurs at 340 K, forming a temperature hysteresis.

(it is expected that there is no change in R in ph tr C-CDW to NC-CDW) The absence of a C-CDW to NC-CDW phase transition at 180 K in very thin films (<9 nm) of 1T-TaS₂ is consistent with a recent report ¹⁰. (why in this C-CDW to NC-CDW phase transition there is no change in R ???)

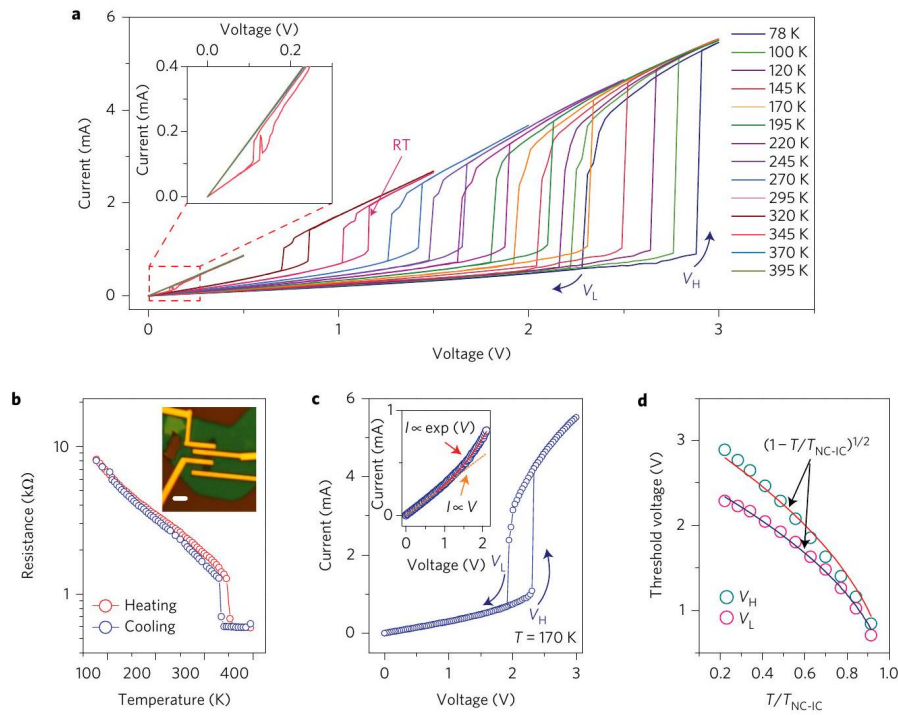


Figure 1 | Electrical characteristics of thin-film 1T-TaS₂.

a, $I - V$ characteristics of thin-film 1T-TaS₂ at different temperatures from 78 to 395 K.

The threshold switching effect is prominent from 78 to 320 K.

The blue arrows indicate the voltage sweep direction for the measurement at 78 K.

For all other temperatures V_H is always higher than V_L .

The hysteresis window is defined as $V_H - V_L$.

The threshold switching is prominent up to 320 K, and becomes less pronounced as the temperature approaches the NC-CDW-IC-CDW transition at 350 K.

As shown in the inset, at 345 K the threshold switching is still measurable.

As the temperature exceeds 350 K, the $I - V$ slope becomes linear.

b, Temperature-dependent resistance measurements for a 9-nm-thick 1T-TaS₂ film.

The NC-CDW-IC-CDW and IC-CDW-NC-CDW transitions happen at 350 and 340 K during the heating and cooling processes, respectively.

The resistance is measured at a low voltage ($V = 20$ mV).

Inset: An optical image of a typical h-BN-capped 1T-TaS₂ device.

The dark purple strip is the 1T-TaS₂ thin film and the larger green region is the h-BN film.

Scale bar, 5 μm.

c, Superlinear $I - V$ characteristics below V_H .

The curve at $T = 170$ K is shown here as an example. Arrows indicate the voltage sweeping directions.

Inset: The current below V_H can be fitted with an exponential component $I \propto \exp(V)$ superimposed on a linear curve $I \propto V$.

d, Temperature-dependent threshold switching voltage.

Both V_H and V_L are proportional to $(1 - T/T_{NC-IC})^{1/2}$, a dependency that is identical to that described by analytical theories of the CDW order parameter¹.

(high V - same value of $I \rightarrow$ same R) Another interesting observation is that the resistance value after electrically induced switching is the same for all temperatures, as seen from the similar slopes of the $I - V$ curves at high field(=high V) in Fig. 1a.

(The resistance at high V (after this switch) and low T is nearly equal to that at high T and low V) (basically it is about the slope on fig. 1a, for high T it is the same at 0, as for low T at the most right of this figure) The resistance extracted from the slope is 580Ω , which matches the low-field (low-field = a small probing voltage is applied, but it is much lower than the threshold voltage) temperature-dependent resistance of 590Ω presented in Fig. 1b at $T > 350$ K.

(The resistance at low V (before this switch) and low T is also equal to that at low T and low V , which is what is seen on the fig. 1a. this is basically a consistency check (since 1b is another experiment with always constant little V), not that important) In addition, the low-field resistances extracted at lower temperatures from the $I - V$ slopes in Fig. 1a are also in agreement with the measured resistance in Fig. 1b(also at lower T), shown in Supplementary Fig. 8.

(R is the same at high T (where we know that there is ICCDW) and at high V with low T -> we can say that we have switched to ICCDW phase) This equivalence in resistance values is consistent with the picture of voltage-controlled switching driving the 1T- TaS_2 between the NC-CDW and the IC-CDW phases.

(or maybe just CCDW domains in NCCDW phase are not more insulating, but the general phase is nearly the same) Another possibility is that the applied field and the resulting current destroy the Mott insulating state within the individual CDW domains while leaving the lattice in the NC-CDW phase.

(V_H scales linearly as length of a sample) We also note that the threshold switching voltage scales linearly with the channel length (Supplementary Fig. 5). (I'll look at it only if needed)

(values of crit. fields, obtained by $E = V/l$) The critical fields E_H and E_L are 28.8 and 22.8kVcm^{-1} at 78 K and decrease to 11.2 and 10.2kVcm^{-1} at room temperature.

(maybe shorter models will have smaller V_H) The length scaling suggests a possibility of further reductions of the threshold voltage for devices with shorter channels.

(below jump - different linear dependences on V , not actually linear) We observe that the $I - V$ characteristics below V_H do not have a simple linear dependence.

(1c - exp component for one selected T) Instead there is an extra exponential component as shown in Fig. 1c.

(V_H and (V_L) also T -dependent with a simple relation) The temperature dependence of the threshold voltages V_H (V_L) follows the relation $(1 - T/T_{\text{NC-IC}})^{1/2}$ below the NC-CDW-IC-CDW transition temperature of 350 K (see Fig. 1d).

(something similar is known from theory and observed in other structural phase of this material) This temperature dependence is the same as that described by analytical theories of the CDW order parameter ¹(analytical theories of the CDW ????) and has recently been observed in $2\text{H} - \text{TaS}_2$ (ref. 20).

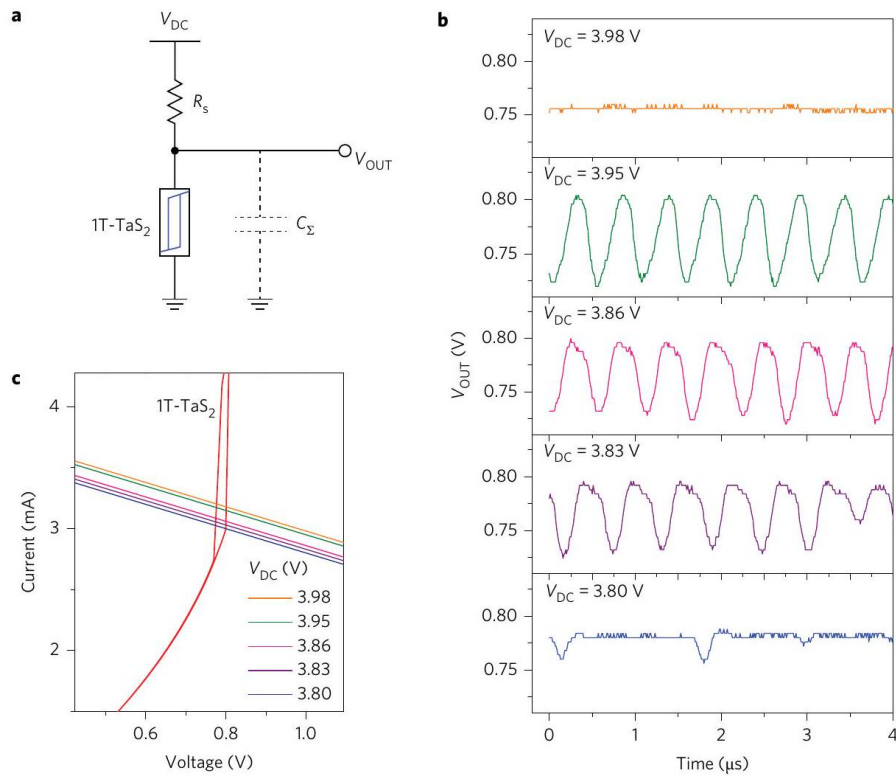


Figure 2 | Oscillator circuit of a **1T** – TaS₂ film with an off-chip load resistor.

(oscillator circuit) a, The circuit diagram of the oscillator consists of the 1 T – TaS₂ film, a seriesconnected load resistor and a lumped capacitance C_{Σ} from the output node V_{OUT} to ground.

(load resistance) The load resistance is $1k\Omega$.

(oscilloscope) The output terminal is monitored by an oscilloscope.

b, Voltage oscillations under different V_{DC} values.

The circuit oscillates when V_{DC} is within the range of 3.83 V to 3.95 V.

The oscillation frequencies are approximately 1.77, 1.85 and 2 MHz when V_{DC} is 3.83, 3.86 and 3.95 V, respectively.

c, Load lines of the resistor at different V_{DC} values.

The blue line, which represents $V_{DC} = 3.8$ V, intersects with V_H of 1 T – TaS₂.

This is the condition at which the circuit is about to oscillate.

(the main schematic and oscillations of V) By connecting this 1T-TaS₂ device with an off-chip $R_L = 1k\Omega$ (it is that R_s on the plot) load resistor (see the schematic in Fig. 2a), we observe stable voltage oscillation at the node between these two components when applying a d.c. bias V_{DC} .

These voltage oscillations, monitored by an oscilloscope, are shown in Fig. 2b. The initiation of oscillations requires V_{DC} values within a certain range.

(very small V -> no oscillations) When V_{DC} is below 3.8 V no oscillations occur.

(small V -> sine oscillations) As V_{DC} increases, the oscillations become sinusoidal.

(why f is dependent on VDC??? see formulas later) The oscillation frequency, f , is dependent on V_{DC} .

In this specific device f was tuned from 1.77 to 2 MHz as V_{DC} changed from 3.83 to 3.95 V.

When V_{DC} becomes greater than 3.98 V, the oscillation stops.

The oscillation mechanism can be understood as the switching of the 1T- TaS₂ device between the IMT and MIT states with the negative feedback from the load resistor R_L .

When V_{DC} is large enough, the d.c. voltage across the 1T- TaS_2 channel reaches V_H and triggers the IMT.

The sudden increment in current results in a large voltage increase across the load resistor.

As V_{DC} is constant, the instantaneous voltage across the 1T- TaS_2 decreases, driving 1T- TaS_2 back into the insulating state.

The current then decreases, reducing the voltage across the resistor and increasing the voltage across 1T- TaS_2 , driving it back into its metallic state.

As long as this voltage can increase to a level higher than V_H the cycle keeps repeating.

Figure 2c provides further explanation.

The intersection of the 1T- TaS_2 curve with the load line is the operation d.c. voltage at the output.

The line representing $V_{DC} = 3.8$ V is on the edge of V_H , where the oscillations just start.

As the oscillation is triggered by IMT-MIT processes, it also can be observed at lower temperature (Supplementary Fig. 6).

(maybe it is possible to do something useful with this theory) Voltage control of an oscillator(VCO) frequency using simple circuitry is highly desirable for numerous miniaturized electronic systems.

(typically a lot of transistors needed) Conventional VCOs usually require multiple transistors and resistors for biasing^{21,22}.

(add G-FET and h-BN -> get a VCO at room T) By monolithically integrating a top-gate graphene field-effect transistor (G-FET)(used to do somehow the controll with voltage (because of somehow change in carrier density in graphene)) (how does it work?) with an h-BN capped 1T- TaS_2 device(just for protection) , we demonstrate a VCO operating at room temperature. (so, it will it work without them, but will be not stable and not be able to control such efficient)

(why exactly G-FET? think more, there is already info in my discussion)

(lithography + etching + evaporation) The gate and contact electrodes for this 2D integrated TaS_2 – h – BN – graphene oscillator were fabricated with electron beam lithography, dry etching(=acid or other chemicals to cut into unprotected parts of a metal surface) and metal evaporation (Supplementary Fig. 3). (I'll be thinking about it only if needed, now it is not a priority)

The device structure and SEM image are presented in Fig. 3a (bottom), b, respectively. The equivalent circuit and the biasing scheme are shown in Fig. 3a (top).

The d.c. bias is applied across the integrated structure whereas the gate voltage of the G-FET is used to change R_L and hence tune the oscillation frequency.

Note that both the 1 T – TaS_2 and graphene sides of the channel are contacted from the edge, forming quasi-1D contacts^{18,23}.

The h-BN entirely covers the 1T- TaS_2 and graphene sides of the channel to protect against environmental exposure.

(it works good) The resulting device demonstrates excellent control of the oscillations using the gate voltage, V_G , of the G-FET.

(V_G turns oscillations) The gate voltage can turn oscillations on and off and tune f monotonically.

(3c -> oscillations for different V_G) As shown in Fig. 3c, no oscillations occur at the output when V_G is set at zero.

(minimal V_G for oscillations) As V_G increases to 0.68 V, the device starts to produce stable oscillations.

For V_G values varying from 0.68 to 1.80 V the frequency can be tuned monotonically from 1.42 to 1.04 MHz.

As V_G increases above 1.80 V the oscillations begin to show missing cycles, indicating that the bias setting exceeds the oscillation requirement. V_{DC} is set at 3.65 V for these measurements.

The tuning mechanism can be understood by examining the load line.

As the slope of the load line changes with V_G and falls within the red hatched region in Fig. 3d, oscillations appear at the output.

The transfer characteristic of the G-FET is shown in the inset to Fig. 3d.

Note that V_{DS} is biased at 2.4 V, close to the value of the voltage drop across the G-FET when the circuit operates at $V_{DC} = 3.65$ V.

The charge neutrality point in this case is at 2.4 V, shifted by the large source-drain voltage of G-FET (V_{DS}).

As V_G increases from zero to 2.1 V, the resistance of the graphene channel monotonically increases, resulting in the oscillation frequency decreasing due to the increased RC time constant, where R and C are the effective resistance and capacitance, respectively. Figure 3e shows the gate voltage tunability of the oscillator frequency. The tuning sensitivity is 0.3MHzV^{-1} , and the oscillation amplitude V_{PP} is ~ 0.2 V. Control of both characteristics will improve dramatically as the technology for handling 2D materials advances.

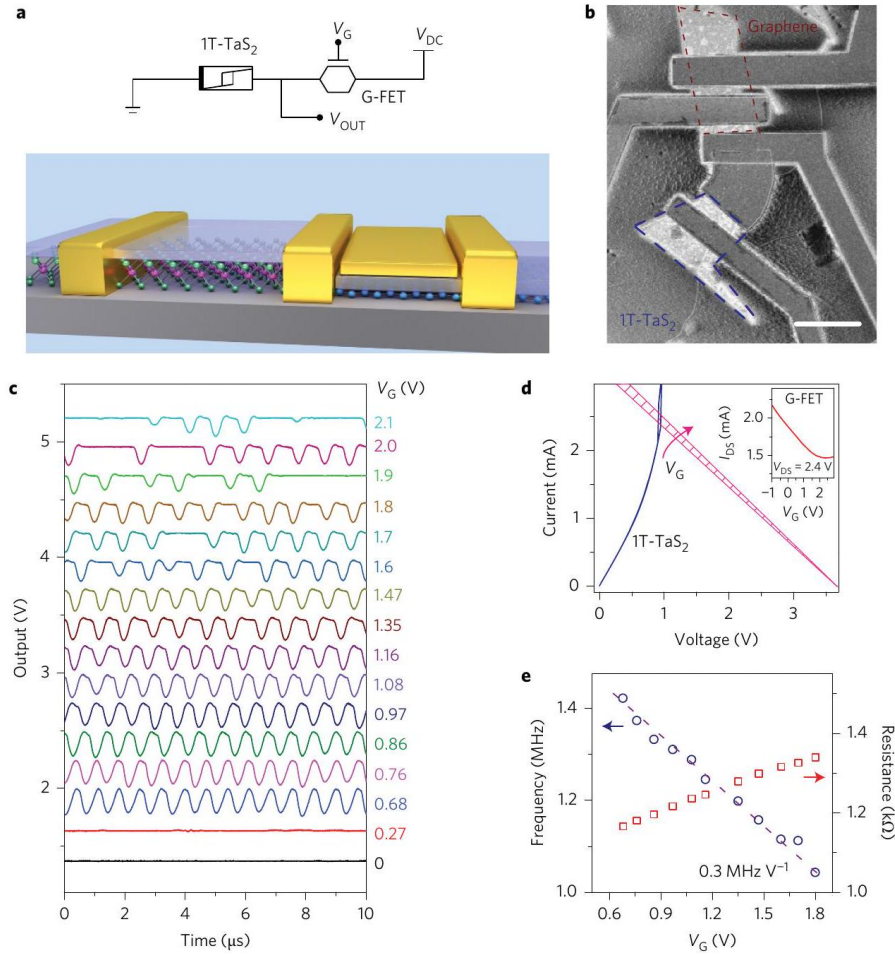


Figure 3 | The integrated 1T- TaS₂ – B N– graphene VCO.

a, Bottom: The device structure of the integrated oscillator consists of a G-FET series connected to 1 T – TaS₂.

Both the graphene and TaS₂ are fully covered with h-BN, which acts as a protective layer against oxidation for the 1T- TaS₂ and as a gate dielectric for the G-FET.

The equivalent circuit and biasing set-up is shown in the top panel.

The V_{DC} bias is applied at the drain terminal of the G-FET and the V_G bias is connected to the gate terminal of G-FET.

The ground is connected to one terminal of 1 T – TaS₂ device and the output port is common to both devices.

b, The SEM image of the integrated 1 T – TaS₂ – BN– graphene VCO. The graphene and the TaS₂ are highlighted by dashed lines. Scale bar, 4 μ m.

c, Output waveforms at different gate biases when V_{DC} is fixed at 3.65V. The oscillation frequency is tunable with gate biases in the range of 0.68 V to 1.8 V. The different waveforms are vertically offset by 0.25 V for clarity.

d, The load line representing the resistance range of the G-FET intersects with the $I-V$ curve of the 1 T – TaS₂ device.

The arrow indicates the slope change of the load line with V_G .

The inset shows the transfer characteristics (source-drain current, I_{DS} , as function of V_G) of the G-FET under a source-drain bias at 2.4 V.

e, The dependence of the oscillation frequency on the gate bias.

Blue circles show the frequency of the oscillation under an increased gate bias.

The frequency can be adjusted monotonically with a tuning sensitivity of 0.3MHzV⁻¹.

The red squares are the resistance values of the G-FET under different gate biases with $V_{DC} = 2.4$ V.

The monolithic integration of a quasi-2D CDW channel with graphene has several advantages. The current carrying capacity of G-FETs²⁴ makes graphene a well-matched load to the low-resistance TaS₂. The oscillations occur when the IMT is triggered in 1T- TaS₂ in the mA range (for the 1–2 μ m wide samples). With similar dimensions to 1T- TaS₂, graphene provides a well-matched current density and resistance. Owing to the linear resistance tunability with the gate voltage of the G-FET at high V_{DS} and high carrier concentrations, the frequency of the oscillator can be tuned linearly by V_G over a wide range. The tuning linearity of VCOs is required for many practical applications²¹. An extra advantage of the CDW-G-FET integrated device is that G-FETs have been demonstrated to operate at very high frequencies of hundreds of GHz^{25,26}, which allows for increased oscillation frequencies. In our proof-of-concept measurements, the frequency is limited by the extrinsic RC time constants of the probe station. The intrinsic resistances and capacitances can be reduced by scaling. The graphene and h-BN layers in the device structure also act as heat spreaders owing to their high thermal conductivity^{27,28}.

From the circuit models in Figs 2a or 3a, the frequency is determined by the charging and discharging time of the capacitance, which is given by

$$1/f = T = C [(R_s//R_{di}) \ln(\alpha_i) - (R_s//R_{dm}) \ln(\alpha_m)] \quad (1)$$

where $\alpha_{m,i} = [V_{DC} - (1 + R_s/R_{dm,di}) V_L] / [V_{DC} - (1 + R_s/R_{dm,di}) V_H]$, m and i represent metallic and insulating states, respectively, R_{di} is the resistance of TaS₂ in the insulating state, R_{dm} is the resistance of TaS₂ in the metallic state, R_s is the load resistance of either the resistor or the G-FET and C is the lumped capacitance between the output node and the ground (Supplementary Fig. 7).

(the notation of two slashes $R_s//R_{di} = \frac{R_1 R_2}{R_1 + R_2}$) $R_s//R_{di}$ is the parallel resistance of the R_s and R_{di} .

The intrinsic geometric capacitances and the resistivities of the 1T- TaS₂ film and the load resistor or transistor set the upper frequency limit of oscillation.

The sheet resistivities of the 1T- TaS₂ in the high and low resistance states are $3\text{k}\Omega\Box^{-1}$ and $740\Omega\Box^{-1}$, respectively.

These values are relatively low, allowing for extremely small RC time constants.

Considering only the parallel plate capacitance to ground of the TaS₂ and graphene, the intrinsic RC-limited frequency given by equation (1) for the $\sim 1\mu$ m scale device shown in Fig. 3b is in the THz regime.

As the RC-limited frequency is so high, the intrinsic fundamental limit on the maximum frequency may be set by the time constants determined by the microscopic switching mechanism between the low- and high-resistance states. The voltage or current driven switching could result from the destruction of the Mott insulating state in the individual NC-CDW domains while leaving the lattice in the NC-CDW state (process a), or it could be accompanied by a reconstruction of the lattice from the NC-CDW state to the I-CDW state (process b). Process a is a purely electronic process and is therefore extremely fast.

The speed of process b is governed by the time constant associated with the relaxation of the lattice. Available femtosecond ARPES data at room temperature suggest a time constant of 700 fs, which provides an upper frequency limit on the order of 1 THz (ref. 29). A lower frequency limit would result from a thermally induced switching mechanism whereby the current heats up the device sufficiently to induce the NC-CDW to IC-CDW transition. Such a mechanism is considered to be the most likely scenario in VO₂ devices^{30,31}. At a fixed temperature, the NC-CDW to IC-CDW transition in samples of different lengths occurs at approximately constant electric fields and constant current densities (and therefore constant power densities). This indicates that thermal effects also play a role in the switching in our device. A study of

V_2O_3 devices found that thermally induced switching could occur at subnanosecond timescales, resulting in GHz frequencies³². In either case, VCOs operating even at lower frequencies (for example, MHz in radio) are important devices with various applications³³. Compact VCOs can also be used as elements in oscillator-based pattern-recognition neural networks^{34,35}.

The physical principles behind the operation of 1T-TaS₂ VCOs are different from those in the MITs used in VO₂ devices^{36–42}. The transition in VO₂ is from the low-temperature monoclinic structure to the rutile structure^{43–45}. The origin of the transition (Peierls versus Mott-Hubbard types) is under debate^{43–45}. The transition in our 1T-TaS₂ devices is from NC-CDW to IC-CDW⁴⁶. As VO₂ is a 3D material, the attempts to deposit it as thin films with small thicknesses ($H < 10$ nm) resulted in excessive strain and correspondingly reduced the phase transition temperature^{47,48}. The phase transition from NC-CDW to IC-CDW in 6-9-nm-thin films of 1T-TaS₂ is almost the same as it is in the bulk (~ 350 K), well above room temperature¹⁰.

Methods

1T-TaS₂ crystal growth.

TaS₂ crystals were grown by an adapted chemical vapour transport method, where the 1T polytype can be isolated by fast quenching from the crystal growth temperature (875–975 °C; ref. 49). Elemental tantalum (20.4 mmol, Sigma-Aldrich 99.99% purity) and sulfur (41.1 mmol, J.T. Baker >99.9% purity) were ground with mortar and pestle and placed in a 17.8×1.0 cm fused quartz ampoule (cleaned by soaking overnight in nitric acid followed by annealing at 900 °C for 24 h). Elemental iodine (J.T. Baker 99.9% purity) was added (~ 88 mg for an ampoule with a volume of ~ 14.0 cm³). The ampoule was evacuated and backfilled three times with argon, with cooling to mitigate I₂ sublimation. Next the ampoule was flame-sealed and heated in a two-zone tube furnace at 10 °C min^{−1} to 975 °C (the hot zone) and 875 °C (the cool zone). These temperatures were held for one week. Then the ampoule was removed from the hot furnace and immediately quenched in a water-ice- NaCl bath. The resulting golden crystals, shown in Supplementary Fig. 1, were characterized as detailed below. The as-grown crystals and their atomic structure are shown in Supplementary Fig. 1. The structure and phase purity were verified by powder X-ray diffraction (shown in Supplementary Fig. 2) and the stoichiometry was confirmed with energy dispersive spectroscopy and electron probe microanalysis (shown in Supplementary Fig. 3 and Supplementary Table 1).

Electrical characteristics of the 1T – TaS₂ devices.

All $I - V$ characteristics were measured in the Lakeshore cryogenic probe station TTPX with a semiconductor analyser (Agilent B1500). The oscillator of the waveform is collected by an oscilloscope (LeCroy WaveAce1012) whereas the d.c. voltage supply of the circuit is biased with a BK Precision 1787B.

31.2 My Discussion

31.2.1 My Conclusion

31.2.2 Most Important General Questions

How does this oscillator circuit work?

The oscillator circuit in Fig. 2a consists of a DC voltage source V_{DC} , a series load resistor R_s , and the 1T-TaS₂ device connected to ground. The output voltage V_{OUT} is measured at the node between R_s and the 1T-TaS₂ device. Since the other terminal of the device is grounded, V_{OUT} is also the voltage applied across 1T-TaS₂. The current through the series resistor is therefore

$$I = \frac{V_{\text{DC}} - V_{\text{OUT}}}{R_s}.$$

For a fixed V_{DC} , this relation gives the straight load lines shown in Fig. 2c, with a slope $-1/R_s$.

The dashed capacitor C_Σ in Fig. 2a represents the total effective capacitance of the output node to ground. It is not necessarily a deliberately added physical capacitor; rather, it includes parasitic contributions from the device, contacts, wiring, probes, and measurement setup. Thus, electrically, C_Σ and the 1T-TaS₂ device are connected in parallel between V_{OUT} and ground.

The capacitance provides the time dependence necessary for the oscillations. When C_Σ charges through R_s , V_{OUT} increases. Once the voltage across 1T-TaS₂ reaches the upper switching threshold, the device switches to its lower-resistance state. The capacitor can then discharge more rapidly through the conducting 1T-TaS₂, causing V_{OUT} to decrease. When the lower switching threshold is reached, the device switches back to its higher-resistance state, allowing the capacitor to charge again. The cycle can therefore be summarized as

C_Σ charges $\rightarrow V_{\text{OUT}} \uparrow \rightarrow$ switch to low resistance $\rightarrow C_\Sigma$ discharges $\rightarrow V_{\text{OUT}} \downarrow \rightarrow$ switch back to high

Repeated switching together with the charging and discharging of C_Σ produces the voltage oscillations observed in Fig. 2b.

Why the G-FET is controlled through the gate?

The graphene field-effect transistor (G-FET) is not required for the basic CDW oscillation itself. A 1T-TaS₂ device connected to a fixed load resistor R_s can already exhibit relaxation oscillations. The purpose of the G-FET is to replace the fixed load with an electrically tunable element, allowing the oscillation frequency to be controlled by an additional voltage.

The main current of the oscillator flows through the graphene channel from source to drain. The top gate provides a separate control terminal. A gate voltage V_G produces an electric field across the gate dielectric and changes the carrier density in graphene. Consequently,

$$V_G \rightarrow n_{\text{graphene}} \rightarrow \sigma_{\text{graphene}} \rightarrow R_{\text{G-FET}}.$$

Changing $R_{\text{G-FET}}$ changes the load line of the 1T-TaS₂ device and therefore changes its charging and discharging dynamics and the resulting oscillation frequency.

The important advantage of applying the control voltage to the gate is that the gate is electrically isolated from the graphene channel by a dielectric. Thus, the gate voltage can control the graphene resistance while drawing very little gate current. The control signal is therefore largely separated from the main current path of the oscillator.

One could instead control the oscillator by changing V_{DC} , as in the simpler circuit containing a fixed R_s . One could also change the voltage applied directly along the graphene channel. However, in the latter case the control voltage would directly modify the current in the main

circuit and the voltage distribution between the graphene and 1T-TaS₂. It would therefore not provide the same independent control parameter. The gate geometry is useful because it provides

an independent voltage control $\rightarrow R_{\text{G-FET}} \rightarrow$ oscillation frequency

without requiring a substantial control current through the gate.

Why does someone need at all this switcher?

(????)

Advantages of charge-density-wave oscillator based on an integrated tantalum disulfide-boron nitride- graphene device

The principal advantage of the 1T-TaS₂ oscillator is that the atomically thin phase-transition material itself provides the abrupt resistance change and hysteresis required for relaxation oscillations. A circuit containing the 1T-TaS₂ device, a load resistance, and a capacitance can therefore convert a constant d.c. voltage into a periodic output without an inductor or a large number of conventional transistors.

Its main potential advantages are the following:

- **Room-temperature use.** The electrically driven resistance switching and the resulting oscillations are observed at room temperature.
- **Compact two-dimensional structure.** The active 1T-TaS₂ layer is only a few nanometres thick, while h-BN protects it from oxidation and serves as the gate dielectric for the graphene transistor.
- **Electrical tunability.** The integrated graphene field-effect transistor acts as a gate-controlled load, allowing the oscillations to be turned on or off and their frequency to be adjusted electrically.
- **Potential frequency scaling.** The relatively low resistance and potentially small geometric capacitance of the two-dimensional components may allow substantially higher frequencies after device scaling.
- **Specialized applications.** Compact mutually coupled oscillators may be useful in neuromorphic circuits, where synchronization and nonlinear dynamics are more important than extremely accurate frequency stability.
- **Radiation tolerance.** Irradiation experiments suggest that 1T-TaS₂ threshold-switching devices may remain operational in high-radiation environments.

These properties make the device particularly interesting as a nonlinear oscillator element for specialized circuits rather than simply as another conventional frequency source.

Disadvantages.

The demonstrated 1T-TaS₂ oscillator does not yet outperform established CMOS oscillators in the characteristics required for ordinary clock or radio-frequency generation. It remains a laboratory prototype with several substantial limitations:

- **Measured frequency.** The experimentally measured frequency is only approximately 1–2 MHz. The terahertz frequency discussed in the original work is an estimate of the intrinsic RC limit and has not been demonstrated experimentally.

- **Small output amplitude.** The output amplitude is approximately 0.2 V, so an additional buffer or amplifier may be required to drive conventional electronic circuits.
- **Restricted operating range.** Oscillations occur only within a limited bias interval. Outside this interval, the device remains permanently in either its high- or low-resistance state.
- **Temperature and device sensitivity.** The threshold voltages depend on temperature, channel dimensions, electrical contacts, oxidation, and local heat dissipation, which may produce substantial device-to-device variability.
- **Joule heating.** Time-resolved measurements indicate that the room-temperature hysteresis has a substantial thermal origin. Heating may therefore limit both the switching speed and the energy efficiency.
- **Incomplete oscillator characterization.** Phase noise, timing jitter, long-term frequency stability, endurance, and reproducibility have not been characterized sufficiently for practical voltage-controlled oscillator applications.
- **Immature fabrication technology.** The reported devices were produced using exfoliated flakes, electron-beam lithography, and transferred h-BN, which are much less scalable than standard CMOS fabrication methods.

Consequently, 1T-TaS₂ oscillators are presently more convincing as research prototypes for specialized coupled-oscillator or radiation-tolerant systems than as replacements for conventional electronic oscillators.

Meaning of the oscillator.

An electronic oscillator converts a constant d.c. supply voltage into a periodically varying output voltage without requiring an external periodic drive. In this work, the term “CDW oscillator” does not mean that the spatial charge-density modulation itself simply moves back and forth. Instead, the oscillation results from repeated switching of the 1T-TaS₂ channel between high- and low-resistance states associated with the NC-CDW and IC-CDW phases. This repeated switching produces a periodic variation of the voltage measured at the output node.

Oscillation mechanism.

The circuit contains the 1T-TaS₂ channel, a series load resistance R_L , and a lumped capacitance C_Σ connected between the output node and ground. The applied d.c. voltage satisfies

$$V_{\text{DC}} = IR_L + V_{\text{TaS}_2}, \quad (31.1)$$

where $V_{\text{OUT}} = V_{\text{TaS}_2}$. Initially, 1T-TaS₂ is in its high-resistance state, so the current and the voltage drop IR_L across the load resistor are small. The capacitance then charges, causing V_{OUT} to increase. When V_{OUT} reaches the upper threshold V_H , an insulator-to-metal transition occurs: the resistance of 1T-TaS₂ decreases abruptly and the current increases. Consequently, the voltage drop IR_L across the load resistor increases. Because V_{DC} is fixed, the voltage across 1T-TaS₂ decreases according to

$$V_{\text{TaS}_2} = V_{\text{DC}} - IR_L. \quad (31.2)$$

When V_{OUT} falls to the lower threshold V_L , the reverse metal-to-insulator transition occurs. The resistance of $1T\text{-TaS}_2$ increases, the current and the voltage drop across R_L decrease, and V_{OUT} begins to increase again. The system therefore repeatedly follows the cycle

$$R_{\text{high}} \longrightarrow R_{\text{low}} \longrightarrow R_{\text{high}} \longrightarrow \cdots . \quad (31.3)$$

The load resistor provides the negative feedback that drives the material back to its initial state, whereas C_Σ introduces a finite charging and discharging time and therefore determines the oscillation period. Without the load resistance, the material would switch once and remain in the conductive state rather than producing continuous oscillations.

Operating range and voltage control.

Oscillations occur only within a limited range of V_{DC} . If the applied voltage is too small, V_{OUT} never reaches V_H , and the device remains in the high-resistance state. If V_{DC} is too large, the device remains in the low-resistance state. With an external $1\text{ k}\Omega$ load resistor, the authors observe oscillations for $V_{\text{DC}} \approx 3.83\text{--}3.95\text{ V}$, with frequencies of approximately $1.77\text{--}2\text{ MHz}$. In the integrated device, the fixed load resistor is replaced by a graphene field-effect transistor. Its gate voltage V_G changes the graphene-channel resistance and hence the effective RC charging time. The gate voltage can therefore turn the oscillations on or off and tune their frequency, making the device a voltage-controlled oscillator.

Purpose and significance.

Electronic oscillators are required for clock generation, radio-frequency signals, phase-locked loops, synchronization, sensing, and networks of coupled oscillators used in neuromorphic computing. The main result of this work is not the invention of a new general function for oscillators, but the demonstration that electrically driven CDW resistance switching can serve as the non-linear element of a compact oscillator operating at room temperature. The integrated graphene transistor additionally provides electrical control of the frequency. Thus, the device is primarily a proof of concept showing how a CDW transition can be converted into a useful periodic electrical signal.

31.2.3 My Questions about Their Methods, Statements and Results

Derivation of $1/f = T = C [(R_s/R_{\text{di}}) \ln(\alpha_i) - (R_s/R_{\text{dm}}) \ln(\alpha_m)]$

(write from GPT later)

31.2.4 Questions about Assumed Knowledge

31.2.5 Things That I Maybe Understood Wrongly

31.2.6 Potential Future Research Directions

How to predict these properties from microscopic theory?

(????????????????)

32 Ultrafast switching to a stable hidden topologically protected quantum state in an electronic crystal by Stojchevska, Vaskivskyi, Mertelj, Kusar, Svetin, Brazovskii, Mihailovic (2014)

Abstract

Hidden states of matter with novel and unusual properties may be created if a system out of equilibrium can be induced to follow a trajectory to a state which is inaccessible or does not even exist under normal equilibrium conditions (bad sentence, but idea is clear: is system is change in a special way) .

Here we report on the discovery of a hidden (H) topologically protected electronic state in a layered dichalcogenide $1T$ -TaS₂ crystal reached as a result of a quench caused by a single 35 fs laser pulse.

The properties of the H state are markedly different from any other state of the system: it exhibits a large drop of electrical resistance, strongly modified single particle and collective mode spectra (plot?) and a marked change of optical reflectivity (plot?) .

Particularly important and unusual, the H state is stable for an arbitrarily long time until a laser pulse, electrical current or thermal erase procedure is applied, causing it to revert to the thermodynamic ground state. (how to prove it?)

Major observed events can be reproduced by a kinetic model describing the conversion of photo excited electrons and holes into an electronically ordered crystal, thus taking into account a dynamic conversion of particles among reservoirs of liquids of electrons and holes, and of an electronically ordered crystal, converting a Mott insulator to a conducting H state. (how to model it???)

Its long-time stability follows from the topological protection of the number of periods in the electronic crystal.

32.1 Article

32.1.1 Theory

Extreme conditions necessary for reaching hidden many body states can be created in the laboratory using laser photoexcitation in condensed matter systems. Typically, the ground state ordering can be temporarily destroyed, but on cooling the system reverts back in a few picoseconds, exceptionally passing through a transient metastable state. So far, a few such metastable states have been shown to persist on timescales between 10^{-9} - 10^{-3} s (1,2,3,4,5,6,7) before recovering to the ground state by a combination of thermal, electronic and lattice relaxation processes (2). Stability of photoinduced states has been demonstrated in a manganite (6) and in chalcogenide glasses (8), where switching occurs between neighbouring thermodynamic states, but no hidden states are involved in these cases.

In this paper, we report for the first time on bistable switching to a hidden (H), spontaneously ordered macroscopic quantum state whose properties are distinct from any other state in the equilibrium phase diagram. The hidden state transition (HST) occurs in a layered quasi-2D chalcogenide $1T$ -TaS₂ crystal, a system which exhibits multiple competing ground states already under equilibrium conditions. Some of the states are shown schematically in Fig. 1A. Near $T_{c0} = 550$ K $1T$ -TaS₂ forms an incommensurate charge-density-wave (IC) with an associated lattice distortion. On cooling these modulations sharpen to form star-shaped polaron clusters (Fig.1 A). Their ordering is thought to be responsible for a variety of phases, causing a transition to a nearly commensurate (NC) state for $T < T_{c1} = 350$ K, and a hysteretic first-order transition to a gapped commensurate (C) phase at $T_{c2} \simeq 183$ K. On heating,

the system develops a triclinic stripe-like ordered state around 223 K which reverts to the NC state at $T_{c2} \simeq 283$ K (9). Further nearby equilibrium states are revealed upon the application of external pressure (10) or doping (11), both of which make $1T$ -TaS₂ superconducting.

To induce the HST, we use a single sub-35 fs Write (W) pulse from an amplified Ti-Sapphire laser at 800 nm with energy $U_W \simeq 1$ mJ/cm². After inducing a HST at 1.5 K, the 4-probe resistance $r(T)$ drops approximately 3 orders of magnitude and *remains in this state indefinitely* at this temperature (Fig. 1B). Upon heating, $r(T)$ is approximately constant up to 60 K, whereupon it increases and merges to the virgin $r(T)$ curve corresponding to the C state above $T_H \sim 100$ K. The I - V characteristic remains linear throughout. Empirically we found that the H state can be *completely* erased (E) by a pulse train of 10^4 50 ps pulses, each with $U_E \simeq 1$ mJ/cm². Alternatively, Joule heating can be used for erasure by passing a ~ 0.1 mA current through the device. In all three cases the system reverts to the C state. Stable switching can be achieved also at intermediate temperatures up to $T \sim 70$ K. The effect is entirely reversible from cycle to cycle, sample to sample, irrespective of the sample growth batch, and there appears to be no limit on the number of W/E cycles that can be performed. (Experimental details on thermal protocols, including ageing effects (12), and a description of the laser lithography used to manufacture the contacts are given in the supplementary material (SM)).

To gain insight into the microscopic nature of the hidden state, we investigate the single-particle and collective excitations, using Pump-probe (P - p) spectroscopy with the P and p pulse energies kept low ($< 10 \mu\text{J}/\text{cm}^2$ and $< 1 \mu\text{J}/\text{cm}^2$ respectively) to ensure minimal disturbance of either state. The sample reflectivity $R(t)$ is simultaneously recorded by the probe (p) beam. In Fig. 2 A to D we first present the transient reflectivity $\Delta R/R$ of $1T$ -TaS₂. In the virgin C state we observe oscillations due to the coherent excitation of the amplitude mode (AM) and phonons which are superimposed on a background from exponentially decaying single particle (SP) excitations across the gap (13). The spectrum $S(\omega)$ obtained by Fourier transformation shows a strong amplitude mode at 2.46 THz, and weaker phonon modes at 2.1, 2.18, 3.2 and 3.85 THz (see Fig.2B). The HST modifies the $\Delta R/R$ (Fig. 2B) and the SP signal is reduced significantly. In the spectrum after the HST shown in Fig.2B the AM peak at 2.46 THz *disappears*, in favour of a new mode at 2.39 THz; intensities of modes at 3.10 THz and 3.85 THz are reduced, and some additional spectral intensity appears between 2 and 2.5 THz. On heating, the spectrum of the H state remains unchanged until ~ 70 K. Above 70 K it gradually reverts back to the C state. Concurrent with the switching of the AM and phonons, we observe a switching of reflectivity R at 800 nm, as shown in Fig. 2 D. All the observations display typical threshold behaviour as a function of U_W : below threshold fluence the resistivity, AM frequency and reflectivity revert to the C state values after the W pulse. Close to threshold fluence, the AM shows bimodal behaviour, which we interpret as incomplete switching. Importantly, no intermediate shift of the AM is observed, indicating distinct two-phase behaviour. The H state spectrum is quite different from the NC state spectrum (Fig. 2 A and B) or the T state spectrum (see SB), indicating that it is not related to the equilibrium states.

We emphasize some remarkable features of the HST: **1.** After photo-excitation the H state spontaneously orders below T_H , as indicated by the narrowness of the AM peak and the fact that *no partial frequency shift* is ever observed even when incomplete switching is caused by near-threshold excitation (see SM). **2.** The switching occurs *only with short pulses*, and the threshold increases with increasing τ_W as shown in Fig. 2 C and - remarkably - can no longer be achieved with $\tau > 4$ ps at any U_W . **3.** The H state is completely stable until erased, or heated above ~ 70 K. Note that T_H has no special significance under equilibrium conditions and is relevant only for describing the transition from the H state to the C state.

To understand these unusual phenomena, we first introduce a scenario for switching based on the current understanding of the electronic ordering in $1T$ -TaS₂ (9,14,15,16), and then describe the results of a minimal phenomenological model which offers insight into how transient

photodoping can lead to a stable ordered state.

The relevant electronic states of $1T$ -TaS₂ in the C state which are within reach of our 1.5 eV laser photons are shown in Fig. 3 C. They are formed predominantly from a single Ta d band which is split into subbands by the formation of a CDW depicted in Fig 1 A. Six of these subbands are filled with 12 electrons per new large unit cell forming a manifold of occupied states up to 0.4 eV below E_F (shown in blue in Fig. 3 C). The 13th left-over electron is localised on the central Ta causing inward radial displacements of 12 neighbours in the shape of a star of David (14,15), thus forming a self-localized polaron. The 13th electron gives rise to a half-filled narrow metallic band straddling the Fermi level; but this band is further split by the Coulomb interaction into two Hubbard bands (plotted green in Fig. 3 C) (15), whereby the upper one merges with the manifold of unoccupied subbands above E_F , while the lower one is ~ 0.2 eV below E_F - still well above the top of the valence band at -0.4 eV, which makes the C state a Mott insulator in the form of a polaronic crystal (10,14,15). In the photoexcited case however, a charge imbalance can cause voids in the polaron lattice which - upon relaxation - leads to the formation of a spontaneously ordered H state. The possibility of both positive and negative discommensurations has been indicated by STM experiments (9), indicating that the system can accommodate both extra holes or extra electrons.

Recent experiments show that the Mott gap rapidly melts within ~ 50 fs after photo-excitation (17), but after $0.5 \sim 1$ ps, the AM oscillations are visible again, indicating the recovery of the C state within a few AM cycles. Since the e - h energy relaxation occurs on a similar timescale ($\tau_E \sim 1$ ps) (13,17), the condensation into the crystalline state competes with $e - h$ recombination.

Photoexcitation initially creates equal numbers of electrons (e) and holes (h) by an inter-band transition, followed by rapid intraband thermalisation via scattering amongst themselves and with the lattice, as well as transitions between different bands, reaching states near the Fermi level and melting the C order on a timescale on the order of 50 fs (17,18,19,20). The maximum effective electronic temperature reached in the process is $T_e \sim 1000$ K, while the lattice reaches ~ 150 K within 3 – 5 ps, whereupon the two are in quasi-equilibrium. (See SM for temperature measurements and model estimates). However, the large asymmetry of the band structure in this compound (14), can also lead to a photodoping effect: the e and h scatter and lose energy at different rates, leading, on the sub-5-picosecond timescale, to a transient imbalance of their respective populations n_e and n_h .

Let's now examine the photodoping effect in more detail. Doping away from half-filling of a conventional Mott-Hubbard state on a rigid lattice leads to a conducting state. But here photo-doping disturbs the polaronic deformations. Let's consider the effect of a photo-doped hole, which annihilates with the localised 13th electron. The annihilation removes the charge at the centre of the polaron, rapidly dissolving the polaronic distortion and leaving a void in its place. In the standard polaron picture (21), its dissolution releases a band state from which the polaron was originally formed, which makes the system conducting. Since some of the 13th electrons have been annihilated by holes, not all ions in these regions are charge compensated, and they have an excess charge. Yet these regions cannot conduct because the remaining 12 electrons are in filled states within the gap formed by the long-range CDW (see Fig. 3 C). The excess charge within these regions will be screened by the electrons which are now transferred to the delocalised bands. At a sufficiently low T and high concentration n_v , these voids are expected to aggregate by diffusion into domain walls. The overall state becomes conducting via the band states released by the annihilated polarons which, if ordered, would form a new incommensurate structure. We can also imagine that photo-excited electrons could squeeze into the structure in between the polarons creating interstitials with a concentration n_i (9). Together with voids with a concentration n_v the total "intrinsic defect" concentration $n_d = n_v - n_i$ may have either sign. Overall charge conservation $n_h + n_v = n_e + n_i$ gives the

imbalance of the current carriers $n_d = n_e - n_h$. Conventionally, photodoping is a transient effect, so once $e - h$ symmetry is recovered, the voids and domain walls disappear and the C state is restored. However, if the voids can be stabilised by collectively ordering into a long-range ordered state, the final state is different than the original one.

Overall charge conservation requires that the concentration n_v of the voids or their walls compensates for the imbalance $n_e \neq n_h$ of electron and hole concentrations in delocalized bands, arresting their mutual recombination and maintaining a metallic state. In either case, local strain causes subsequent self-reorganisation of these voids (or extra electrons), giving rise to a long-range ordered structure with an excess of charge carriers with respect to the C state.

Now we outline a plausible minimal model for the metastable state, which may have phenomenological implications beyond our detailed speculations on the nature of microscopic processes in this particular material. The model details, the calculation and more results are presented in the Appendix.

The free energy $F_d(n_d)$ appropriate for the formation of the charge-ordered state outlined above (16) needs to include the effect of repulsion between the domain walls, their crossings (16,22,23), and should reproduce the first order nature of the transition (16,23). The $F_d(n_d)$ based on these considerations and existing models (16,23) is plotted in Fig. 3 B.

To obtain the time dependencies of concentrations $n_e(t)$, $n_h(t)$ and of the electronic temperature $T(t)$ we consider the recombination rates of e and h across the spectral gap and into the new ordered state. Apart from the densities, the rates depend on the separate chemical potentials $\mu_i(t) = \partial F_i / \partial n_i$ for the electrons, holes and defects (we assume that the sub-systems are more or less equilibrated internally (19)). The difference in chemical potentials gives the energy released when particles are exchanged among the reservoirs which determines the temperature evolution. In equilibrium, the μ_i for all the three reservoirs must be equal, so the intersection of the three surfaces μ_e , μ_h and μ_d , as functions of n_e and n_h and subject to the constraint $n_d = n_h - n_e$ gives the thermodynamically stable end points of the system. These are shown in Fig. 3 D, plotted for an arbitrary intermediate temperature $0 < T < T_H$. The condition $\mu_h = \mu_d = -\mu_e$ gives two stable points, which correspond to the free energy minima shown in Fig. 3 B: point C where $n_e = n_h$, and point H , where $n_e - n_h = n_d \neq 0$. The third intersection U is unstable since it corresponds to a maximum of the free energy.

The relaxation processes between the charge reservoirs considered by the model are shown schematically in Fig. 3 C (See the Appendix for more details). In Figs. 4 A - C we show the calculated trajectories of $n_e(t)$ and $n_h(t)$ after a laser pulse excitation plotted as a function of time t in the form of parametric plots for different cycles. The plots include the lines of intersections between the pairs of chemical potential surfaces from Fig.3 D, indicating the possible end points (H or C) corresponding to the temperature at the end of the cycle. In the W cycle, we start in the C state at low T where $n_e = n_h \simeq 0$ (point O). For excitation above threshold $U_W > U_T$ (Fig. 4 A), the laser pulse causes the electronic temperature to increase and the system trajectory initially follows the C state line (where $n_e = n_h$), then makes a loop and ends at point H (where $n_d \neq 0$). In this cycle, the system trajectory goes around the energy maximum point U behind which the H point is hidden.

Below threshold ($U_W < U_T$), the system initially follows the same path, but the final temperature reached by the system is too low for there to be an intersection of all three chemical potentials, so the system returns back to state C (Fig. 4 B). The appearance of a switching threshold observed in the experiments is thus described by the model. In the E cycle we start from the hidden state at point H (Fig. 4 C). Increasing T above a critical value causes the system to follow curve **1** towards the commensurate state C' at an elevated temperature $T > T_H$. Cooling thereafter causes it to return via **2** to the stable point C , reproducing the cycle performed in our experiments.

We can now also understand why switching does not occur for $\tau > 4$ ps: Electron-hole

asymmetry may be present as long as the entire electronic system is out of equilibrium with the lattice (up to $3 \sim 5$ ps). With pulses longer than a critical length which is related to the electron/hole energy relaxation time, the H state can no longer form. Changing the W pulse length τ within our model and plotting the threshold U_T as a function of pulse length τ , we obtain the curve shown in Fig. 2 C. The model closely follows the observed behaviour, whereby no stable H point is reachable for pulses longer than a critical value τ_c , observed experimentally at ~ 4 ps.

The main nontrivial observations, namely the appearance of a switching threshold for the W pulse fluence, its critical pulse-length dependence, the threshold temperature for the E cycle, and the high conductance can thus be reproduced. Moreover, the narrow AM spectrum is a direct consequence of the predicted homogeneous long range order in the H state. The observation of a mid-gap spectral feature following sub-threshold photoexcitation as reported recently (19,24,25) is consistent with a transient change of polaron density.

The reason for the remarkable stability of the H state over an arbitrarily long time is that it is topologically protected: The domain wall density n_d cannot change continuously, but can do so only in discrete steps, only when the number of periods of the electronic crystal changes, which is quantized. Such an effect as has been demonstrated in 1D CDWs (26,27). This constraint - and its energetically costly resolution by proliferation of topological plane and line defects - resembles the protection and inhibited decay of super-currents in superfluids and superconductors where the intrinsic defects are phase slips and vortices. Here, on a microscopic level, proliferation of new domain walls provides a mechanism for spectral flow of particles across the spectral gaps which converts polaronic states to/from band states. The creation and motion of such extended objects will be substantially slowed down by the presence of intersecting discommensurations and finally arrested by pinning to lattice defects. The E cycle may be explained by the creep of extended defects which is known to be promoted by heating above an irreversibility line characteristic of pinning phenomena.

Previous time-resolved experiments in $1T$ -TaS₂ failed to detect switching because they were performed either with insufficient fluence (18), or the ambient temperature was too high (20). The mechanism for the creation of a topologically protected state by a nonequilibrium quench is generic and is likely to be found in other charge-ordered materials with multiple electronic reservoirs. The switching is caused by relatively weak and short pulses, which - considering the large change in resistance and optical reflectivity - has obvious application potential. The effect also opens the way to the search for new generations of room temperature non-volatile memory elements in electronically ordered materials. As a memory element, switchable by sub-35 fs pulses, our device is already comparable to, or exceeds the current speed record of 40 fs in magnetic materials (28).

32.1.2 Appendix 1: the calculation of the system trajectory

The theory was developed on a basis of a phenomenological approach which leads to a minimal and computationally treatable model, and which is compatible with existing microscopic pictures. Our model is independent of underlying microscopic details and can be only complicated further, but this was not necessary as shown by the successful numerical solutions of the equations below.

The focus is upon three reservoirs of electrons: electrons and holes as mobile charge carriers with concentrations n_e and n_h and the crystallized electrons with the concentration $1 - n_d$ where $n_d = n_v - n_i$ is the relative density of intrinsic defects (interstitials "i" and voids "v" as explained above; both are known to be present (9). Altogether, the concentrations are subject to the charge conservation law $n_e - n_h = n_v - n_i = n_d$. The crystalline density, hence the concentration of its defects, can be changed only by proliferation of topological defects, akin to

vortices in superfluids, which is allowed at high T of initial dynamics but is arrested at low T of the already formed H state.

The total free energy, which we shall consider additive, $F(n_d, n_e, n_h) \approx F_d(n_d) + F(n_e) + F(n_h)$ determines the partial chemical potentials $\mu_j = \partial F / \partial n_j \approx \mu_j(n_j)$ (these are also functions of the temperature) of the reservoirs which must be all equilibrated in the static regime. The electrons and the holes from the nominally empty and filled band states will be considered as particles with 2D spectra $\epsilon_{e,h}(p) = \Delta_{e,h} + p^2/2m_{e,h}$ characterized by their activation energies - the gaps $\Delta_{e,h}$ and by effective masses $m_{e,h}$ giving constant densities of states $N_{e,h} \sim m_{e,h}$ above the respective gaps. That yields the chemical potentials as

$$\mu_{e,h}(n) = \Delta_{e,h} + k_B T \ln(\exp(n_{e,h}/(k_B T N_{e,h}) - 1). \quad (32.1)$$

The necessary free energy $F_d(n_d)$ of the crystalline reservoir can be taken just to satisfy the fact of the first order phase transition in equilibrium between the C and IC phases, which is the experimental fact as well as the results of thermodynamical calculations. We went a bit further to justify the chosen form of F_d by referring to a general theory (23) of weakly incommensurate triangular lattices. Assuming the symmetry between vacancies and interstitials, i.e. with respect to the sign of n_d , we choose the parametrization

$$F_d(n_d) = E_{DW}(C_0|n_d| + C_1|n_d|e^{-1/(\xi|n_d|)} - C_2\xi n_d^2 + C_4\xi^3 n_d^4) \quad (32.2)$$

where C_n are numeric constants. Here ξ is the domain wall width, E_{DW} is its energy scale per a constituent defect. The first two terms are standard for a picture of the 2nd order C - IC transition: in thermodynamic equilibrium, the coefficient $C_0 < 1$, as a function of T , reduces the DW energy and for $C_0 < 0$ the walls start to be created but their concentration is stabilized by the repulsion given by the second term $\sim C_1$. The next term $\sim C_2$ appears for non-collinear arrays of domain walls which now intersect in points with a concentration $\sim n_d^2$. A key point (23) is that this energy is expected to be negative, which we took into account with the sign "-" of the term $\sim C_2$ in (32.2). Together with the last stabilizing term $\sim C_4$ to take into account the repulsion between the crossings, we obtain the desired non-monotonous curve for F_d shown in Fig. 3A. The chemical potential of the crystalline reservoir is then:

$$\mu_d(n_d) = E_{DW}(C_0 + C_1(1 + \frac{1}{\xi|n_d|})e^{-1/(\xi|n_d|)} - 2C_2\xi|n_d| + 4C_4(\xi|n_d|)^3)\text{sign}(n_d). \quad (32.3)$$

The three surfaces of chemical potentials $-\mu_e$, μ_h and μ_d as a function of n_e , n_h and $n_d = n_e - n_h$ respectively are shown in Fig. 3B. (μ_h and μ_d , as both counting the electron's deficiencies, should be always taken with an opposite sign with respect to μ_e .)

Mutual transformations among the reservoirs, together with the concomitant heat production, are dictated by imbalances of three partial chemical potentials μ_j . The corresponding kinetic equations are chosen in a simplest form satisfying to the condition that the exchange rate among any two reservoirs vanishes when the corresponding chemical potentials become equal $\delta\mu_{i,j} = 0$. To model the nonequilibrium evolution, we need to consider the relaxation kinetics between the three reservoirs.

The rates R_{ij} of particles' exchange among the reservoirs may be complicated functions of n_j , μ_j , and T and we need to make physically motivated assumptions. It is common, from physics of semiconductors to gapful correlated systems, to take the bi-particle form of the e-h recombination $R_{eh} \sim n_e n_h$. The linear relations $R_{hd} \sim n_h$ and $R_{ed} \sim n_e$ imply that the band particles can transform themselves into defects without meeting another particle, e.g. the holes can annihilate with a main part of polarons rather neglecting the small concentration of defects. In principle the bi-modal parts $R_{ed}^{bm} \sim n_e n_d$ and $R_{hd}^{bm} \sim n_h n_d$ can be also present which we shall

not consider here keeping the minimalistic approach. Next we use the most general principle that, as functions of potentials mismatches, R_{ij} changes the sign passing through zero when the potentials coincide: $\delta\mu_{i,j} = 0$. Again, we take it into account in a simplest form of the linear dependence $R_{ij} \sim \delta\mu_{i,j}$. Finally, kinetic equations for the time evolution of $n_h(t)$ and $n_e(t)$ acquire the form:

$$\frac{dn_h}{dt} = -k_{eh}n_en_h(\mu_e + \mu_h) - k_{hd}n_h(\mu_h - \mu_d) + P(t) \quad (32.4)$$

$$\frac{dn_e}{dt} = -k_{eh}n_en_h(\mu_e + \mu_h) - k_{ed}n_e(\mu_e + \mu_d) + P(t) \quad (32.5)$$

where k_{ij} are the coefficients of the recombination rates $R_{i,j}$ after extracting dependencies on $n_{i,j}$ and $\delta\mu_{i,j}$, $P(t)$ is the temporal profile of particles production. As a justification, notice a distant resemblance of these equations with basic ones describing the photo-voltaic devices (see e.g. (29,30); superficially, n_d can be compared with a part of electrons trapped by impurities or lattice defects.

The temperature evolution is taken into account by the energy balance equation

$$J = C_T dT/dt = \sum_j \mu_j (dn_j/dt), \quad (32.6)$$

where C_T is the heat capacity. The formulas (32.4,32.5) and (32.6) form a complete set of equations governing the system evolution. Their solution yields the trajectory of the Fig. 3, and the partial time dependencies in Fig. 32.5.

In these equations, the time is in ps and k_{ij} are in ps^{-1} , the laser pulse length is $\tau = 0.035$ ps. Other quantities are dimensionless: n_j as concentrations per enlarged unit cell of one star; the energies as given in units of the electrons' gap Δ_e . The parameters used for calculation presented in the main text and in Fig. 32.5 below are as follows. The hole gap is taken as $\Delta_h = 1.4$ (following a prevailing information from experiments and band calculations that the Fermi level is closer to the upper rim of the gap), and the densities of states are $N_h = 1.2$, $N_e = 1$. For electrons there may be an uncertainty because we do not know for sure if they thermalize to the bottom of the conduction band or to the upper Hubbard level which positions look to be close, see (31) and rfs. therein. Also the electronic states are not accessible to photo-emission experiments. Still, it is known from STS (32) and optics (33) that the total gap is $\Delta_e + \Delta_h = 0.6\text{eV}$, so our energy unit is 0.25eV .

Parameters in Eqs. (32.2,32.3) are adjusted such that the free energy F_d shows the appropriate minimum as shown in Fig. 3A: $C_0 = 0.22$, $C_1 = 1$, $C_2 = 1$ and $C_4 = 2$. The domain wall size is $\xi = 3$, in lattice units, and the domain wall energy scale is $E_{DW} = 2$. So the energy to initiate one defect is taken as $E_d = C_0 E_{DW} = 0.44\Delta_e = 0.11\text{eV}$. $k_{eh} = 20 \text{ ps}^{-1}$, $k_{hd} = 20 \text{ ps}^{-1}$ and $k_{ed} = 10 \text{ ps}^{-1}$; their magnitudes are estimated from the observed single particle relaxation rate in Fig. 2B. The trajectory is very robust with respect to parameters k_{ij} , changing their magnitude by a factor of 2 has a minor effect on the plots, provided that $k_{hd}/k_{ed} > 2$. For these parameters, the threshold laser pulse energy for switching to the H state is $U_T = 0.8$.

The temporal evolution of n_e , n_h , n_d and T is plotted in Fig. 32.5 above and below U_T , corresponding to the trajectories shown in Fig. 3. Notice that the temperature saturates quite fast while the evolution of concentrations keeps a longer time towards H state and much longer time towards the C state.

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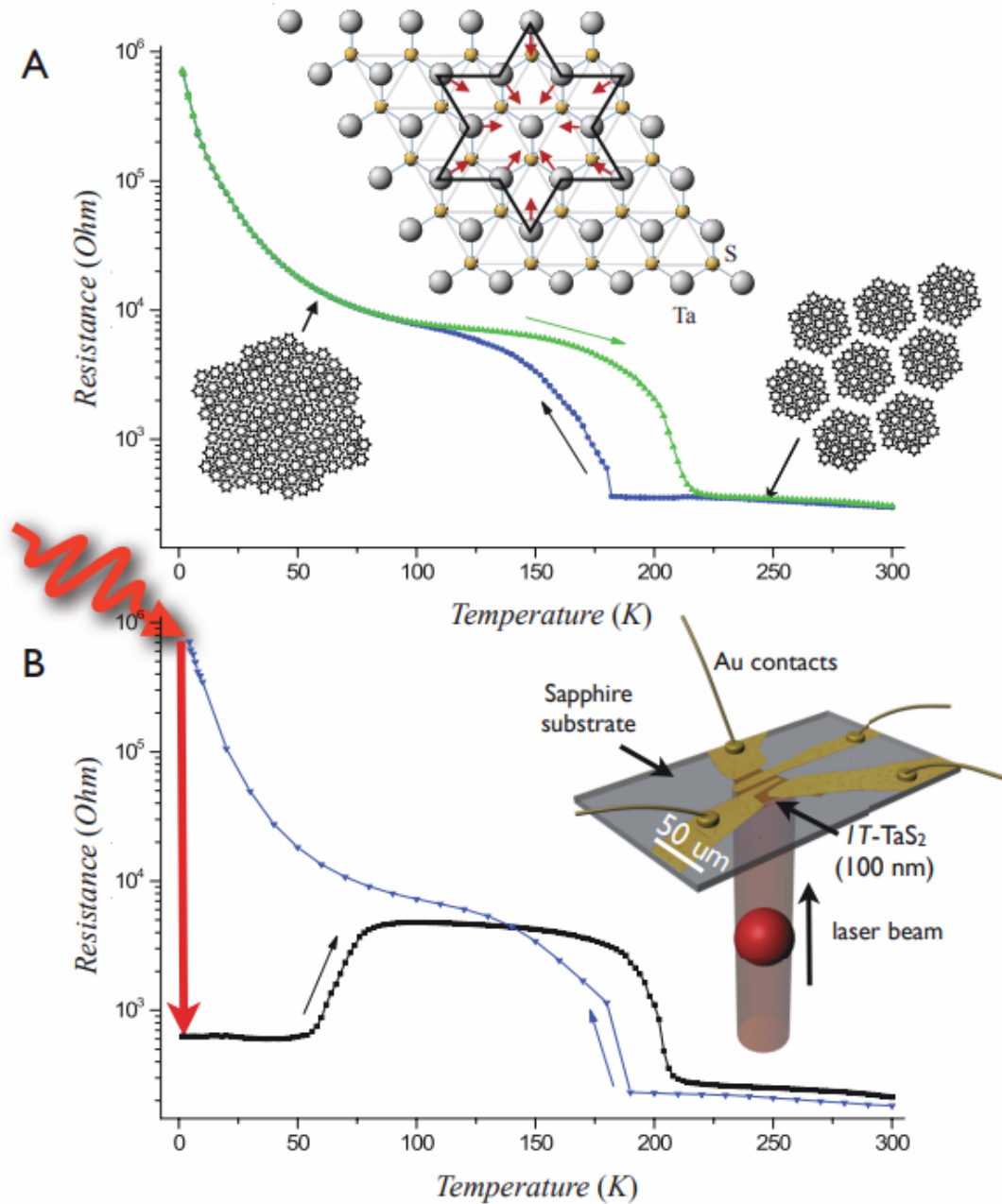


Figure 32.1: **Fig. 1.** Resistivity switching of 1T-TaS₂ by a 35 fs laser pulse at 800 nm. (A) The T -dependence of the 4-probe resistance $r(T)$ on temperature cycling. The inserts show schematically the lattice distortions associated with an individual polaron and their ordering in the NC and C states respectively. (B) The drop of r at 1.5 K after a single pulse with $U_w > U_T$ (red arrow). On heating the resistance reverts back between 60 and 100 K (black curve). The insert shows a schematic of the sample and contacts, which are from an optical microscope image.

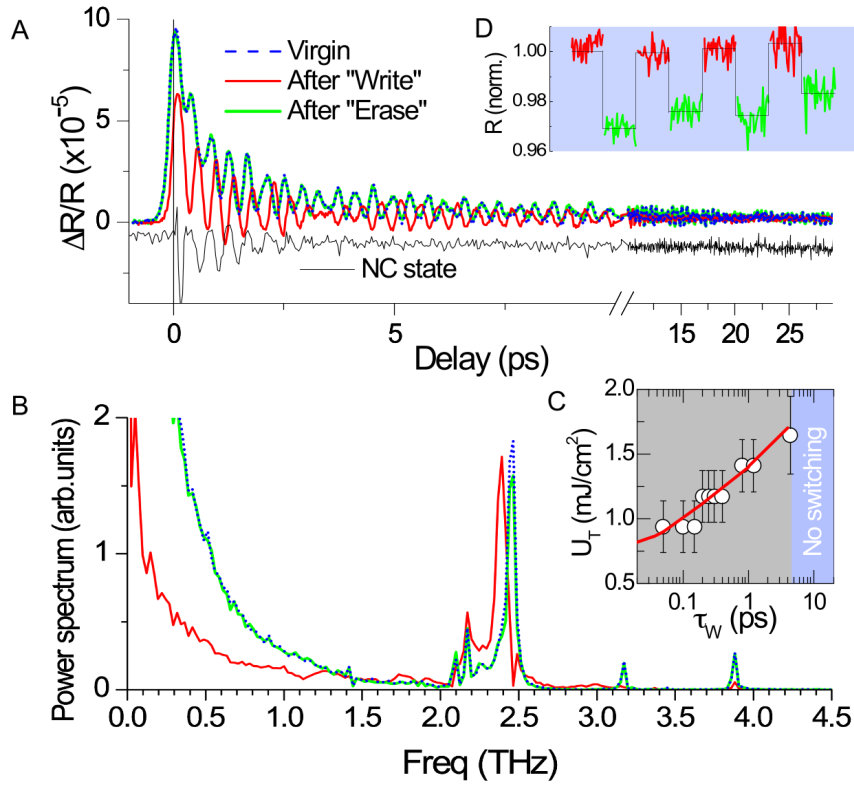


Figure 32.2: **Fig. 2.** (A) The transient reflectivity $\Delta R(t)/R$ of $1T$ -TaS₂ in the virgin state (blue dashed line), after exposure to a 50 fs W pulse (red line), and after an E pulse (green line). For comparison, the thin black line is the data in the *NC* state at 220 K recorded on cooling (the trace is offset for clarity). (B) The corresponding FT spectra $S(\omega)$ using the same color notation. Note the complete disappearance of the AM at 2.46 THz in the *H* state, and clean switching back after the E pulse. The switching is also observed for the modes at 2.3, 3.2 and 3.85 THz. The *NC* state spectrum, as well as the *T*-state spectrum recorded at 240 K on heating (not shown) are qualitatively different than either the *C* or *H* state spectra. (C) The switching threshold fluence U_T as a function of pulse length τ_W measured optically with the Pump-probe experiments. The red line is predicted by the model calculation. (D) The reflectivity at 800 nm recorded with the photodiode during a sequence of alternating W and E pulses. (The noise is from the laser.)

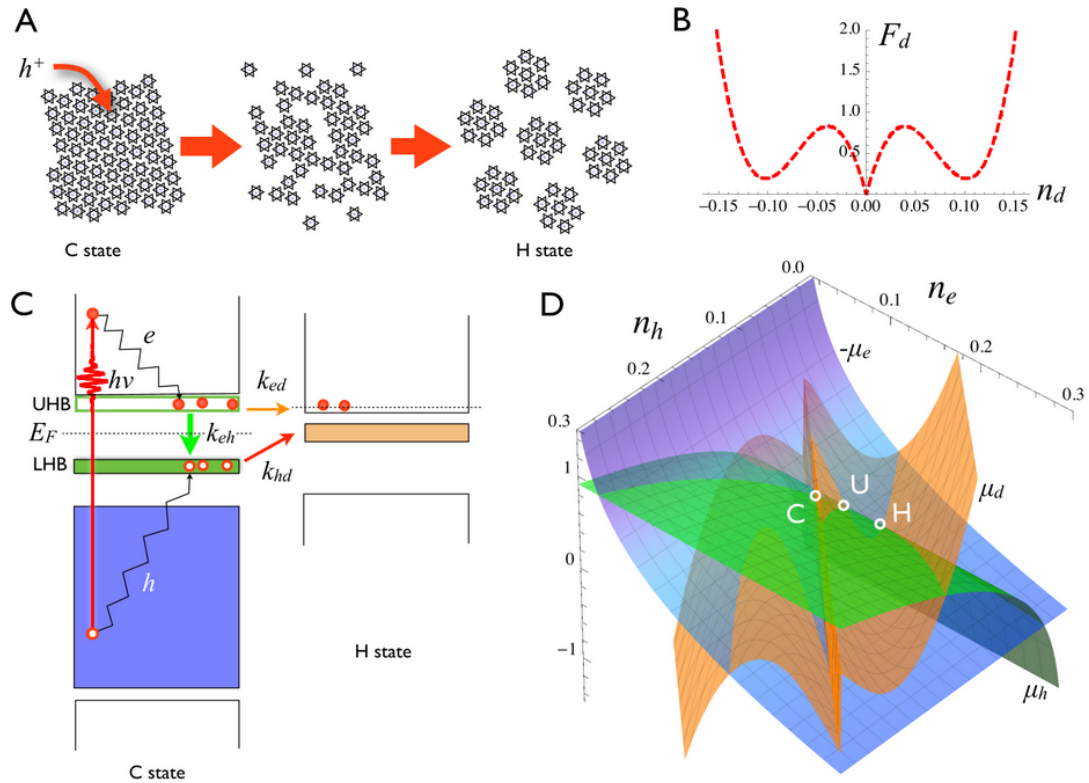


Figure 32.3: **Fig. 3.** (A) A schematic diagram of the reordering following a laser pulse. First a hole annihilates with a polaron, causing voids in the structure, which reorganise into a long-range ordered structure with a wavevector shift δq is related to the number of defects by charge conservation $\delta q/\pi \simeq n_d$. Loosely, the structure may be thought of as polaron clusters separated by domain walls. (B) The CDW free energy F_d (dashed red line) as a function of n_d . (C) A schematic energy levels diagram of the C state based on refs. (14,15,28). Occupied bands in blue are those from Ta atoms within each polaron in Fig. 1. The Hubbard bands are shown in green. Photoexcitation, initial energy relaxation and subsequent relaxation processes of the e and h amongst themselves and to a new incommensurate H state are shown schematically. (D) The chemical potential surfaces $-\mu_e$ (blue), μ_h (green) and μ_d (orange) respectively as a function of n_e and n_h . The intersections C and H are commensurate and incommensurate stable points of the system respectively.

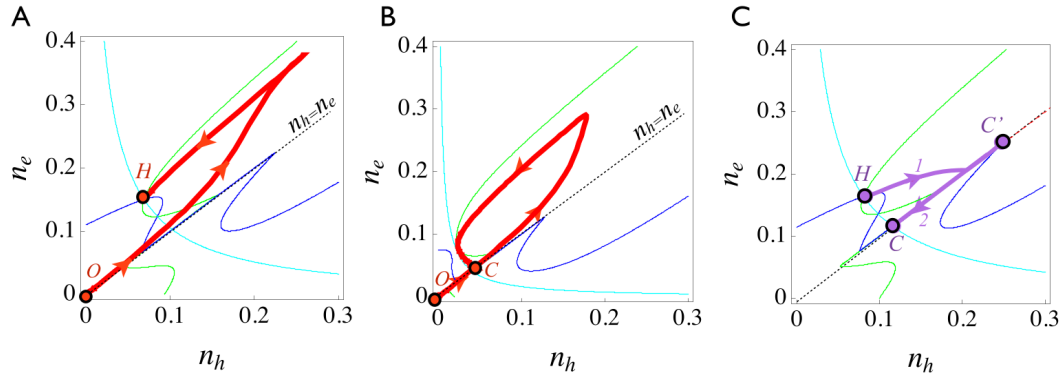


Figure 32.4: **Fig. 4.** (A) The system trajectory system (thick red line) above switching threshold $U_W > U_T$ on a parametric plot of $n_e(t)$ and $n_h(t)$ as a function of time superimposed on lines of partial equilibria given by the intersections $\mu_e = -\mu_d$ (green), $\mu_h = \mu_d$ (blue) and $\mu_e = -\mu_h$ (cyan) drawn for the final temperature after the system has stabilized. (B) Same as (A) except below threshold $U_W < U_T$. The system now returns to the C state. (C) Model trajectory of erasure by heating in the H -state (purple line): the trajectory first leaves the H -point, then joins the commensurate line. After reaching a maximum at C' , on cooling the system returns to point C .

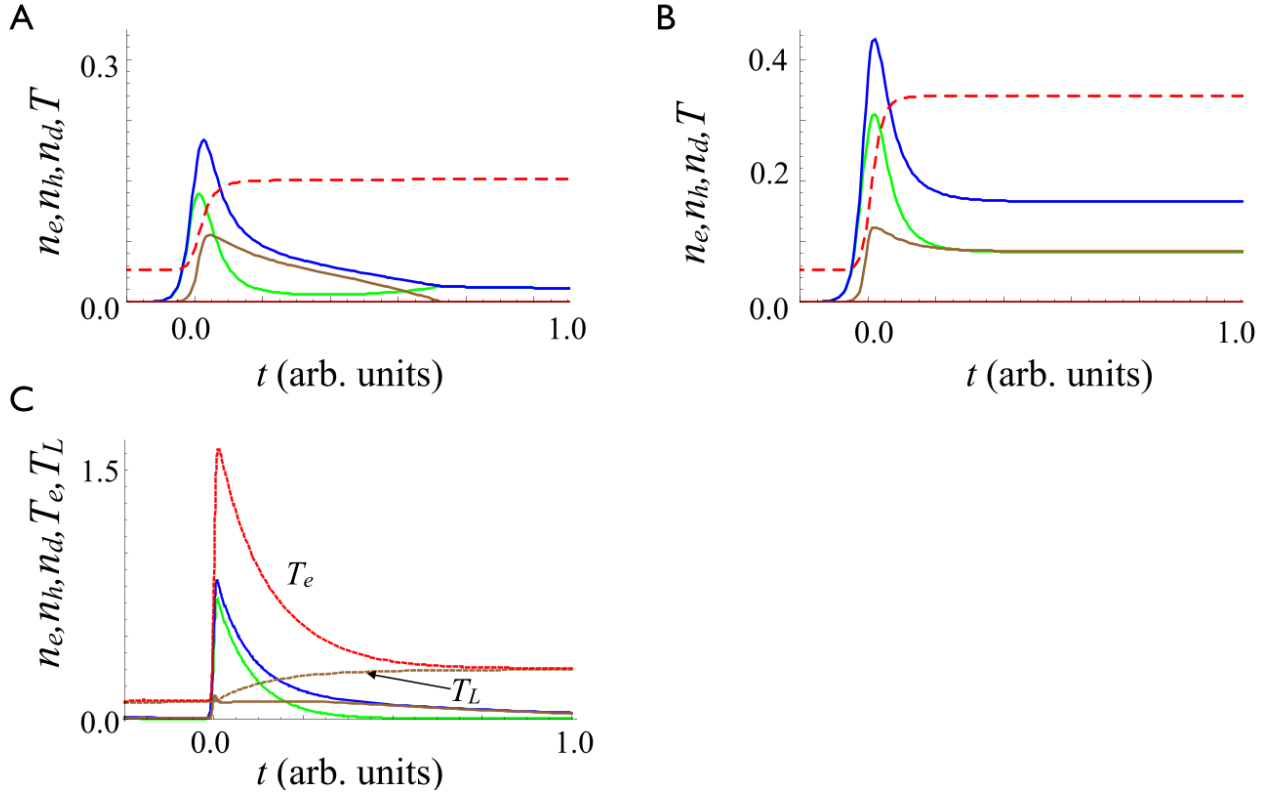


Figure 32.5: The calculated n_e (blue), n_h (green), n_d (brown) and the temperature T (red dashed) as functions of time using the equations (32.4,32.5) and (32.6): a) below threshold ($U_W < U_T$) and b) above threshold ($U_W > U_T$). The initial temperature was taken as $T = 0.1\Delta_e/k_B$. The corresponding parametric plots of n_e and n_h are shown in Figs. 3 D and E respectively. Note that the calculation does not discuss the cooling part of the cycle, so the temperature remains high after all the pulse energy is transferred. In C we show the results of a calculation which includes the two-temperature model for $U_W > U_T$. n_e (blue), n_h (green), n_d (brown) are qualitatively similar to the results of the simple model calculation (B). The electronic and lattice temperatures T_e and T_L are shown by the red-dashed and brown-dashed lines respectively.

32.1.3 SM

I. Sample Details

Numerous samples of two different origins were used to check for consistency of the results. Fresh $1T - \text{TaS}_2$ samples were grown by P. Sutar and A. Mrzel by first synthesizing TaS_2 powder from the elements (99.9%Ta foil, 99.98% S powder) in a stoichiometric ratio (with 99.98% iodine as transport agent) in a quartz ampoule and heated in a multiple zone furnace $750^\circ\text{C} - 850^\circ\text{C}$ for 5 days. The ampoule was subsequently opened and resealed with a small quantity of C_{60} powder as getter, then heated in a multiple-zone furnace with a temperature gradient of $900^\circ\text{C} - 800^\circ\text{C}$ for 6 hours, subsequently reversing the gradient to $750^\circ\text{C} - 850^\circ\text{C}$ for 8 days. Finally, the ampoule was quenched into water. The single crystals, up to $5 \times 5 \times 0.1$ mm in size were checked by Raman, resistivity and XRD to be the $1T - \text{TaS}_2$ polytype. $1T - \text{TaS}_2$ samples from G. Berger were grown at EPFL as described in [1]. They were already used for measurements in 2002 [2, 3]. No significant difference was observed in the data from the two sets of samples.

II. Experimental Details

The samples were mounted on a cold finger of a liquid-He flow optical cryostat equipped by CaF_2 windows.

For the optical measurements, all the laser beams were derived from a 250 – kHz-repetitionrate regenerative Ti : Al_2O_3 laser amplifier with 50 fs pulse length. Acousto-optic modulators (AOM) were used to modulate the beams. The modulators for W and E beam were controlled by a programmable function generator synchronized to the laser in order to pick a desired number of pulses from the original pulse train. The modulator for the pump (P) beam was controlled by a lock-in amplifier using a standard 2 -pulse pump-probe detection scheme.

The W-pulse length was increased from the original length of 50 fs either by increasing the accumulated dispersion in the amplifier by varying the number of the amplifier round trips or adjustments of the post-amplification optical pulse compressor, that was used also to compensate the dispersion of the AOMs . The E pulses of $\sim 50\text{ps}$ length were derived from the uncompressed amplifier output by bypassing the compressor.

For the resistance measurements, a single pulse from an amplified Ti:Sapphire laser (Coherent Legend) was used with a 35 fs pulse length. The sample was illuminated from the back side through the sapphire substrate to achieve uniform illumination and to ensure that there is no unilluminated gap between the contacts and the sample.

The resistance $r(T)$ was measured by the standard 4-contact technique. Gold contacts $\sim 10\mu\text{m}$ apart were manufactured by laser lithography using a LPKF ProtoLaser LDI machine, which allows lithography on samples deposited on an insulating substrates using a 2-layer photoresist (Allresist ARP 5480/ARP3510). The samples used in the experiments were 80 – 100 nm thick exfoliated $1T-\text{TaS}_2$ single crystals which were previously deposited on a sapphire substrate by exfoliation from sticky tape. (The temperature dependence of the resistivity for thinner samples is no longer characteristic of $1T-\text{TaS}_2$, from which we conclude that the strain caused by the contraction mismatch between the substrate and the sample modifies the system to such an extent that we are no longer dealing with characteristic $1T-\text{TaS}_2$ material.) The I-V characteristics were measured at each temperature, and were linear in a range $\pm 100\mu\text{A}$. Erasure by Joule heating was achieved by passing a current of 1 mA .

$1T-\text{TaS}_2$ is known to have slow relaxation dynamics associated with pinning and/or intersecting discommensurations which can strongly affect the measurements unless a proper protocol for thermal cycling is followed [4,5]. We have used a thermal cycling protocol which gave us consistent results: all cooling cycles were done starting at room temperature, and temperature was changed at a rate of 2 K/ minute or slower. Once switched, thermal annealing was done by heating to room temperature. Interrupting the thermal cycle at intermediate temperatures gave unpredictable results.

Importantly, the threshold measurements were done by measurement of the AM switching. This means that the same volume is switched and probed, as determined by the optical penetration depth, which is equal for both the W excitation and the probe. For the resistivity measurements, we need to illuminate from the back, because illuminating from the front creates shadows. However, since the thickness is greater than the penetration depth, we need to use higher fluences with back illumination, to ensure that the contact region is illuminated above threshold. Typically this is found to be 3 – 4 times the the threshold fluence as determined from optical measurements. The entire sample is thus exposed to above-threshold excitation, which gives us the reproducible resistance switching characteristics.

III. Calculation of the Electronic and Lattice Temperatures After a Write (W) Pulse

The temperature after photoexcitation can be estimated using Newton's law of cooling, with the electrons and the lattice assumed to be described by effective temperatures T_e and T_L respectively:

$$\gamma_e T_e \frac{dT_e}{dt} = -\gamma_L (T_e - T_L) + P(t) \quad (1)$$

$$C_L(T) \frac{dT_L}{dt} = \gamma_L (T_e - T_L) \quad (2)$$

By meticulously taking into account the T -dependent specific heats $\gamma_e(T)$ and $C_L(T)$, the optical absorption coefficient α and reflectivity R of $1T - \text{TaS}_2$ at 800 nm, the uncertainty of the calculated T_e and T_L can be significantly reduced. $P(t) = (1 - R) \frac{E_0}{\sqrt{2\pi}w} \exp\left[-\frac{(t-t_0)^2}{2w^2}\right]$ is the normalized W pulse intensity, where $\tau_W = 2\sqrt{2\ln 2}w$ is the W pulse width. $\gamma_L = 3\hbar\lambda_{e-p} \langle\omega^2\rangle \gamma_e / \pi k_B \simeq 300\text{psK}^{-1}$ is the energy relaxation rate [6], and $\gamma_e = 4.2\text{mJmol}^{-1} \text{K}^{-2}$

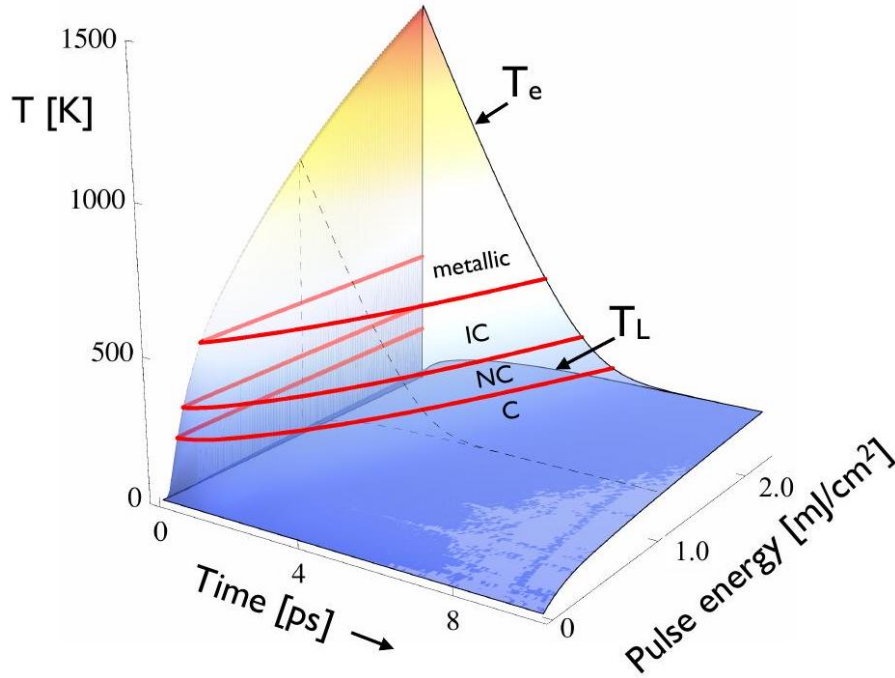


FIG. S1: The estimated temperatures T_e and T_L after excitation calculated using the 2TM as a function of pulse energy U_W . The dashed line represents the threshold value of U_W for the transition to the H state. The red lines indicate the transition temperatures T_{c0} , T_{c1} and T_{c2} respectively.

is the electronic specific heat coefficient [7]. $C_L(T)$ is the lattice specific heat and $R = 0.6$ is the reflectivity at 800 nm [8]. Using an electron-phonon interaction constant $\lambda_{e-p} \sim 0.25$, a Debye model fit of the experimental $C_L(t)$ [9] and an estimated second moment of the Debye frequency $\langle\omega^2\rangle \sim 10\text{THz}^2$, we obtain the evolution of $T_e(t)$ and $T_L(t)$ as a function of E_0 and τ_W shown in Fig. S1. At the threshold for switching, the calculated T_L is $\sim 150 \text{ K}$. T_e initially reaches 1400 K, but becomes comparable to the lattice temperature on a timescale of $\sim 3\text{ps}$.

To test the accuracy of the calculation, we compare the calculated T_L to the measured temperature of the lattice obtained from the time dependence of the amplitude mode frequency

ω_{AM} measured using the 3-pulse technique [20], and its independently determined temperature-dependence. We see that the calculated and measured T_L agree to better than 10 K (Fig. S2).

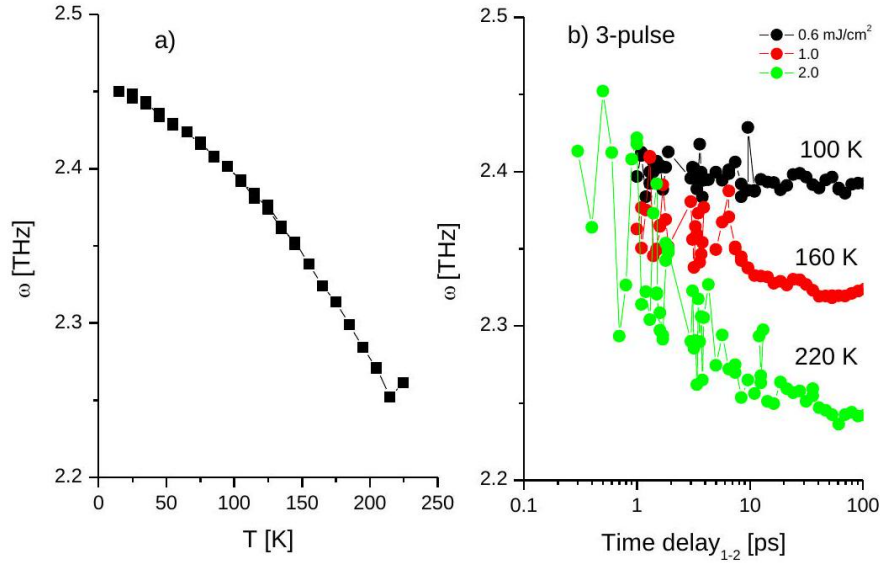


FIG. S2: a) The measured frequency of the AM as a function of temperature using the Pump-probe technique (see also ref. [2]). b) The frequency of the AM as a function of time after a W pulse of different magnitude measured as a function of time delay by the Pump-probe method. The three curves correspond to $U_W = 0.6, 1.0$ and 2.0 mJ/cm², using 50 fs pulses shown by black, red and green data points respectively. The lattice temperature reached after 100 ps for the three pulse energies are approximately 100 K, 160 K and 205 K respectively. The middle curve corresponds to the threshold value of U_w . The measured temperatures are in remarkable agreement with the calculated ones on the basis of the two temperature model shown in Fig. S1. Note that the large oscillations at early times are not noise, but rather they are order parameter oscillations which occur at early times[20].

IV. Calculation of the Temperature After the Erase (E) Pulse Burst

The average surface temperature between the transient T spikes during a long burst of pulses can be approximated by solving a steady state anisotropic heat conduction model [10]. We need to take into account the strong T -dependence of the heat conductivity [11] below T_{c2} . Furthermore, an absence of experimental data on the out-of-plane heat conductivity means that the diffusive heat transport perpendicular to the surface can only be qualitatively estimated. Using the average power density for the the case of erase pulses, the in-plane heat

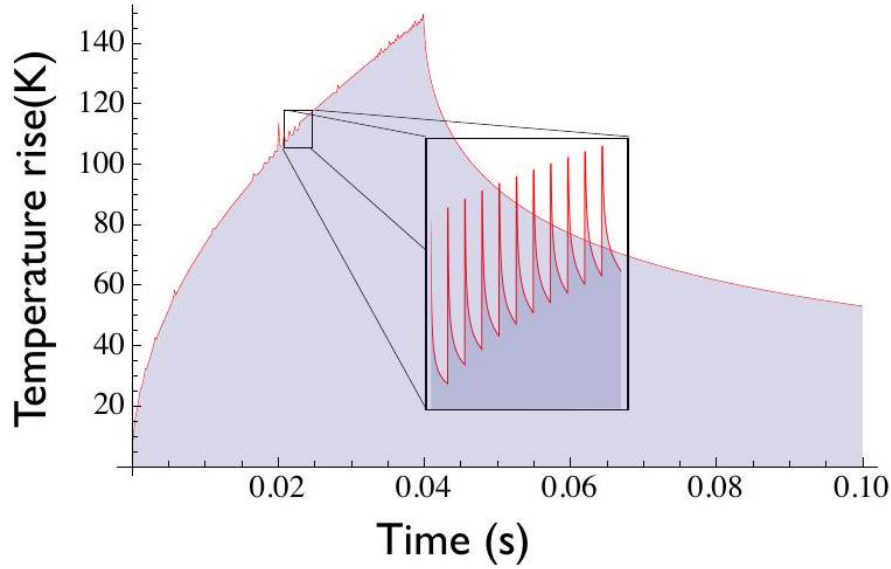


FIG. S3: The calculated lattice temperature rise ΔT_L as a result of the E burst, a pulse train of 10^4 pulses, each $\tau = 50$ ps in length and 4μ s apart. The constants are $K_c = 0.01$ W/cm – K, $\rho = 6$ g/cm³. The value of K_c is an estimate from the measured in-plane thermal conductivity of $K_{ab} = 0.1$ W/cm – K[11]. The uncertainty in estimated temperature comes mainly from the uncertainty in thermal conductivity perpendicular to the sample surface.

conductivity at 100 K, $K_{\text{par}} \simeq 0.1$ W/cmK, [11] and assuming, that the out-of-plane heat conductivity, K_{perp} , is 10-100 times smaller than K_{par} , we obtain the surface temperature rise in the 40 – 120 K range.

Let us next estimate the time for the temperature to drop below T_H after absorption of a single pulse. Initially the energy is absorbed within the optical penetration depth, $\lambda_{\text{opt}} \simeq 20$ nm, thick layer [8]. Since the beam diameter, $w_{FWHM} = 86 \mu$ m, is much larger than λ_{opt} the diffusion is effectively 1D. The characteristic diffusion length is estimated from the ratio of the internal energies, $\xi \simeq \lambda_{\text{opt}} U(T_0)/U(T'_c)$, obtained by extrapolating the heat capacity data[9] using Debye model, where T_0 is the initial temperature immediately after the system thermalizes. Assuming the same anisotropy as above we estimate the thermal diffusivity, κ_{perp} , to be in the $\sim 2 \cdot 10^{-4} - 4 \cdot 10^{-3}$ cm/s² range between T_p and room temperature, resulting in the characteristic time for diffusion $\tau_{\text{SP}} = \xi^2/4\kappa_{\text{perp}}$ in the $\sim 2 - 300$ ns range. Here the longest τ_{SP} corresponds to the smallest κ_{perp} and $T_0 \simeq 300$ K corresponding to the case of erase pulse. In the case of the write pulse at the threshold $T_0 \sim 200$ K, giving $\tau_{\text{SP}} < 30$ ns.

Bearing this in mind, the surface temperature rise resulting from the E pulse burst is calculated using a solution to the diffusion equation with appropriate boundary conditions[10]. Simplifying the pulse shape to a square hat top, the surface temperature rise from the accumulated heat, expressed as a summation over the whole pulse train of N pulses is given by:

$$\Delta T_L = \frac{2U_E(1-R)}{\tau_W K} \sqrt{\frac{\kappa\tau}{\pi}} \sum_{n=0}^N \Theta[(x - t_0 - \tau)] \text{Re} \left[\sqrt{\frac{x - nt_0}{\tau}} - \sqrt{\frac{x - nt_0}{\tau} - 1} \right] \quad (3)$$

where Θ is the heaviside theta function, t_0 is the time between pulses, τ is the individual pulse duration, R is the reflectivity, K is the thermal conductivity, $\kappa = K/\rho c$ is the thermal diffusivity, c is the specific heat capacity and ρ is the density of 1T-TaS₂[7]. The temperature

dependence of K arising from the thermal conductivity and specific heat are explicitly taken into account, just as in the W pulse calculation. The estimated $\Delta T(t)$ is plotted in Fig. S3.

V. The Calculation of the System Trajectory

We present a plausible phenomenological theory with the aim of elucidating the underlying physics. The main requirements are that (1) it should be as simple as the problem allows, (2) it is still computationally treatable, which is not trivial considering the highly non-linear nature of the phenomenon which it needs to describe, (3) it needs to be compatible with the existing microscopic picture of this material and (4) it needs to describe the three main remarkable observations of the experiment. The proposed model is independent of underlying microscopic details and can be elaborated and extended further, but the minimal model which we give here satisfies the requirements above and the numerical solutions of the equations presented below are successful in describing the system trajectories for the different cycles performed in the experiments.

We need a mechanism by which a new ordered state forms under nonequilibrium conditions, rather than the system simply returning to the ground state. The important fundamental insight of the model is the necessity for a transient electron-hole asymmetry at the Fermi level, which allows a transient photodoping effect to occur just long enough for a new hidden state to form. The energy relaxation timescale for photoexcited carriers where the asymmetry originates also relates to the switching timescale observed in our experiments. Once the state is established, its collective nature protects it from dissipating.

The focus of the model is on three reservoirs of electrons: electrons and holes as mobile charge carriers with concentrations n_e and n_h and the crystallized electrons with the concentration $1 - n_d$ where $n_d = n_v - n_i$ is the relative density of intrinsic defects (interstitials " i " and voids " v " as explained in the main text; both of which are known to be present [12]). All together, the concentrations are subject to the charge conservation law $n_e - n_h = n_v - n_i = n_d$.

The total free energy, which we shall consider additive, $F(n_d, n_e, n_h) \approx F_d(n_d) + F(n_e) + F(n_h)$ determines the partial chemical potentials (in photo-physics of semiconductors they are also referred to as quasi-Fermi levels) $\mu_j = \partial F / \partial n_j \approx \mu_j(n_j)$ (these are also functions of the temperature) of the reservoirs which must be all equilibrated in the final static regime. The electrons and the holes from the nominally empty and filled band states will be considered as particles with 2D spectra $\epsilon_{e,h}(p) = \Delta_{e,h} + p^2/2m_{e,h}$ characterized by their activation energies - the gaps $\Delta_{e,h}$ and by effective masses $m_{e,h}$ giving constant densities of states $N_{e,h} \sim m_{e,h}$ above the respective gaps. That yields the chemical potentials as

$$\mu_{e,h}(n) = \Delta_{e,h} + k_B T \ln \left(e^{n_{e,h}/(k_B T N_{e,h})} - 1 \right) \quad (4)$$

The necessary free energy $F_d(n_d)$ of the crystalline reservoir can be taken just to satisfy the fact of the first order phase transition in equilibrium between the C and IC phases, which is the experimental fact as well as the results of thermodynamical calculations. We went a bit further to justify the chosen form of F_d by referring to a general theory [13] of weakly incommensurate triangular lattices. Assuming the symmetry between vacancies and interstitials, i.e. with respect to the sign of n_d , we choose the parametrization

$$F_d(n_d) = E_{DW} \left(C_0 |n_d| + C_1 |n_d| e^{-1/(\xi |n_d|)} - C_2 \xi n_d^2 + C_4 \xi^3 n_d^4 \right) \quad (5)$$

where C_n are numeric constants. Here ξ is the domain wall width and E_{DW} is its energy scale per constituent defect. The first two terms are standard for a picture of the $C - IC$ transition [13]: in thermodynamic equilibrium, the coefficient $C_0 < 1$, as a function of T , reduces the DW energy and for $C_0 < 0$ the walls start to be created but their concentration is stabilized by the repulsion given by the second term $\sim C_1$. The next term $\sim C_2$ appears for

non-collinear arrays of domain walls which now intersect in points with a concentration $\sim n_d^2$. A key point [13] is that this energy is expected to be negative, which we took into account with the sign "-" of the term $\sim C_2$ in (5). Together with the last stabilizing term $\sim C_4$ to take into account the repulsion between the crossings, we obtain the desired nonmonotonous curve for F_d shown in Fig. 3 B of the main text. The chemical potential of the crystalline reservoir is then:

$$\mu_d(n_d) = E_{DW} \left(C_0 + C_1 \left(1 + \frac{1}{\xi |n_d|} \right) e^{-1/(\xi |n_d|)} - 2C_2 \xi |n_d| + 4C_4 (\xi |n_d|)^3 \right) \text{sign}(n_d) \quad (6)$$

The three surfaces of chemical potentials $-\mu_e, \mu_h$ and μ_d as a function of n_e, n_h with $n_d = n_e - n_h$ respectively are shown in Fig. 3 D of the main text. (μ_h and μ_d , as both counting the electron's deficiencies, should be always taken with an opposite sign with respect to μ_e .)

Recent experiments show that the Mott gap rapidly melts within ~ 50 fs after photoexcitation [14], but after $0.5 \sim 1$ ps, the AM oscillations are visible again, indicating the recovery of the CDW state within a few AM cycles. Since the $e - h$ energy relaxation occurs on a similar timescale ($\tau_E \sim 1$ ps) [2,14], the condensation into the crystalline state competes with $e - h$ recombination.

Mutual transformations among the reservoirs, together with the concomitant heat production, are dictated by imbalances of the three partial chemical potentials μ_j . To model the nonequilibrium evolution, we need to consider the relaxation kinetics between the three reservoirs. The corresponding kinetic equations are chosen to have the simplest form which satisfies the condition that the exchange rate among any two reservoirs vanishes when the corresponding chemical potentials become equal $\delta\mu_{i,j} = 0$. A schematic diagram of the relaxation processes is shown in Fig. 3C of the main text.

The rates R_{ij} of particles' exchange among the reservoirs may be complicated functions of n_j, μ_j , and T and we need to make physically motivated model assumptions. It is common in the physics of semiconductors, as well as gapped correlated electron systems, to take the bi-particle form for the $e - h$ recombination $R_{eh} \sim n_e n_h$ [18, 19]. Linear terms $R_{hd} \sim n_h$ and $R_{ed} \sim n_e$ imply that the band particles can transform into defects without meeting another particle, e.g. holes can annihilate with polarons neglecting the small concentration of defects. In principle the bi-modal parts $R_{ed}^{bm} \sim n_e n_d$ and $R_{hd}^{bm} \sim n_h n_d$ can be also present, but we will neglect such higher order terms to keep the model simple. Next we use the most general principle that, when the potentials are mismatched, R_{ij} changes sign, passing through zero when the potentials coincide: $\delta\mu_{i,j} = 0$. Again, we use the simplest form of the linear dependence $R_{ij} \sim \delta\mu_{i,j}$. Finally, kinetic equations for the time evolution of $n_h(t)$ and $n_e(t)$ acquire the form:

$$\begin{aligned} \frac{dn_h}{dt} &= -k_{eh} n_e n_h (\mu_e + \mu_h) - k_{hd} n_h (\mu_h - \mu_d) + P(t) \\ \frac{dn_e}{dt} &= -k_{eh} n_e n_h (\mu_e + \mu_h) - k_{ed} n_e (\mu_e + \mu_d) + P(t) \end{aligned} \quad (8)$$

where k_{ij} are the coefficients of the recombination rates $R_{i,j}$ after extracting dependencies on $n_{i,j}$ and $\delta\mu_{i,j}$, $P(t)$ is the temporal profile of particles production. As a further justification of the equations above, notice a distant resemblance of these equations with the basic equations describing photo-voltaic devices (see e.g. [18, 19]); superficially, n_d can be compared with electrons trapped by impurities or lattice defects.

The temperature evolution during the cycle is taken into account by the energy balance equation

$$J = C_T dT/dt = \sum_j \mu_j (dn_j/dt) \quad (9)$$

where C_T is the effective heat capacity of the electronic system. To keep the model as simple as possible, we consider here the part of the cycle which is relevant for establishing the ordered state. (The subsequent cooling of the electronic system to the lattice can be treated separately by lowering the temperature externally to the model, by introducing additional lattice bath into the system of equations via the two-temperature model (Eqs. (1) and (2)), or even extending it to take into account thermal diffusion processes; later we discuss the inclusion of the two-temperature model). The formulas (7,8) and (9) form a complete set of equations governing the system evolution on transition to a charge ordered state under photodoping conditions. Their solution yields the trajectories shown in Fig. 4 of the main text. The time dependencies of n_e, n_h and n_d are shown in Fig. S4.

In these calculations, the time is in ps (defined by the rate constants k_{ij} which are in ps^{-1}), the laser pulse length is taken as $\tau = 0.035\text{ps}$. Other quantities are dimensionless: n_j as concentrations per enlarged unit cell of one star; the energies as given in units of the electrons' gap Δ_e . The parameters used for calculation presented in the main text and in

Fig. S4 below are as follows. The hole gap is taken as $\Delta_h = 1.4$ (following a prevailing experimental information and band calculations that the Fermi level is closer to the upper band edge). The densities of states are $N_h = 1.2, N_e = 1$ (from indications on the bandwidths in the literature). For electrons there may be an uncertainty because we do not know for sure if they thermalize to the bottom of the conduction band or to the upper Hubbard level whose positions are close to each other, see [15] and refs. therein. Also the electronic states are not accessible to photo-emission experiments. But still, it is known from STS [16] and optics [17] that the total gap is $\Delta_e + \Delta_h = 0.6\text{eV}$, so our energy unit is 0.25 eV .

Parameters in Eqs. (5,6) are adjusted such that the free energy F_d shows the appropriate minimum as plotted in Fig. 3 B of the main text: $C_0 = 0.22, C_1 = 1, C_2 = 1$ and $C_4 = 2$. The domain wall size is $\xi = 3$, in lattice units, and the domain wall energy scale is $E_{DW} = 2$. So the energy to initiate one defect is taken as $E_d = C_0 E_{DW} = 0.44\Delta_e = 0.11\text{eV}$. $k_{eh} = 20\text{ps}^{-1}, k_{hd} = 20\text{ps}^{-1}$ and $k_{ed} = 10\text{ps}^{-1}$; their magnitudes are estimated from the observed single particle relaxation rate in Fig. 2 B of the main text. The trajectory is very robust with respect to parameters k_{ij} , changing their magnitude by a factor of 2 has a minor effect on the solutions, provided that the asymmetry $k_{hd}/k_{ed} > 2$. For these parameters, the threshold laser pulse energy for switching to the H state is $U_T = 0.8$.

The temporal evolution of n_e, n_h, n_d and T is plotted in Fig. S4 above and below U_T , corresponding to the trajectories shown in Fig. 4 A and B of the main text. Notice that the temperature saturates quite fast while the evolution of concentrations requires a much longer time to reach the H state (Fig. S4 A), and an even longer time towards the C state (Fig. S4 B).

The cooling part of the cycle has so far not been addressed in the model. In principle, we need to discuss the energy relaxation to the lattice bath, (such as in the two-temperature model described in Sec. III) and the eventual thermal diffusion out of the photo excited volume. Including the two-temperature model in the relaxation process (Eqs. (1) and (2)) requires solving them together with Eqs. (7) and (8). In Fig. S4 C we show the calculation of n_e, n_h, n_d , as well as the electronic and lattice temperatures T_e and T_L , respectively for such a model. We observe that for n_e, n_h, n_d qualitatively similar behaviour is seen as in the minimal model.

The stability of the final H state in the final stage of relaxation is protected by the form of the free energy (5), which ensures the stability of a charge ordered state with $n_d \neq 0$ and $\delta q \neq 0$.

Recovery to the ground state ($n_d = 0$ and $\delta q = 0$) involves the introduction or removal of additional periods in the electronic crystal order, which is energetically costly, and is thus inhibited as discussed in the main text. Further discussion of the system evolution in this regime, and associated thermal relaxation is beyond the scope of the present experimental data

set.

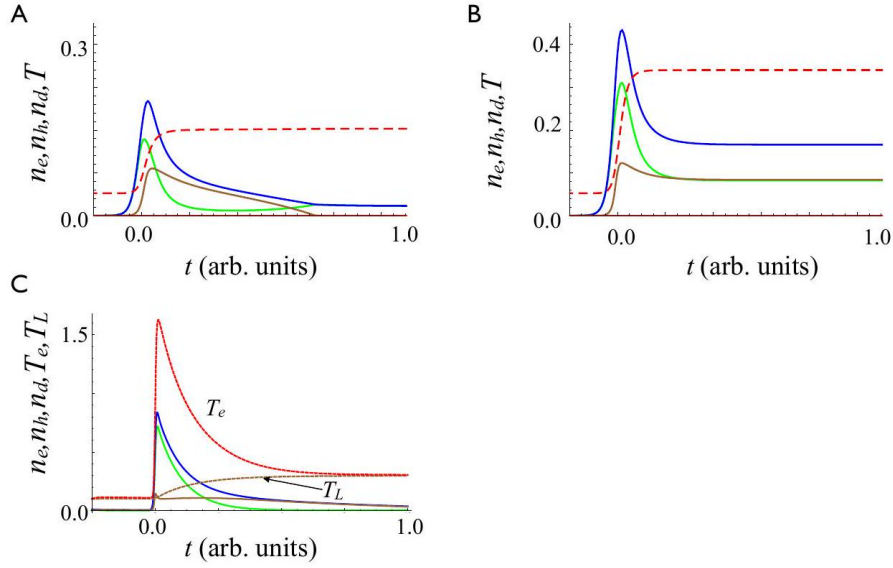


FIG. S4: The calculated n_e (blue), n_h (green), n_d (brown) and the temperature T (red dashed) as functions of time using the equations (7,8) and (9): a) below threshold ($U_W < U_T$) and b) above threshold ($U_W > U_T$). The initial temperature was taken as $T = 0.1\Delta_e/k_B$. The corresponding parametric plots of n_e and n_h are shown in Figs. 3 D and E respectively of the main text. Note that the calculation does not discuss the cooling part of the cycle, so the temperature remains high after all the pulse energy is transferred. In C we show the results of a calculation which includes the two-temperature model (Eqs. (1) and (2)) for $U_W > U_T$. n_e (blue), n_h (green), n_d (brown) are qualitatively similar to the results of the simple model calculation (B). The electronic and lattice temperatures T_e and T_L are shown by the red-dashed and brown-dashed lines respectively.

VI. Bimodal Switching and Power Dependence in Stroboscopic Experiments

Additional insight into the switching mechanism may be obtained from measurements of the dependence of the collective mode spectrum on the laser pulse fluence U_W , particularly near threshold fluences. In Fig. S5 A and B we first show the transient reflectivity and the resulting FT spectra measured by increasing the power of the pump pulse with the standard Pump-probe technique. The spectra do not show any clear switching behaviour. Instead, the spectrum broadens and some spectral weight shifts towards lower frequency. Upon reducing the pump power, the spectrum measured thereafter with low power reverts to the H state spectrum, as shown in Fig. 2 B of the main text. For comparison, we also show the reflectivity transients after exposure to single W pulses with different fluences, measured with standard (low-power) Pump-probe spectroscopy. We observe a clear bimodal distribution for the AM with two modes at 2.39 and ~ 2.45 THz, and no spectral density in between. The higher frequency modes are also shown. The threshold behaviour is quite pronounced.

VII. Comparison of Mode Frequencies Observed by Raman and Coherent Phonon Spectroscopy in Different Phases of TaS₂.

To show that a light-induced structural transition to a known thermodynamic phase is not taking place, we can compare the spectra of the H state (shown in Fig. 2 of the main text) with Raman spectra of all known phases and polytypes of TaS₂ at different temperatures listed in Table 1. From the absence of any correspondence between the published fingerprint

spectra and the measured H state spectrum we conclude that structural switching to any known thermodynamic phase does not take place. Note that the IR modes should not be observable in our coherent phonon spectra, where only Raman-active modes are allowed.

Further, to demonstrate that the H state spectrum is different from the NC state (on cooling) or the T state (on warming), we show the spectra measured by coherent phonon spectroscopy with the Pump-probe technique in Fig. S6. Two major things are different between the NC and the H state: (1) there is no exponential background in the NC state, which is quite pronounced in the H state and (2) the spectrum of the NC state is quite

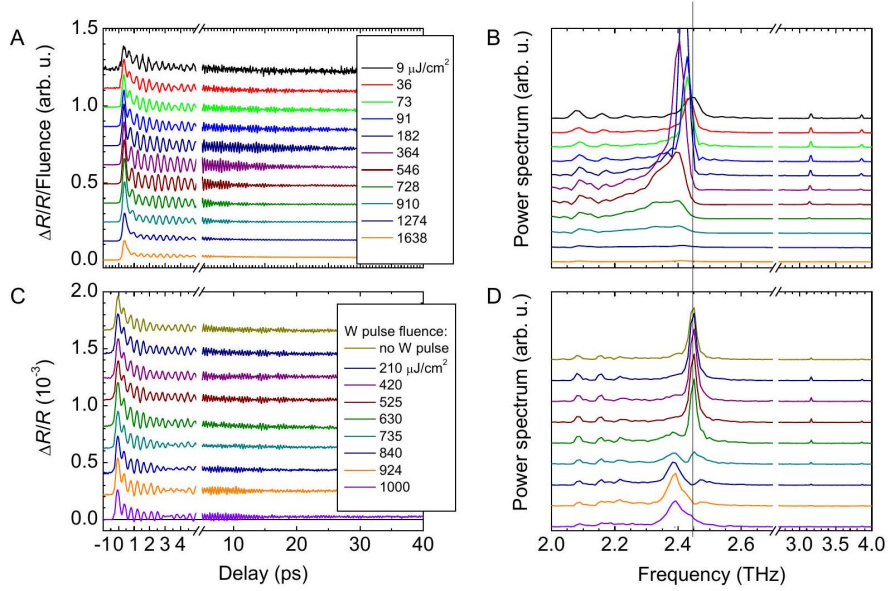


FIG. S5: A. Transient reflectivity traces at different pump power measured by a stroboscopic pump-probe experiment at a 250 kHz repetition rate. B. The corresponding power spectra show a broadening and a shift to lower frequency with increasing pump power. The data are normalised to pump power. C. The reflectivity traces in three-pulse measurements: The fluence of the (single) W pulse is varied, but the measurements are made with a pump-probe sequence with very low pump and probe power. D. The corresponding power spectra show bimodal switching behaviour between 2.39 and 2.46 THz . For W near threshold two distinct modes are observed, but no spectral density in between. All the data were obtained with 50 fs pulses at 800 nm .

different. It is weak, and exhibits a relatively broad spectral feature centred around 2.1 THz . The NC and T states are thus quite different from the H state, which - at least regarding the mode spectra - is more similar to the C state than either of the high-temperature states.

$1T - \text{TaS}_2^*$	$H - \text{TaS}_2$	$1T - \text{TaS}_2$	$1T - \text{TaS}_2$	$1T - \text{TaS}_2$	$2H - \text{TaS}_2$	$4Hb - \text{TaS}_2$	$1T - \text{TaS}_2$
		CCDW	NCDW, $T_c = 310$ K	ICDW, $T_c = 370$ K			CCDW
coh. ph.	coh. ph	Raman	Raman	Raman	Raman	Raman	IR
						19	
					27		
	42 (1.27)						
					48		48
							54.5
		56					
	59 (1.79)						58.5
		62					
	63.8 (1.93)						63
			64			64	
							66.5
		68		68			68
68.9 (2.089)	68.9 (2.089)						
71.5 (2.167)	71.5 (2.167)	71.5				72	72
75.6	75.3	75			75		
		78				78	
	78.9 (2.39)						
							80
81.2(2.46)							
		82					
		84					
		87.5				88	
							89
		92.5					
	96.35	95				96	
	99.7	98.5					100
		103				103	
104.4 (3.165)							
		106					106
		110					
		114					
		119					
							121
		124					
		127					
127.9 (3.875)	127.9 (3.875)						
						129	129
							134

TABLE I: Frequencies of the observed modes in the low frequency region for different polytypes of TaS_2 and their different phases[21-24]. Note that the laser power is significantly lower in timeresolved Pp spectroscopy than in Raman spectroscopy, which can explain the slightly higher frequencies of the coherent phonons compared to the Raman spectra. All energies are in wavenumbers $16 \text{ (cm}^{-1}\text{)}$. The numbers in brackets for the coherent phonons are in THz .

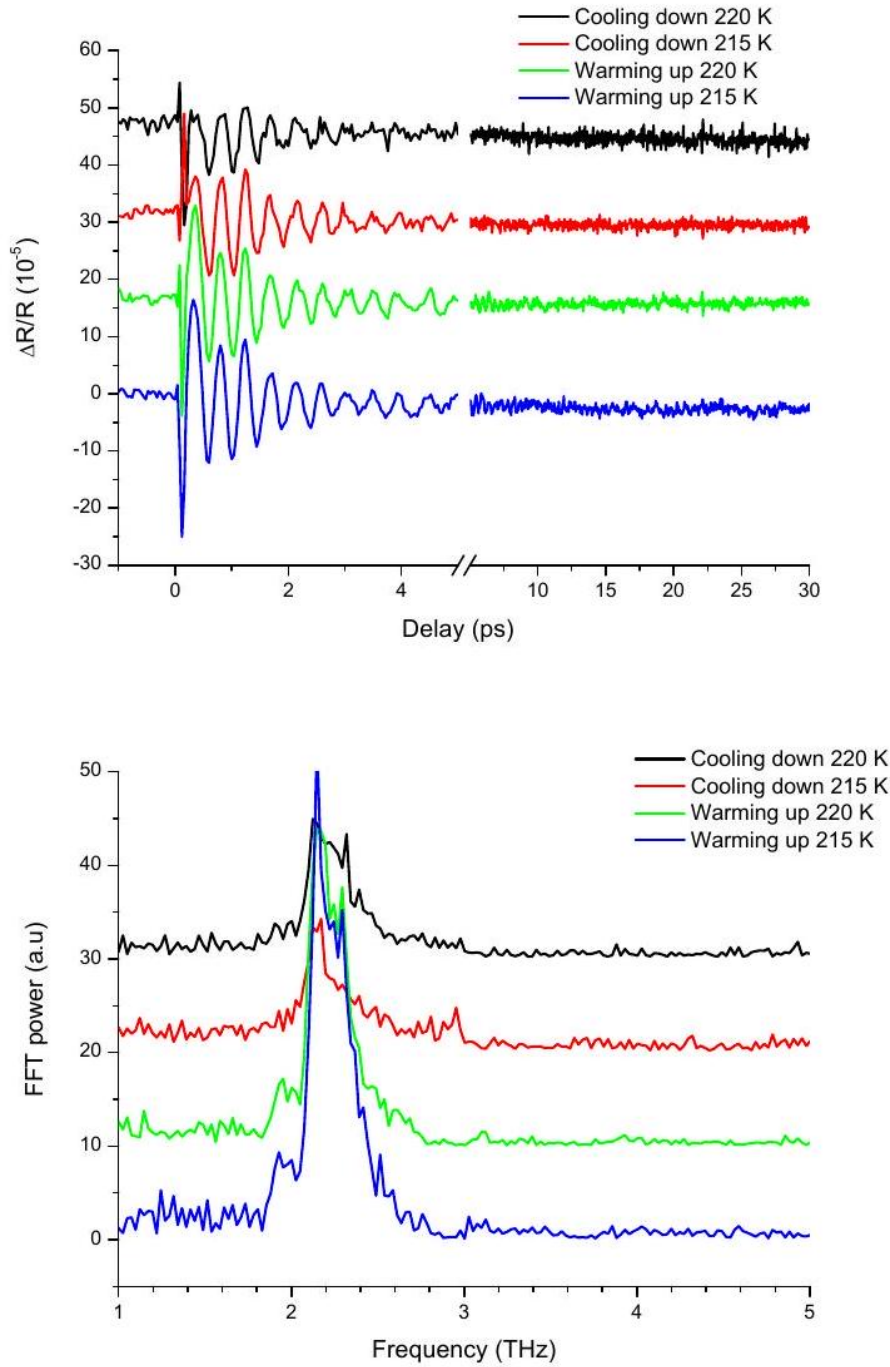


FIG. S6: Top: Transient reflectivity traces at different pump intensities measured by a pump-probe experiment in the NC state on cooling and the T state on warming. Note the absence of an additional exponentially decay component which could be attributed to single particle (SP) excitations. For comparison, the SP spectra are quite evident in the spectra shown in Fig. S5. Bottom: The corresponding power spectra show a relatively broad mode centered at 2.1 THz. Note that mode is not observed in either the H state spectra, or in the C state spectra.

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excita-

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32.2 My Discussion

32.2.1 My Conclusion

32.2.2 Most Important General Questions

32.2.3 My Questions about Their Methods, Statements and Results

32.2.4 Questions about Assumed Knowledge

32.2.5 Things That I Maybe Understood Wrongly

32.2.6 Potential Future Research Directions

33 Fast electronic resistance switching involving hidden charge density wave states by Vaskivskyi, Mihailovic, Brazovskii, Gospodaric, Mertelj, Svetin, Sutar, Mihailovic

Abstract

(intro to physics of computer elements) The functionality of computer memory elements is currently based on multi-stability, driven either by locally manipulating the density of electrons in transistors (how exactly??) or by switching magnetic or ferroelectric order. (how exactly??)

(also switching between metallic and insulating phases can be used in a computer) Another possibility is switching between metallic and insulating phases by the motion of ions, but their speed is limited by slow nucleation and inhomogeneous percolative growth.

(charge density wave system + pulsed current = fast resistance switching) Here we demonstrate fast resistance switching in a charge density wave system caused by pulsed current injection.

(pulsed current changes insulator to unstable metal state with DWs) As a charge pulse travels through the material, it converts a commensurately ordered polaronic Mott insulating state in 1 T – TaS₂ to a metastable electronic state with textured domain walls, accompanied with a conversion of polarons to band states, and concurrent rapid switching from an insulator to a metal. (why is the charge pulse doing so???)

(it is fast, resistance changes a lot, little energy is needed) The large resistance change, high switching speed (30 ps) and ultralow energy per bit opens the way to new concepts in non-volatile memory devices manipulating all-electronic states. (so how they are supposed to work?)

33.1 Article

33.1.1 Introduction

(A first-order transition can provide competing metastable states separated by an energy barrier and therefore hysteresis. This is useful for memory) Systems with first-order transitions between competing states in the phase diagram are obvious candidates for resistive memories. (maybe SRAM is using 1st order ph transition) (why exactly first-order transitions are needed for memory devices???)

(obviously, first 1 or tr do not imply that switching between the states is fast)

(people studied hidden state with laser) In the last few years, pulsed laser experiments have led to an improved understanding of non-equilibrium phase transitions^{1–4} and metastable hidden (H) states^{1–3,5}.

(there are some limitations in optical memory) Optical memory, even though it can be switched with short pulses (35 fs) in charge density wave (CDW) systems² would be severely limited by associated disk-based technology (limited by associated disk-based technology???) .

(what is known about optical memory???)

(there is also a problem of switching of CDW systems) Electrical switching of CDW systems on the other hand has until now met the fundamental problem that injected charge does not directly couple to the order parameter (injected charge does not directly couple to the order parameter??? read something else to understand it) .

(electric field gives motion of CDW) Instead, an applied electric field usually causes an incommensurate (IC) CDW to slide (slide of CDW???)⁶, and in experiments so far the system invariably(=in the same way) reverts back to the original state when the external field is switched off^{7,8}.

(Pulsed current injection means that charge is transported through the sample for a finite time: electrons enter through one electrode and leave through the other, producing electron- and hole-like excitations near opposite contacts. The electrons do not simply accumulate inside the sample, and injection through the stated ohmic contacts does not necessarily involve tunnelling.) In this study we describe ultrafast non-volatile resistance switching with short pulsed current injection in 1 T – TaS₂, where injected charges create domain walls (DWs) via coupling to gradients (coupling to gradients?) of the CDW order parameter, converting the material from an insulator to a metal at low temperatures.

(pulsed current injection = they inject a lot of carriers (el+holes) at ones, which have some current, which is present for some time)

(why not only electrons, but also holes move? are there are formulas for exactly this? which will show that only electrons are not enough to explain physics?)

(promise of ultrafast memory devices) From a technological viewpoint, this opens up the possibility of low-temperature ultrafast memory devices, whose absence has so far seriously impeded progress of ultrafast energy-efficient superconducting computing, for example⁹.

33.1.2 Results

Thermal phases of 1T – TaS₂.

(they analyze 1 T – TaS₂) The experiments were performed on 1 T – TaS₂, which at high temperatures is a simple metal with a single Ta *d* electron (reminder: learn why it is *d* electron???) band crossing the Fermi level.

(temp of ph. trns.) At $T_{c0} = 543$ K, it forms an IC CDW.

(descr. of well-known ph. tr. to NCDW) On cooling below $T_{c1} = 350$ K, in trying to conform with the underlying lattice, the IC structure forms a nearly commensurate (NC) state in which electrons on each 13th Ta atom localize, leading to a regular hexagonal array of NC polaron clusters separated by DWs (illustrated in Fig. 1a).

(descr. of well-known ph. tr. to CCDW) Below $T_{c2} = 183$ K, the DWs vanish and a fully commensurate (C) hexagonal polaronic superlattice forms, which is believed to be a Mott insulator with an energy gap $\Delta_{\text{Mott}} \simeq 0.1\text{eV}$ (refs 10,11).

(IMPORTANT CLARIFICATION OF FIG. 1B!!!!). In Fig. 1b, each curve corresponds to a separate current pulse with a different amplitude. For $I < I_T$, the voltage approaches $V = IR_{\text{HI}}$, and no switching occurs. When $I > I_T$, the voltage initially rises as expected for R_{HI} and then suddenly decreases while the applied current remains approximately constant. This voltage drop therefore indicates the switching $R_{\text{HI}} \rightarrow R_{\text{LO}}$. When the pulse ends, the current becomes zero and hence $V = IR = 0$, but this does not mean that the resistance has immediately returned to R_{HI} . At 150 K, the metastable low-resistance H state persists for approximately $\tau_R \sim 10$ ms, not $10 \mu\text{s}$, before relaxing back to the equilibrium high-resistance C state. Since the pulse itself lasts only $1 \mu\text{s}$, the H state survives approximately 10^4 times longer than the writing pulse. At lower temperatures, its lifetime becomes much longer, and it can therefore behave as a practically stable memory state on the experimental timescale.)

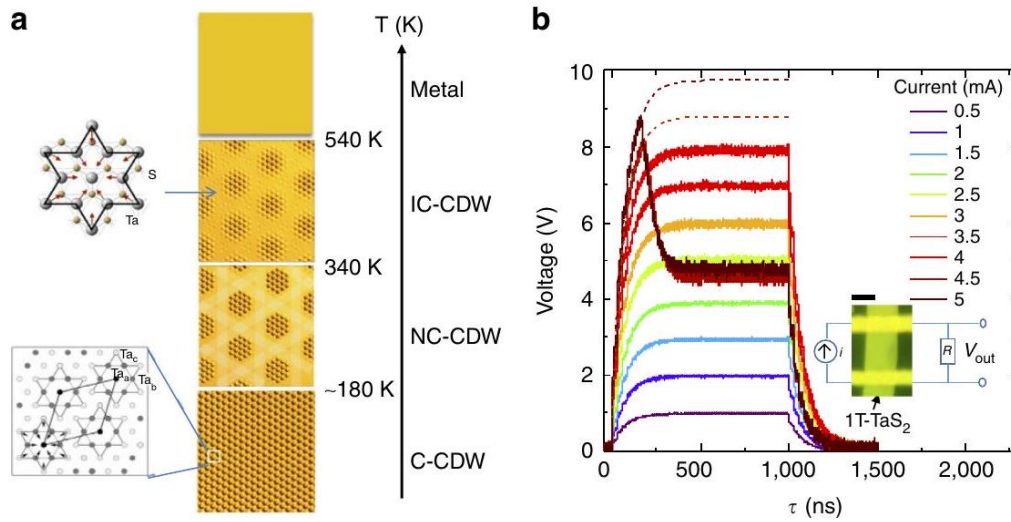


Figure 1 | (phases and switching) The equilibrium phases of 1T – TaS₂ and demonstration of switching behaviour.

(states of TaS₂) (a) An illustration of the different CDW states in 1T-TaS₂ at different temperatures.

(voltage as f. of time when they apply current) (b) Temporal behaviour of switching from HI to LO (high to low) resistance in response to a pulse from a current source.

The extrapolated voltage in the absence of switching is shown by the dashed lines.

(formula for fast rise of V for the case of no switching) The time-response $V_{out} = V \left(1 - e^{-\frac{t}{RC}} \right)$ is determined by $\tau_{RC} = RC$ where R is the two-terminal circuit resistance and changes from 53 to 44 ns.

Fits of the relaxation times show that the difference between τ after switching (=time when R drops) and τ_{RC} (= time at the end during which V goes to 0) at the end of the pulse is < 0.3 ns, setting a limit on the intrinsic speed of the device.

(circuit) The insert shows the measuring circuit.

(small oscillations are kind of noise) The small superimposed oscillations are due to ringing of the circuit. Scale bar, 2μ m.

$$I_0 = I_R + I_C = \frac{V}{R} + C \frac{dV}{dt}.$$

(reminder: $\frac{dV}{dt} + \frac{V}{RC} = \frac{I_0}{C}$)

$$V(t) = I_0 R \left(1 - e^{-t/(RC)} \right).$$

Switching by current pulse.

(low T, one layer and some parameters of experiment) The switching experiments were performed in the Mott state on thin (50-100 nm) single crystal flakes of 1 T – TaS₂ on sapphire substrates, with electrical contacts deposited over the crystal using laser direct lithography, typically $1 - 8\mu$ m apart.

(different pulse lengths were also used, but see SM for them) Electrical measurements were made in the C state with pulse lengths between 1 s and 40 ps (see Methods section, Supplementary Note 1 and Supplementary Fig. 1 for details).

(important plot of voltage after pulse) In Fig. 1b, we show the voltage across the sample at 150 K as a function of time after the application of a 1μ s pulse from a current source for different magnitudes of pulse current.

(*RC constant gives the time of drop of voltage*) At low pulsed currents, the voltage across the sample follows the source, with rise and fall times defined by the RC constant of the circuit $\tau_{RC} = R_{HI}C = 53$ ns, where R_{HI} is the initial (high) value of circuit resistance.

(*this sharp drop of voltage = switching*) With increasing current, above a certain threshold current, the voltage across the sample drops sharply to $\sim 60\%$ of its expected value (dashed) and remains constant until the end of the pulse.

(*switching $\rightarrow \tau_{RC}$ decreases, because R there is smaller*) After switching, τ_{RC} decreases to 44 ns, consistent with the change of sample resistance (to a value designated as R_{LO}) after switching.

(*falling times after switching and at the end of pulse are the same*) Comparing exponential fits with the fall time τ_s after switching and the fall time after the end of the pulse we find that they are indistinguishable from each other to within ± 0.3 ns, defining an upper limit on the intrinsic switching time.

(*also, later the R will go to the previous high R , and here is a time for this switch*) The recovery of R to the initial value R_{HI} occurs within $\tau_R \sim 10$ ms, consistent with relaxation time data at 150 K (*it is about experiment of ref. 5*), which changes with temperature T as $\frac{1}{\tau_R} \propto \exp(-E_A/k_B T)$ (*there is an idea of overcoming energy barrier of the free energy, so the time is connected to this probability, this is why this formula is such*), with $E_A = 280 \sim 2,300$ K (*it is meant E_A/k_B . maybe the substrate gives such a big range of values, see cited papers to be assured in it*) (*why there is such a big range?*) (*why is $E_A = 280 \sim 2,300$ K so? derive.*), depending on the sample substrate⁵, k_B is the Boltzmann constant.

(*they use different pulses and measure R init. and fin. to get switching speed*) To investigate the switching speed, we apply current pulses of different duration and measure the initial and final resistance with a low current after each pulse.

(*they used standard electrical pulse generator and metal-semiconductor-metal pulse source + laser (fig. 2c)*) For $\tau_{\text{pulse}} > 25$ ns, we used a standard electrical pulse generator, whereas for $\tau_{\text{pulse}} < 25$ ns we used a 35-fs optical pulse-triggered 30 ps risetime (~ 40 ps full width at half maximum) metal-semiconductor-metal pulse source with the 1 T – TaS₂ sample mounted in a $50 - \Omega$ transmission line circuit (shown in Fig. 2c).

(*for currents about some threshold, there is no dependence on how R drops on the length of a pulse (before $\tau_{\text{pulse}} < 0.1$ s)*) Remarkably, provided that $I > I_T$ (*it should be provided that $I < I_T$*), we observe switching between R_{HI} and R_{LO} , irrespective of the duration of the applied pulse over the interval $40\text{ps} \lesssim \tau_{\text{pulse}} < 0.1$ s (summarized in Fig. 2a).

(*higher times $\rightarrow$ less switching to low R state, then no this switching*) For $\tau_{\text{pulse}} > 0.1$ s, switching is incomplete (*how is it, incomplete?*) and does not occur at all for $\tau_{\text{pulse}} > 1$ s.

(*now, at low T we can have a material in low R state. low R switches to high R for long pulses in time*) Repeating the same experiment, but starting in the low resistance state R_{LO} , switching from R_{LO} to R_{HI} occurs for $\tau_{\text{pulse}} > 0.1$ s (Fig. 2b).

(*switching forward is for $\tau_s < 30$ ps, since this pulse is already enough to get the switching*) The implication of these measurements (*=from this we can conclude that*) is that the $R_{HI} \rightarrow R_{LO}$ switching is caused by the leading edge of the pulse, in a time $\tau_s < 30$ ps.

(*reminder: switching back to high R happen for 10 ms times (at 150K). The HI-to-LO transition already occurs for the shortest pulses, whereas long pulses suppress this transition and can return an initially LO sample to HI through Joule heating. Therefore, writing is attributed to the leading edge of the pulse.*)

(*also this pulse heats the system a lot, and this higher T state easier relaxes, because with higher T, it is easier to get through energy barrier to local minima, where there is a high R*) On the other hand, the reverse switching $R_{LO} \rightarrow R_{HI}$ with $\tau_{\text{pulse}} \geq 0.1$ s is consistent (*consistent = so this amount of heating can be from this current and change of R , maybe someone will derive*

it later) with Joule heating above 100 K, where the lifetime is sufficiently short to relax the H (=hidden) state (where there is a low R)⁵.

(labels write (W) and erase (E)) We label the two cycles described above as write (W) and erase (E).

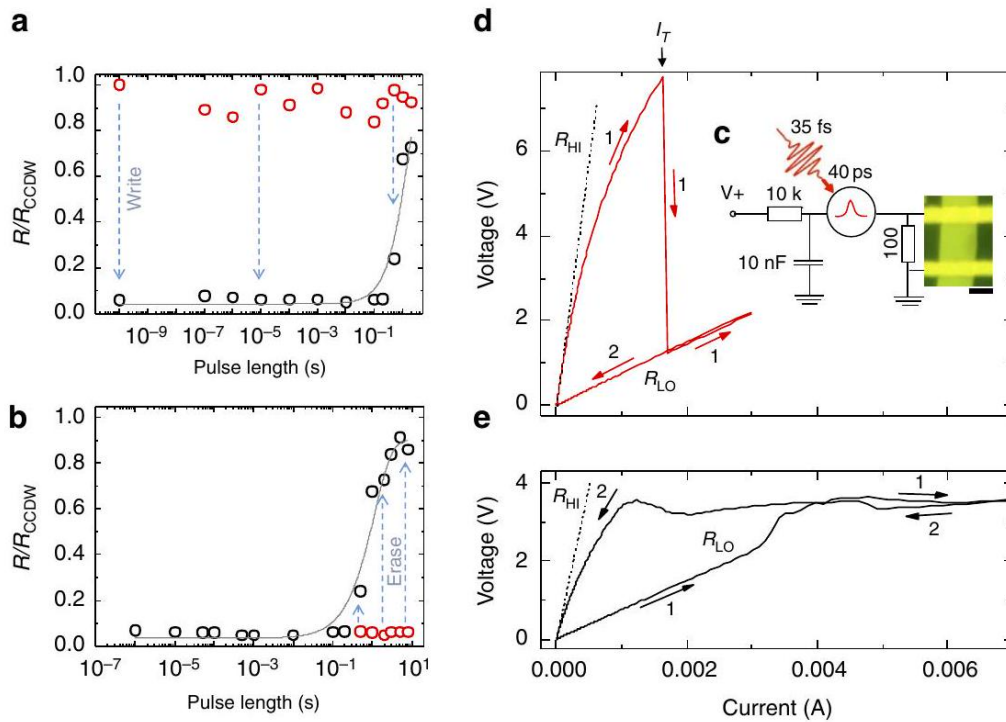


Figure 2 | Switching speed and threshold behaviour.

(how R goes to low values for different pulses) (a) Switching resistance ratio measured with a single pulse above threshold I_T , each time starting from the HI resistance state (red circles). (some maybe experimental errors are the reasons why red circles are not at one line. GPT can give a lot of potential reasons)

Black circles show resistivity after current pulse.

(how R goes to low values for different pulses. not always we get to the high R at all) (b) Erasing with 1-s pulses, each time starting from the LO resistance state (red circles).

Black circles show resistivity after applying erase pulse.

The data were obtained by alternating write/erase cycles and increasing the pulse length.

(circuit for fast pulses) (c) The circuit used for the 30-ps measurement with an metal-semiconductor-metal (MSM) device as the current source.

(d) The voltage V measured during each pulse, first incrementally increasing and then decreasing the pulse current I , shown by paths (1) and (2), respectively.

Above the threshold current I_T , V abruptly drops between two consecutive current values.

(increase current and then decrease, look at V) (e) Same as in d, but starting from the low resistance state increasing I_{pulse} along path (1) and then reducing I_{pulse} along (2).

(mistake in the article! there is 14K in the text, but 20K in the caption) In all cases $T = 20$ K and the pulse length was 10μ s (in the text it is written that it is 50μ s). Scale bar, 2μ m.

(reminder: threshold current is the current when there is already a switch to low R just because of the current)

(we'll test many currents) To systematically measure threshold current I_T , we incrementally increase and then decrease the current pulse magnitude, while simultaneously recording the voltage across the sample.

(we apply a lot of pulses of a current of different strengths and measure V , we get fig. 2d. the sys is stayed in the final state with new R after this current) The resulting hysteretic $I - V$ curve measured at 14 K for a 80-nm-thick crystal with $8\mu\text{m}$ between inner contacts and $\tau_{\text{pulse}} = 50\mu\text{s}$ is shown in Fig. 2d.

Before switching, the $I - V$ curve shows an unusual exponentially increasing I with V :

$$\frac{I}{I_0} = \exp\left(\frac{V}{V_0}\right). \quad (1)$$

(it is like log, if we look at $V(I)$)

(then there is a drop) Increasing I beyond a critical value I_T , we observe a sharp drop in V .

(then linear curve) Thereafter, the $I - V$ curve becomes ohmic over a large range of I .

(we got this little R) On the return cycle (and subsequent cycles as long as $I < 2I_T$), the $I - V$ curve is linear, with a slope $R_{\text{LO}} = \left[\frac{dV}{dI}\right]_{I \rightarrow 0}$ (it is not just $R = V/I$, because actually the law is more general, $V = RI + V_{\text{offset}}$ or there could be some exper. errors because of V_{offset} . a lot of tiny reasons can give this error, it is not worth of thinking about it. maybe even fundamentally this tiny R should be there...) at the origin that is two to three orders of magnitude smaller than R_{HI} in the C state (Fig. 2a).

(same for low $R \rightarrow$ fig. 2e) Repeating the measurement cycle, but starting with the sample in the low resistance state R_{LO} , the response departs from linearity beyond $I \sim I_T/2$ (Fig. 2e).

(see fig. 2e, slow increase of V , then it is nearly constant) Thereafter, V increases very slowly with I , becoming nearly independent of current above 4 mA.

(descr. of back cycle of 2e) In the return part of the cycle, the nearly I -independent behaviour remains until $\sim 1\text{ mA}$, whereupon the system reverts to the original C state with R_{HI} below 1 mA.

(see also SM) More details are presented in Supplementary Fig. 2.

Temperature dependence of the switching.

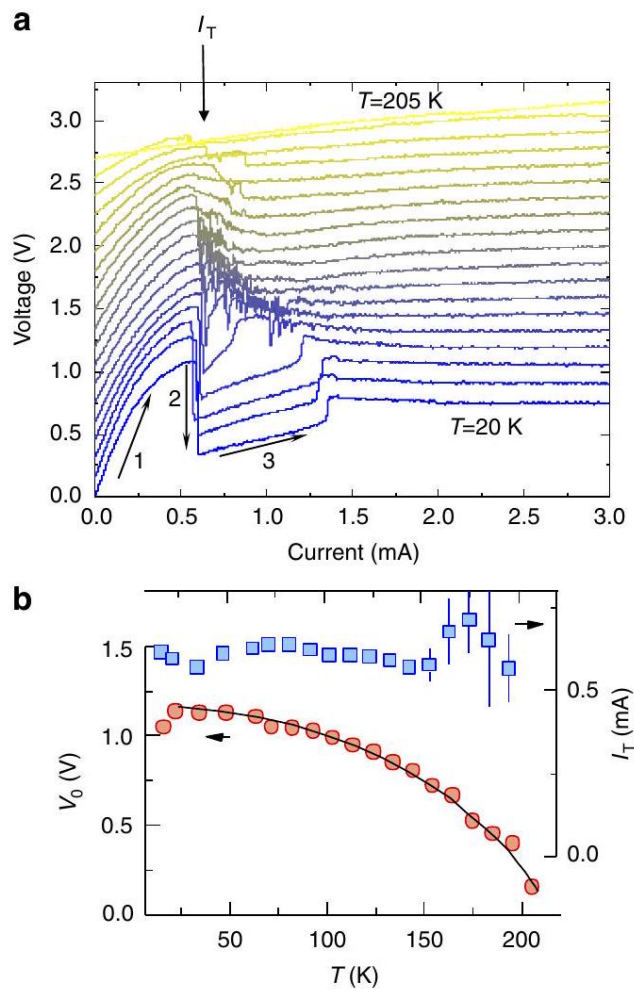


Figure 3 | The T-dependence of switching.

(V-I for diff. T) (a) The pulsed V-I characteristic as in Fig. 2, measured at different temperatures and at 10 K intervals with $\tau_{\text{pulse}} = 50\mu\text{s}$.

(the same experiment was done) The $V - I$ curve is measured in pulsed mode, by increasing the current incrementally and measuring the voltage at each point.

The resistance drops sharply in a few consecutive measurements at the critical value of I_T .

The sample was reset in between each $V - I$ curve by heating it above 310 K and then cooling down to the indicated temperature for the next measurement.

(b) (two plots as function of T. the word "current" is for 3a plot, not for I_T) I_T and V_0 as a function of temperature. (note that currents are above 0.5 mA! the Y axes goes up.)

(errors for I_T) Error bars are obtained from fitting the data with the exponential function.

(all here will be about fig. 3. Reminder: before, we had this plot only at 14K, now, there are a lot of them for other temperatures) The temperature dependence of the switching is shown in Fig. 3a for $20\text{ K} < T < 205\text{ K}$.

(details of state of sample preparation: it was slowly cooled in the beginning) For 150 K and below, each curve is measured on a freshly ordered CDW state, prepared by slowly cooling the sample from 150 K to the indicated base temperature before each measurement.

(obvious sentence, we know that T is in range from 20 to 205, so T is also in range 150 and 205) Above 150 K, the temperature was gradually increased.

($T < 55\text{K} \rightarrow$ there is a switch) For T up to $\sim 55\text{ K}$, the behaviour is similar to that described above for $T = 14 \sim 20\text{ K}$ (Fig. 2d,e).

($55 < T < 165\text{K} \rightarrow$ bigger I_T , fluctuations of voltage) In the range $55 \sim 165\text{ K}$, an instability is observed above I_T , where the voltage fluctuates with each pulse between R_{HI} and R_{LO} .

($T > 165\text{K} \rightarrow$ fluctuations and switching slowly disappear) Above 165 K , these fluctuations disappear and the switching ratio $R_{\text{HI}}/R_{\text{LO}}$ eventually disappears completely above 195 K .

(fit and critical current is on fig. 3b) The T -dependence of I_T and V_0 (V_0 is just a constant scale for the V in the fit formula) obtained from a fit to the data using equation (1) is shown in Fig. 3b.

(V drops, I_T is almost a constant) Remarkably, fits to the $I - V$ curves below threshold show that I_T is almost completely independent of T , whereas V_0 gradually drops with T .

(there is also info in SM) (The details of the fitting are given in the Supplementary Note 2 and Supplementary Fig. 3.)

(maybe there is still a low R state, but it can decay so fast, so we can't measure it) The latter behaviour is probably not entirely intrinsic, as at high temperatures the measurement time becomes comparable with the relaxation lifetime τ_R of the low resistance state⁵. (measurement time = whole time of a one experiment, when we do all measurement)

(at high T -s, high currents, dV/dI changes from negative to positive slowly) We also note the rather remarkable behaviour in Fig. 3a at high currents, displaying a cross-over from negative differential resistance (DR) through zero DR to a slight positive DR with increasing temperature up to 200 K .

33.1.3 Discussion

(intro) Before discussing the switching mechanism, we first highlight the unusual observations.

(REMINDER: THERE IS NO CLEAR EXPLANATION OF WHY EXACTLY CURRENT GIVES THE SWITCH)

(it is not because of dielectric lines inside the material because it is fast and all the system is changed) The switching is remarkably fast and works as a latch(=a mechanical or electronic fastener used to hold something shut or store data) with a very sharp current threshold, which cannot be associated with dielectric breakdown into filamentary(filament = thin, flexible thread, wire) paths(=conducting lines in this material) involving ionic motion (there are several atoms or defects which move), as in chalcogenide glasses^{7,12}, manganite Mott insulators¹³ or band insulator memristors such as TiO_x (ref. 14)(= in some other materials it is present) (how do they know that in some other materials it is present?) .

(The authors argue that the low resistance is not caused only by conduction along narrow DWs. According to their interpretation, the commensurate domains between the DWs also become metallic, so the resistance of the entire switched state decreases. nothing is explained about it)

(also, it is not confirmed that the total material is homogeneously dielectric. this is the view of authors)

(some other effects are also not there) Zener tunnelling and avalanche breakdown can also be eliminated, because they do not exhibit metastability(=can't have this switchings) .

(some sliding and de-pinning are ruled out) The pulsed $I - V$ curve below switching threshold is also qualitatively different from the observed behaviour for sliding and de-pinning of a CDW^{6,15,16}.

(dissipationless CDW sliding conductivity may occur in this material) On the other hand, well above I_T , the negative DR behaviour gradually crosses over to a small positive DR with increasing temperature, which is reminiscent of dissipationless CDW sliding conductivity (Frölich

conductivity) observed in blue bronze at similar current densities ¹⁷.

(there were other switching experiments, but with optics) In previous optical switching experiments, electrons (e) and holes (h) are homogeneously photoexcited and spatially overlapping ².

(before: spectral analysis was also done (for photoexcited H state) showed one peak -> the material is macroscopically homogeneous in this state) The combination of narrow spectral width and unchanged spectral intensity of the collective amplitude mode in the photoexcited H state compared with the C state indicate that the two states are comparably homogeneous. (think more about this argument that tight peak means only macroscopically homogeneous system. why? draw examples) (where is this plot of spectra?)

(so, there should not be a macroscopic inhomogeneity, only a microscopic one. this somehow stems from the prev. experiment)

(now something it is not a photoexcitation, so we'll have inhomogeneous state. it is not clear what exactly is different here) Presently, the e and h(which are already not created by laser, but by tunneling to and out of the material) are spatially separated at either electrode so the optical mechanism does not apply and we expect the structure to be less homogeneous. (I don't really understand this argument, homogeneous or not electrons and holes, I'll read the cited paper if needed)

(actually, we know just the STM of it, so we know DWs) Scanning tunneling microscope (STM) images of the sample surface after current injection (Pulsed current injection means that charge is transported through the sample for a finite time: electrons enter through one electrode and leave through the other, producing electron- and hole-like excitations near opposite contacts. The electrons do not simply accumulate inside the sample, and injection through the stated ohmic contacts does not necessarily involve tunnelling) by an STM tip confirm this: they show an irregular meander(=winding curve or loop in a river for example) of DWs rather than a regular array of DWs (see Supplementary Figs 4 and 5) ^{18,19}.

(different pulses create different different DWs -> diff. Rs) In our experiments we find that different R_{LO} with different relaxation properties can be reached with different pulse voltages near threshold (see Supplementary Note 3 for a few examples), indicating that different DW configurations can be created under different conditions.

(also, there is a free energy and maybe we have electron glass) The free energy landscape of H states in 1T- TaS₂ clearly has multiple minima-consistent with the notion of an electronic glass(revise this theory of electronic glass) .

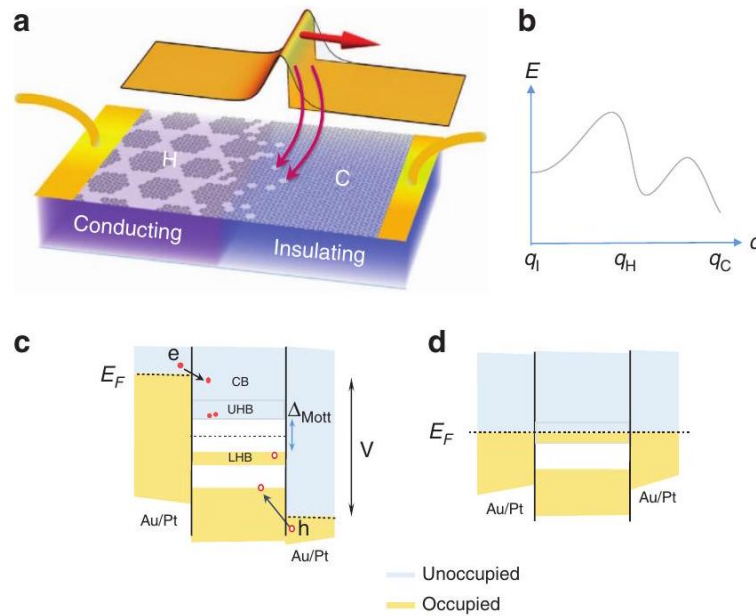


Figure 4 | An illustration of carrier trapping and DW formation after carrier injection.

(a)(how current creates H state) The injected charges are trapped in the C structure causing the formation of a textured glassy electronic state.(they confused and draw H state as symmetric NC state by the way)

(organe - current, red - direction of traveling) The charge density ρ is depleted at the leading edge of the pulse as it travels through the sample.

(b)(sketch of free energy which they imagine) The free energy as a function of CDW wavevector based on the model of Nakanishi and Shiba²⁰ (I am not sure that it is possible to prove that that confusing article give approximately this free energy) .

(q for left and right E .) (nothing is written about if it should be a function of q or of n , maybe there is some complicated transformation) q_C and q_I are the q -vectors of the undoped commensurate (when there are no extra carriers) and IC states, respectively.

(H state has a vector btw both before) The q -vector in the H state q_H is determined by the density of carriers forming the DWs.

(band structure at high R (c) (when there is already a V, but not I yet) and low R (d) state. this is what they imagine) (c) A depiction of the charge injection at the electrodes in the C state and (d) the band structure after the Mott-to-band state conversion process.

(q is an effective wave vector of CDW. if we speak about H state, we average it. If there is a DW, then there is a gradient of phase, which adds effectively to the q . also, existence of DW is reflected in density n , this is why q is connected with n)

(coupling to CDW: $\sim e \left(\psi \frac{\partial \psi^*}{\partial x} \right)$) From a Landau theory viewpoint, charge (=extra charge that is injected by current) cannot couple directly to the order parameter ψ of the CDW ($\psi = Ae^{i\phi}$ is the complex CDW order parameter, not the charge density itself. The physical density modulation can be written schematically as $\rho(\mathbf{r}) = \rho_0 + \text{Re}[\psi(\mathbf{r})e^{i\mathbf{Q}\cdot\mathbf{r}}]$), but can couple through Lifshitz-invariant spatial gradient terms in the free energy $\sim e \left(\psi \frac{\partial \psi^*}{\partial x} \right)$, which are present at DWs. (learn this theory of free energy. it is another big topic. some ideas of invariance are here.. I haven't seen this theory and this terminology (Lifshitz-invariant spatial gradient) yet)

(current creates DWs, this is another paraphrasing of it.) We propose that as the pulse of charges propagates through the sample, the energy of the system is lowered by charge carriers dynamically creating DWs.

(DWs are actually more charged than CCDW around them and repel) As the DWs are charged (with respect to the CDW background), they repel each other, creating a periodically textured stripe structure, an effect that is well known in correlated electron systems.

(suddenly, we also discussing periodicity of DWs)

(DON'T LOOK AT THEIR SM, THERE IS A WEAK AND UNCLEAR THEORY. THEY DON'T HAVE A GOOD THEORY, JUST A TOY MODEL WITH AN IDEA WHICH DOES NOT PREDICT ANYTHING NEW)

(free energy is complicated and has a lot of minima even without current) The free energy F for such a system includes terms from the IC CDW formation and the DW repulsion, and has a number of minima, corresponding to states with different CDW and DW order (Fig. 4b) already in the absence of additional charge ²⁰. (²⁰ is a strange paper with complicated formulas)

(they somehow show in SM that extra charge changes system to periodic DW array. I looked at it and I am not convinced that it is a real derivation. there are a lot of words and few formulas, I don't see how their theory is connected to their cited papers) In the Supplementary Notes 4-5 and Supplementary Figs 6-7, we consider the situation in detail, showing that on charge injection the C state is unstable towards the formation of a periodic DW array, IC with the underlying lattice structure.

(here, it looks like an imitation of explanation, nothing is explained, we still don't know anything about $F(n)$) The origin of this instability lies in the negative curvature of the inverse compressibility $k = d^2F/dn^2 < 0$ arising from the shape of $F(n)$, which in turn is a consequence of the Coulomb repulsion between DWs.

(they continuing imagining their free energy, but now as function of effective CDW wave vector q . for some q it is C, for some H phase) The periodicity of the DWs is directly related to the injected charge density $n_i = n_e - n_h$: the resulting structure is commensurate if $n_i = 0$ and IC otherwise, with a wavevector $q_H = n_i/\pi$ corresponding to the minimum in the free energy (Fig. 4b).

(they imagine DWs as periodically ordered and connect it with the density of state) The DW structure in the current-injection-induced H state is thus similar to the NC state, but with a periodicity that depends on n_i .

(they think that maybe there are a lot of charges, so a lot of DW structures will give something which is seen in experiment, where there are approximately random DWs) Inhomogeneity of charge injection will naturally lead to spatially inhomogeneous DW structures observed in experiments.

(they also imagine all the material metallic(because of some STM/STS reports gap closure inside DWs). they think that for some reason CDW inside DWs should also be metallic. it is just their guess. Also, the proposed microscopic conversion of localized polarons into conducting band states is an interpretation rather than a derived mechanism.) Nevertheless, the state conversion from polarons to band states means that it is not only the DWs, but the entire state that is metallic.

(simple homogeneous one-band Mott-Hubbard picture -> no DWs) Microscopically, a simple Mott-Hubbard picture ²¹ is inadequate for a description of the DW formation ¹⁸. (why "Mott-Hubbard picture -> no DWs"?)

(Mott-Hubbard + Coulomb -> some insights about DWs) However, if we also take into account the effect of long-range Coulomb repulsion and consider pulsed carrier propagation through a commensurate polaronic crystal (Fig. 4a), we can qualitatively understand the origin of the textured state(state with DWs) also from the microscopic viewpoint.

(if we put electrons to the sys, they lose energy very fast) The carriers launched at the electrodes first lose their excess energy $eV = E_e - E_h = 1 \sim 10\text{eV}$ (Fig. 4c,d) within $< 1\text{ps}$.

(avalanche multiplication factor is produced) Taking into account scattering and energy loss to phonons of these energetic carriers gives an avalanche multiplication factor (avalanche multiplication factor???) $f_m \sim \frac{(E_e - E_h)}{\Delta_{\text{Mott}}} = 10 \sim 100$. (f_m takes into account that 1 carrier (el or hole) can create 10-100 carriers. Somehow. This is their imagination without any reasoning) (also check notation of n , is it a density or a number of carriers? maybe it was before the density)

(order-of-magnitude estimation of carriers in the system by the end of a pulse) By the time the e and h reach the upper Hubbard band (UHB) and lower Hubbard band (LHB), respectively, the number (same notation, but a different value, now n is not density) of carriers injected by a 40 – ps pulse is $\sim n_i \simeq \frac{f_m}{e} \int_0^{\tau_{\text{pulse}}} V/R_{\text{HH}} dt = 10^6 \sim 10^7$.

(there are holes, they can annihilate with CDW standing electrons, thus voids can be created. again, it is just an abstract idea, no formulas are written) Occupancy of the Hubbard bands is unstable, so as they propagate in the applied electric field, the holes annihilate with the localized electrons at the centre of each polaron, leading to the creation of voids in the polaron lattice, accompanied by a dynamic conversion of polaronic (Mott-Hubbard) states to conducting band states as the wave travels through the sample (Fig. 4a).

(The cited STM experiment found that only one voltage polarity efficiently created the textured state. This polarity dependence was interpreted as evidence that hole accumulation is more effective than electron injection, although heating and transient electron injection were not completely excluded.) (I am not sure about it, if needed see cited paper) (STM studies suggest that electrons are not expected to show the same effect as holes¹⁸.)

(how to find out, if we have a motion of el-s or holes?)

(somehow they calculated holes from STM of the DW state, and it is a big number) From the STM images (see Supplementary Note 6 for details), the number of holes n_h that can be accommodated in the DWs is very roughly between $\sim 1/4$ and $1/3$ of all the available polaron sites; thus, for our typical sample of volume $3\mu\text{ m}^3$ we estimate $n_h \approx 10^6 \sim 10^7$.

(this number of holes is similar to that one unjustified number before, which was obtained from current + multipl. factor) This is consistent with the number of injected charges in the pulse n_i .

(reminder that hidden phase is not homogeneous) However, rather than forming a homogeneous patch of voids at the electrode, as a result of the Coulomb interaction, a textured state forms (Fig. 4a).

(reminder that DWs form very fast) The time for such an DW state to form after melting is known to be $\tau_{\text{form}} \sim 1\text{ ps}$ (ref. 22), which is consistent with the observed speed of the switching process.

(DWs (which give R) are maybe formed by the carriers in the leading edge of the pulse) The observed independence on pulse length can thus be understood: the DWs are formed by the carriers in the leading edge of the pulse. (why DWs are formed by the carriers in the leading edge of the pulse? it is not explained theoretically, it is just from different pulses)

(repetition of the conclusion from fig. 2a) Above a certain threshold, the entire sample is converted and further added charges have no additional effect; thus, the trailing edge of the pulse has no further effect.

(The authors attempt to explain the sub-threshold exponential I – V curve by tunnelling of individual carriers through a hypothetical real-space electrostatic barrier produced by a charged DW. This is distinct from the collective barrier in the free energy $F(n)$.) Importantly, the unusual exponential I – V curves below threshold described by equation (1) can be understood within this picture in terms of carrier tunnelling through barriers (which tunnelling through barriers???) resulting from the transient DW structure.

(useless formula for intermediate quantity for the current. we know how current grows, so

we tune this model to explain it, and this is a very approximate formula, which is consistent with the current) We show in the SM that the tunnelling("tunnelling" is in British English) rate within such a state leading to equation (1) is $R \sim \exp(V/V_0)^\beta$ (it is not explained, if β is inside or outside of the exp, most likely inside) where $\beta \sim 1$, where the barrier energy V_0 is related to the C state order parameter, giving rise to its T -dependence shown in Fig. 3b.

(connection of current and tunneling rate:

$$dQ = e\Gamma dt.$$

$$I = \frac{dQ}{dt} = e\Gamma.$$

then they do a big approximation to WKB without much explanation.)

(maybe here they have another barrier, not for the free energy, but for electron in the charged DW (such that it is a parabolic potential), it should tunnel through barrier that depends on the strength of CDW, and the tunneling rate gives the current. BUT WE DON'T SEE ANY BARRIER AT THE EXPERIMENT, WE KNOW NOTHING ABOUT IT)

(anyway all this theory is unusable for explanation of why we have such a fast switching)

(repetition of intro that they obtained something important) The experiments introduce a paradigm of all-electronic switching between CDW states for data storage applications beyond current concepts^{12,14,23–28,29}.

(maybe one can create a net of such memory elements) Devices based on CDW state switching in 1 T – TaS₂ could be scaled and integrated into commonly used cross-bar configurations³⁰. (maybe here is an important citation about how to use such memory element to create more than 1 bit memory)

(the write speed is very fast) The demonstrated write speed ~ 30 ps is externally limited, but is an order of magnitude faster than the previous record for non-volatile memory^{14,25}.

(maybe the real switch is way faster) The intrinsic speed appears to be < 1 ps. (GPT said that the work by Eichberger et al. explains what this limit is?)

(they also propose these devices to be small and not energy costly for writing) With $\tau_W = 30$ ps, the expended energy per bit is estimated to be $E_B < \frac{\tau_W V_T^2}{R_{HI}} = 0.25$ pJ (that formula for power $P = V^2/R$) (this energy will finally be transferred to heat) for a device with an area $2 \times 2 \mu\text{m}^2$ (shown in Supplementary Fig. 8), which is extremely small, comparable with current magnetic random access memory (MRAM) devices³¹. (discussion of possible sizes is not present. we don't know the smallest possible size of it)

(just idea about why we are not using shorter pulse of a current: here is an unclear idea that we need to transfer some charge to get the material switched. so they could use shorter pulse, but then there should be more charge per fraction of second. this can break the device, so they just use 30 ps pulse. but maybe it is not fully true and we don't need to increase charge linearly if we decrease time of a pulse to keep switching...)

(smaller device -> less energy will be needed) As both V_T and R_{HI} scale linearly with distance between contacts (see Supplementary Fig. 9), E_B scales linearly with size along the contact direction and can be reduced by making the devices smaller.

(it can be a memory device) From a practical device viewpoint, it functions as a latch at low T .

(erasing also can be done fast and it heats the sample) The reverse $M - I$ transition is caused thermally, which requires that the device is heated momentarily above T_{c2} (sounds like a problem) - which can be done on a sub-nanosecond timescale with appropriate design²⁵.

(somehow in general it is maybe possible to erase a lot of cells at the same times, so erasing speed shouldn't be a problem) Moreover, in practical devices bulk Erase is used where entire blocks are erased simultaneously; thus, E speed is not a limiting device operation speed.

(temperature range is a problem) The device operating temperature appears to be limited by T_{c2} (Fig. 3a).

(maybe if you add Se, the T_c will be higher.) It is known that this can be increased significantly by Se substitution: $1\text{ T} - \text{TaS}_{1.5}\text{Se}_{0.5}$ has a $T_{c2} > 300\text{ K}$ (ref. 32), introducing the possibility of room temperature operation, whereas the relaxation time τ_R has been recently shown to be controllable by compressive strain⁵ tuning the data retention time of the device. (they didn't use this material for their experiment. they don't explain why? sounds like a nice idea of the next paper: the same but for the better material with higher T_c) (no explanation and further comments about this new material are given)

(so a lot of people are working on memory devices, it is a big special field of condensed matter. a lot of ideas and slight improvements are done there constantly. maybe someone is using this information really for creation of memory devices)

33.1.4 Methods

Sample preparation

(obtaining a sample) $1\text{ T} - \text{TaS}_2$ crystals were grown by chemical transport method with iodine as a transport agent with the average lateral dimensions $1 - 5\text{ mm}$ and thicknesses $\sim 100\mu\text{ m}$.

(obtaining a layer) Thin flakes were obtained from single crystal by exfoliating with sticky tape.

(substrate) The obtained $50 - \text{ to } 100\text{-nm-thick}$ flakes were deposited on sapphire substrate.

(how electrodes were put) Four gold electrodes were deposited on top of the flake by laser-direct lithography with initial 10-nm-thick Au/Pd layer.

Electrical measurements

(how V was measured) DC transport measurements were performed using standard four-point technique (four-point technique???? 15 min maybe is enough to learn what is it, but it is not important now) .

(always they started in CCDW state (high R), obviously, because this is the idea (fig. 1b)) All switching experiments were performed starting from the C Mott phase by applying single electrical pulse.

(device for production of long current) The pulses in the range $100\text{ ns} - 1\text{ s}$ were produced by a standard pulse generator.

(device for production of short current) For $40 - \text{ ps}$ full width at half maximum pulse we used metal-semiconductor-metal current source triggered by a $35 - \text{ fs}$ laser pulse.

33.2 My Discussion

33.2.1 My Conclusion

33.2.2 Most Important General Questions

Is this development going somewhere now? If no, why?

(????? I'll think later. seems that no, it is an advanced question)

Comparison with conventional computer memory.

Writing to an SRAM processor cache typically takes approximately $0.5 - 2\text{ ns}$, whereas random access to DRAM takes approximately $50 - 100\text{ ns}$.

Neither SRAM nor DRAM requires a separate erase operation, since a stored bit is erased simply by overwriting it.

In an NVMe solid-state drive, a write request typically takes 10–100 μs , while programming a NAND page may require 0.1–1 ms, and erasing a NAND block takes approximately 2–10 ms.

By comparison, the current-induced transition in $1T\text{-TaS}_2$ occurs within approximately 30 ps. However, this value describes only the physical switching of an individual experimental device and does not include addressing, driving, and readout circuitry.

The demonstrated erase process is considerably slower: spontaneous recovery at 150 K takes approximately 10 ms, while electrically induced thermal erasure requires pulses of approximately 0.1–1 s. Thus, the device demonstrates exceptionally fast writing but a much slower and highly asymmetric erase process.

what are the limits of size of this memory cell?

maybe 10-100 nm, since we need several SODs.

This is an unanswered question.

So how to store/read memory in it?

Is it finally known, why the current gives the switch?

(??? check some future articles)

So how to create an array of memory of such elements?

(it is not explained, I can only guess)

So how to create a computer from it?

Comparison of the proposed CDW memory cell and they already working one

(??? I'll compare later, what is better, what is worse?)

Comparison of the proposed CDW memory cell and they already working one

(??? I'll compare later, what is better, what is worse?)

Who needs the ps memory and why?

(maybe no one needs it, this is what I know now)

(GPT:)

1. **Developers of superconducting digital computers.** Josephson-junction logic can operate on picosecond time scales, whereas conventional memory would become a speed and power bottleneck. A fast cryogenic memory could therefore store intermediate results without forcing the processor to wait.
2. **Developers of cryogenic control electronics for quantum computers.** They need classical memory close to the quantum processor for instructions, calibration parameters, and measurement results. Here the principal advantages would be low-temperature operation, non-volatility, low dissipation, and reduced wiring; picosecond switching itself would usually be beneficial but not essential.

3. **Researchers studying unconventional electronic switching.** For them, the device is valuable even without an immediate commercial application because it demonstrates that information may be stored by reorganizing an electronic ordered state rather than by moving ions, atoms, or magnetic domains.

Ordinary personal computers and conventional data centres do not presently need this particular memory: existing semiconductor memories are sufficiently fast, operate at room temperature, and are vastly easier to manufacture and integrate. Thus, there is no established mass-market demand for the specific $1T$ -TaS₂ device described in this paper. Its most credible application is as a possible memory element for future superconducting cryogenic computers, while the broader “picosecond memory” claim should be regarded as a proposed niche application rather than as a demonstrated technological necessity.

Comparison of memory cell and they already working one

Limitations of the proposed $1T$ -TaS₂ memory device.

Despite its exceptionally fast resistance switching, the proposed device has several important limitations.

1. **Cryogenic operation and limited retention at elevated temperatures.** The hidden low-resistance state is long-lived only at low temperatures, whereas its relaxation time decreases rapidly upon heating. Later experiments indicate reliable stability below approximately 40 K. *Status in 2026: not resolved for $1T$ -TaS₂.* The device is now primarily considered as a possible cryogenic memory rather than a replacement for room-temperature computer memory. Room-temperature switching has recently been demonstrated in other CDW materials, such as EuTe₄, but this does not remove the temperature limitation of the $1T$ -TaS₂ hidden state.
2. **Strong asymmetry between writing and erasing.** Writing the low-resistance state can be non-thermal and extremely fast, whereas erasing it requires Joule heating sufficiently strong to destabilize the hidden state. Consequently, erasing is slower, dissipates substantially more energy, and may heat neighbouring cells. *Status in 2026: not resolved.* Pulse and thermal engineering can accelerate the erase cycle, but recent device studies still identify erase as the most energy-consuming operation and often assume that many cells are erased simultaneously.
3. **Incomplete microscopic understanding of switching.** The 2016 explanation based on carrier injection, polaron destruction, charged domain-wall formation, and a Mott-to-band conversion was qualitative and did not predict the threshold current, resistance change, switching time, or retention. Later imaging has established that CDW reconfiguration, lattice strain, stacking changes, defects, and, in some operating regimes, Joule heating all contribute to switching. *Status in 2026: partially improved but not resolved.* The switched structure is now characterized much more directly, but there is still no generally accepted predictive microscopic model connecting the applied pulse to the final resistance state.
4. **Uncertain homogeneity and state-to-state variability.** The hidden state is a glassy domain configuration with many metastable minima, so nominally identical pulses can produce different domain networks, resistance values, and relaxation times. Recent spatially resolved photoemission measurements have found metallic regions coexisting with regions that remain gapped after current pulsing. *Status in 2026: not resolved.* Such multiplicity may be useful for analogue or multilevel memory, but it complicates reliable binary storage and requires statistical characterization across many devices.

5. **The original speed and energy claims were not directly established.** The 2016 experiment demonstrated switching with an approximately 30 ps pulse, whereas the claimed intrinsic time below 1 ps was inferred from optical measurements. Its quoted energy below 0.25 pJ was also an upper estimate of the energy deposited in a single element, excluding the pulse generator, addressing circuitry, reading, and thermal erasing. *Status in 2026: largely improved at the single-device level.* Subsequent work demonstrated switching with a single 1.9 ps electrical pulse and reported switching energies of a few femtojoules, although complete circuit-level energy and erase costs remain considerably less favourable.
6. **Limited evidence for scalability and array integration.** The 2016 work studied isolated micrometre-scale devices and merely suggested compatibility with cross-bar architectures. Later devices were fabricated with dimensions down to approximately 40 nm, and multibit structures and coupling to superconducting nanowire drivers have been demonstrated. *Status in 2026: partially resolved.* Nanoscale operation is therefore plausible, but a dense independently addressable 1T-TaS₂ memory array with selectors, suppression of sneak currents, peripheral circuits, and CMOS-compatible fabrication has not been demonstrated.
7. **Endurance, reproducibility, and material integration.** Later experiments reported endurance of at least approximately 10⁶ switching cycles, showing that rapid failure is not inevitable. Nevertheless, these tests were performed on a limited number of research devices, whereas commercial memory requires tightly distributed thresholds and resistance levels across very large arrays, long retention, high fabrication yield, and substantially more extensive qualification. Device behaviour also depends on defects, contacts, strain, crystal thickness, and interlayer stacking. *Status in 2026: partially improved but not technologically resolved.* Most demonstrated devices still rely on exfoliated or specially prepared flakes rather than a mature wafer-scale fabrication process.

Thus, the later work has substantially strengthened the evidence for picosecond writing, femtojoule-scale single-cell operation, nanoscale fabrication, and good endurance. However, cryogenic retention, thermally expensive erasing, incomplete control of the metastable state, and the absence of a fully integrated memory array remain major obstacles. The technology is therefore considerably more credible as a specialized cryogenic memory concept than as a general-purpose replacement for conventional room-temperature memory.

Is a memory lifetime of 10 ms useful?

The reported lifetime at 150 K is approximately 10 ms, not 10 μ s. Such a retention time is clearly insufficient for archival storage: a file that must remain available for several years should be stored in an SSD, flash memory, or a magnetic disk, not in this device. However, not every computer memory is intended to retain information for years. Working memories store data only while it is actively being processed; conventional DRAM also requires periodic refreshing because its stored charge gradually leaks away. A 10 ms lifetime could therefore be used only with frequent refresh operations, although the required refresh circuitry and energy would reduce the advantages of the device.

Moreover, the 10 ms value was measured at 150 K, whereas the proposed application is low-temperature superconducting computing. The relaxation is thermally activated, so at much lower temperatures the H-state lifetime becomes substantially longer. The intended role of the device is therefore an ultrafast cryogenic working-memory element or latch, rather than permanent storage for personal files. Nevertheless, unless sufficiently long and reproducible retention is demonstrated at the actual operating temperature, calling the device a practical non-volatile memory is premature.

33.2.3 My Questions about Their Methods, Statements and Results

What is the proposed tunnelling barrier?

The tunnelling discussed by the authors is not tunnelling through the electrical contacts and is distinct from crossing a collective barrier in the free energy $F(n)$ or $F(q)$. The contacts are assumed to be ohmic. Instead, the authors propose that carriers tunnel in real space across transient charged domain walls, or charged stripes, and between neighbouring polaron clusters.

A domain wall visible in an STM image is not itself a drawing of a potential barrier. The proposed potential arises because the authors assume that the wall contains uncompensated electric charge. Any spatial charge distribution produces an electrostatic potential through Poisson's equation. In a one-dimensional approximation,

$$\frac{d^2\Phi}{dx^2} = -\frac{\rho(x)}{\varepsilon},$$

where x is the coordinate perpendicular to the wall. If the charge density is assumed to be approximately constant within a wall of finite thickness, $\rho(x) \simeq \rho$, integrating Poisson's equation twice gives

$$\Phi(x) = \Phi_0 - \frac{\rho x^2}{2\varepsilon},$$

up to constant and linear terms. The parabolic potential is therefore not an additional experimentally observed structure: it is the electrostatic potential inferred from the assumed uniform charge density inside a finite-width domain wall. A different microscopic charge profile would produce a different potential shape.

The model does not necessarily imply one parabolic potential extending across the entire sample. Rather, each charged wall is supposed to produce a local potential barrier. A carrier moving through the sample perpendicular to the walls must cross a sequence of such barriers, so the total voltage drop may be regarded as the sum of the drops across individual charged stripes. A domain wall may simultaneously conduct well along its length and act as an electrostatic barrier for motion across it,

$$\sigma_{\parallel} \gg \sigma_{\perp}.$$

Thus, the fact that a domain wall can contain conducting states does not prevent its uncompensated charge from producing a transverse potential barrier.

For an electron, the relevant potential energy is $U(x) = -e\Phi(x)$, with the sign determining whether a particular charged wall acts as a barrier or a well. The authors apply a WKB-like approximation to tunnelling across this proposed real-space barrier and use it to motivate the observed exponential current-voltage relation. However, the microscopic charge distribution $\rho(x)$, the barrier shape, and its width are not independently obtained from the experiment. Consequently, tunnelling across charged domain walls is a qualitative model for the sub-threshold I - V behaviour rather than an experimentally established microscopic mechanism.

Why is tunnelling introduced in the domain-wall picture?

The presence of domain walls does not by itself require tunnelling. If the domain walls form a continuous conducting network connecting the two electrodes, carriers can propagate along this network without crossing an electrostatic barrier,

$$\text{electrode} \longrightarrow \text{conducting DW network} \longrightarrow \text{electrode}.$$

The tunnelling mechanism is introduced by the authors specifically to explain the exponential I - V characteristic observed below the switching threshold, before the fully metallic H state has formed. Their simplified one-dimensional model assumes that transient charged stripes are oriented across the direction of current and separate different polaronic regions. A carrier travelling between the electrodes must therefore cross these charged stripes or move between neighbouring polaron clusters. The electrostatic potential associated with the uncompensated charge of a stripe is treated as a tunnelling barrier.

This geometry is an assumption of the model rather than a necessary consequence of the observed domain-wall structure. In the real two-dimensional material, carriers might instead propagate along connected domain walls, bypass charged regions, or move through junctions in a percolating domain-wall network. If such a continuous conducting path exists, tunnelling across every wall is unnecessary.

The authors choose the tunnelling picture because a suitable barrier model can reproduce the empirical dependence

$$I \sim \exp\left(\frac{V}{V_0}\right).$$

Above the threshold, they assume that the barriers cease to limit transport and the entire sample is converted into the metallic H state. Thus, tunnelling across charged domain walls is a proposed explanation of the sub-threshold transport, not an experimentally established consequence of the existence of domain walls.

if the state drops to the low R, then why we are speaking about some metastability of it? in fig. 2d, 2e there is a metastable state, why is it not in fig. 1b?

(GPT:)

Metastability concerns the free energy and lifetime of a state, not whether its electrical resistance is high or low. The low-resistance H state is metastable because it corresponds to a local minimum of the free energy: it can persist after the writing pulse, but the equilibrium state is still the high-resistance C state, to which the system eventually returns. In Fig. 1b the low-resistance state is already present after the voltage drop and remains until the end of the pulse. However, the measurement is performed at 150 K, where its lifetime is only about 10 ms, and after the current pulse ends the measured voltage immediately approaches zero, so the persistence of the resistance cannot be read directly from that trace. Figures 2d and 2e were measured at much lower temperature, where the H state survives long enough to produce an obvious hysteretic I - V curve.

do I understand correctly that 1b has different R_{HI} ? Not the same R_{HI} for the different current?

(GPT:)

No. The curves in Fig. 1b correspond to the same sample initially prepared in essentially the same R_{HI} state. What changes between the curves is the magnitude of the applied current pulse. Consequently, before switching the expected voltage is different for each trace, $V = IR_{HI}$, even though R_{HI} is approximately the same. The dashed curves show the voltage that would be expected for each applied current if no resistance switching occurred.

Fig 1b: what if R is the same but current decreases, that is why the voltage decreases? Not because R increases?

(GPT:)

The programmed source current does not decrease at the moment of the sharp voltage drop: it remains approximately constant during the flat part of the pulse. Therefore, the sharp decrease of voltage cannot be explained by a decrease of the externally applied current. For an approximately constant current, $V = IR$, so the observed voltage drop indicates that the resistance decreases. The RC response of the measuring circuit broadens the observed transition, but it does not change the direction of the resistance change.

why did they do two experiments (on fig. 1b and on fig. 2c)? Why the one on 1d is not enough?

(GPT:)

Figure 1b and Fig. 2c serve different purposes. Figure 1b shows the measured voltage response to a $1\ \mu\text{s}$ current pulse and demonstrates the abrupt resistance drop in real time. Its time resolution is limited by the approximately $50\ \text{ns}$ RC response of the circuit, so it cannot determine whether switching is possible with a picosecond pulse. Figure 2c is not a second switching-result plot but the special circuit used to generate and deliver an approximately $40\ \text{ps}$ pulse. The metal–semiconductor–metal source and transmission-line geometry are required to test switching far below the time resolution available in Fig. 1b.

fig. 2a: why there is a high R at bigger pulses?

(GPT:)

Here “bigger” refers to a longer pulse duration, not necessarily a larger current amplitude. The leading part of the pulse can create the low-resistance H state, but a sufficiently long continuation of the current produces Joule heating. Heating shortens the lifetime of the H state and allows it to relax back toward the equilibrium high-resistance C state during the same pulse. Consequently, switching becomes incomplete for pulse durations above approximately $0.1\ \text{s}$ and is absent in the final measured state for pulses longer than approximately $1\ \text{s}$.

switching: is it from very low R to the constant pretty high R, or from pretty high R to the very high R? or both are meant?

(GPT:)

The paper uses two principal resistance states. Writing means $R_{\text{HI}} \rightarrow R_{\text{LO}}$, whereas erasing means $R_{\text{LO}} \rightarrow R_{\text{HI}}$. The absolute measured values can vary between samples, temperatures, and different metastable H-state configurations, and incomplete switching can produce intermediate resistances. Nevertheless, “HI” and “LO” always refer to the high- and low-resistance states relative to one another; the authors are not defining two distinct high-resistance states as separate logical states.

Fig. 2b: erase is for 10 s, is it a big problem? It is so long.

(GPT:)

Figure 2b uses $1\ \text{s}$ erase pulses, not $10\ \text{s}$. The reverse $R_{\text{LO}} \rightarrow R_{\text{HI}}$ transition begins to occur for pulse durations above approximately $0.1\ \text{s}$, but the experiment does not resolve the intrinsic duration of the actual transition during such a pulse. Nevertheless, the demonstrated erase procedure is enormously slower than the picosecond write operation and requires substantial heating, so it is a genuine practical disadvantage. The authors suggest that optimized nanoscale thermal design and block erasing could make erasure faster, but sub-nanosecond erasure was not demonstrated in this experiment.

finally, how they explain that high $R \rightarrow$ low R is for any short pulse, and for low $R \rightarrow$ high R the low pulses are not doing anything?

(GPT:)

The two directions are attributed to different physical mechanisms. The $R_{\text{HI}} \rightarrow R_{\text{LO}}$ transition is proposed to be a rapid non-thermal electronic process: carrier injection destabilizes the commensurate polaronic state and creates a textured H state during the leading part of the pulse. By contrast, $R_{\text{LO}} \rightarrow R_{\text{HI}}$ is attributed to thermal relaxation. A short pulse does not deposit enough heat for a sufficiently long time to destabilize the H state, whereas a long pulse heats the sample, shortens the H-state lifetime, and allows relaxation to the equilibrium C state. Thus, the strong asymmetry between writing and erasing is intentional in the authors' interpretation rather than a contradiction.

why exactly the circuit for fig. 2c is exactly this one for this experiment?

(GPT:)

A conventional electrical pulse generator was used for pulses longer than 25 ns, but it could not provide the approximately 40 ps pulse required for the fastest measurement. In Fig. 2c, a 35 fs laser pulse activates a metal–semiconductor–metal photoconductive source, which produces the ultrashort electrical current pulse. The sample is incorporated into a 50 Ω transmission-line circuit so that such a fast pulse can propagate to the sample with reduced reflections and waveform distortion. This circuit is therefore chosen to generate and deliver a controlled picosecond electrical pulse, not because it represents the intended architecture of a final memory device.

why at all do we need to do experiment on figs 2a, 2b, 2c, 2d? Why experiment on fig. 1b is not enough to do the proposal of a memory device?

(GPT:)

Figure 1b demonstrates an abrupt voltage and resistance drop during one 1 μs pulse, but this alone does not establish the essential properties of a memory element. Figure 2a shows that writing occurs over a wide range of pulse durations and extends the demonstrated operation down to the picosecond regime. Figure 2b demonstrates the reverse erase operation. Figure 2c shows the apparatus that makes the picosecond test possible. Figure 2d establishes a sharp threshold and hysteresis, showing that the resistance depends on the previous pulse history and that the low-resistance state can be read at small current. Together these measurements provide evidence for writing, erasing, bistability, a threshold, state retention, and ultrafast operation; Fig. 1b alone provides only the initial observation of switching.

why in 3a the drop is at 0.6 mA and on 2d the drop is at 2mA?

(GPT:)

The curves were obtained from different devices and experimental series, so the numerical threshold currents need not coincide. The threshold depends on sample thickness and width, contact geometry, contact separation, strain, defects, and the detailed pulse conditions. Current density and electric field are therefore more physically transferable quantities than the absolute current measured in milliamperes. Figure 2d reports one 80 nm-thick crystal with 8 μm between the inner contacts, whereas Fig. 3a studies the temperature dependence using another device. The difference between approximately 0.6 mA and 2 mA is consequently not evidence of an internal inconsistency.

fig. 3a: do we start with the high R state?

(GPT:)

Yes. Each temperature-dependent I - V curve is intended to begin from the freshly prepared commensurate C state with R_{HI} . The current-pulse magnitude is then increased incrementally. Once the threshold is crossed, subsequent points in the same sweep can probe the switched state and therefore depend on the preceding pulses. Between complete temperature-dependent curves, the sample is reset by heating it to approximately 310 K and cooling it to the next measurement temperature.

fig. 3b: why from theoretical side V_0 has such change in T?

(GPT:)

In the authors' qualitative tunnelling model, V_0 characterizes the electrostatic barrier associated with transient charged domain walls or stripes in the commensurate state. At low temperature, the commensurate polaronic order is strong and the assumed uncompensated sheet charge, and therefore the barrier, is largest. As the temperature approaches the transition to the conducting nearly commensurate phase, the C-state order parameter and the corresponding excess sheet charge are assumed to decrease, so V_0 also decreases. This is only a qualitative association: the paper does not derive $V_0(T)$ microscopically from a measured domain-wall charge distribution, and the Supplementary Information describes its relation to the C-state order parameter as loose.

fig. 1b: do we see there that the erasing time is big? I don't see it. Why it is not there it it is not?

(GPT:)

No, the long erasing or recovery time is not directly visible in Fig. 1b. When the current pulse ends, the voltage falls to zero with the RC response of the circuit, regardless of whether the sample remains in R_{LO} or has returned to R_{HI} . Once $I = 0$, the relation $V = IR$ gives $V = 0$ for either resistance, so the voltage trace cannot reveal the subsequent resistance recovery. Measuring the recovery requires a separate small read current applied after controlled delays. The reported recovery time of approximately 10 ms at 150 K comes from such relaxation measurements and is different from the 44–53 ns electrical RC fall times visible in Fig. 1b.

33.2.4 Questions about Assumed Knowledge

Why is hysteresis useful for memory devices?

Hysteresis is useful because it makes the state of a device depend on its history. At the same small read current I_{read} , the material can remain in either the high-resistance state R_{HI} or the low-resistance state R_{LO} , depending on which pulse was previously applied. The corresponding voltages are $V_{\text{HI}} = I_{\text{read}}R_{\text{HI}}$ and $V_{\text{LO}} = I_{\text{read}}R_{\text{LO}}$, allowing the two states to represent the logical values 0 and 1.

Without hysteresis or another form of metastability, the resistance would be uniquely determined by the instantaneous current or voltage. After the writing pulse ended, the system would return to the same equilibrium state and the stored information would be lost. Thus, hysteresis is not itself the purpose of the device; it is evidence that two distinguishable states can persist under the same read conditions. Hysteresis is not required for every type of memory: SRAM, for example, maintains bistability through electronic feedback, whereas the device discussed here stores information directly in metastable states of the material.

33.2.5 Things That I Maybe Understood Wrongly

33.2.6 Potential Future Research Directions

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33.3 References from Generally Main Articles

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