Giant renormalization of correlation strength in 1T-TaS$_2$ by lattice vibration

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The lattice thermodynamics of a 1T-TaS$_2$ layer, e.g. the spontaneous formation of a $\sqrt{13} \times \sqrt{13}$ commensurate charge density wave (CCDW) and vibrations around the equilibrium position, is calculated by ab initio molecular dynamics. Based on that, we examine how the ground-state electronic structure is renormalized by lattice temperature. We show that the band gap within the density functional theory plus onsite-U correction shrinks by half when the temperature raises from 0 K to 200 K. The gap size reduction is one order of magnitude larger than the temperature variation in energy. This giant temperature dependence is closely related to the CCDW-triggered Mottness in 1T-TaS$_2$, and is expected to result in unconventional thermodynamic properties.

1T-TaS$_2$ has perhaps the richest electronic phase diagram of all transition-metal dichalcogenides because of the intertwined lattice, charge, orbital and spin degrees of freedom [1]. While the low-temperature commensurate charge density wave (CCDW) order and the accompanied metal-to-insulator transition have been investigated for a long time by diffraction [2], transport [3], scanning tunneling microscopy (STM) [4–6] and angle-resolved photoemission [7–9], the absence of magnetic susceptibility of the insulating phase remains puzzling [10]. The possibility of a quantum spin liquid state due to the lattice frustration was proposed recently [11], which aroused revived theoretical interest and stimulated a series of recent experiments [12–16].

The general consensus [17] is that below 200 ± 20 K ($T_{\text{CCDW}}$), the $\sqrt{13} \times \sqrt{13}$ CCDW order is fully established [Figs. 1(a)(b)]. The Ta atoms are grouped into 13 atoms clusters with a “Star-of-David” (SD) arrangement. It is widely perceived that such a 2D layer can be viewed as a cluster Mott insulator - each SD acts effectively as a cluster Mott insulator - each SD acts effectively as a

For a CCDW cell containing 13 Ta atoms and 26 S atoms, a full tight-binding description using the atomic-orbital basis is apparently inefficient. Our previous maximally localized Wannier function analysis in combination with low-temperature scanning tunneling spectroscopy (STS) characterized two types of molecular orbitals capturing the low-energy physics [18]: one is associated with the central Ta atom of a SD ($|c\rangle$), which suffers from a strong onsite Coulomb repulsion ($U_c$); the other consists of six hybridized orbitals along the edges of the SD ($s\alpha=1,...,6$), which are much more delocalized. A schematic summary is shown in Figs. 1(c)(d). These seven orbitals in together accommodate 13 unpaired Ta d-electrons, with the topmost band half filled. The corresponding multi-orbital Hamiltonian takes the form:

$$H = \Delta_{cs} \sum_i c_i^\dagger c_i + t_{cs} \sum_{i\alpha} (c_i^\dagger s_{i\alpha} + \text{h.c.}) + \sum_{i\alpha,j\beta} t_{i\alpha,j\beta} s^\dagger_{i\alpha} s_{j\beta} + U_c \sum_i c_i^\dagger c_i^\dagger c_i c_i,$$

in which $c_i^\dagger$ and $s^\dagger_{i\alpha}$ are the creation operators of $|c\rangle$ and $|s\alpha\rangle$ in the unit cell labeled by $i$. $\Delta_{cs}$ is the onsite energy difference between $|c\rangle$ and $|s\alpha\rangle$, and $t_{cs}$ ($t_{i\alpha,j\beta}$) are the hopping amplitude between the central and surrounding orbitals (two surrounding orbitals).

A parallel can be drawn between $|c\rangle$ ($|s\alpha\rangle$) and the Cu $d_{x^2−y^2}$ (O p-orbitals) in high-Tc cuprates [19]. On one hand, the localized orbital spawns the strongly-correlated physics. On the other hand, the less localized orbitals are fully occupied, but still play an important role in mediating hopping and superexchange.

Despite the formal similarity, the Mott physics in 1T-TaS$_2$ is distinct in three aspects:

(1) The electrons live in a triangular lattice. In contrast to a square lattice, antiferromagnetism is geometrically frustrated;
(2) $t_{cs}$ and $U_c$ are roughly one order of magnitude smaller [c.f. Tab. 1 in the Supplementary Materials (SM)]
than p-d coupling in cuprates and the Hubbard U of the Cu d-electron [19]. Consequently, a rather soft Mott gap ([18, 20, 21]) is observed.

(3) Unlike the p-d onsite energy difference in cuprates, \( \Delta_{\alpha \sigma} \) is not a “chemical” property, but is induced by CCDW. Without CCDW, there is no differentiation between SD center and surrounding.

Current investigations on 1T-TaS\textsubscript{2} largely concentrate on the first two aspects. The first aspect serves as the basis to discuss the quantum spin liquid physics [11–16], while the second renders sensitive experimental tunability, e.g. via pressurization [1], doping [22–26], ionic liquid gating [27], voltage pulsing [27, 28] and likely layer stacking [29]. Below, we aim to highlight the significance of the last aspect.

If it is possible to further downfold Eq. (1) into an effective single-orbital Hubbard model:

\[
H_{\text{eff}} = t \sum_{\langle ij \rangle} c_{i \sigma}^\dagger c_{j \sigma} + \tilde{U}_c \sum_i \left( c_{i \uparrow}^\dagger c_{i \downarrow}^\dagger c_{i \downarrow} c_{i \uparrow} - \frac{1}{2} \right),
\]

the effective correlation strength of the low-energy electrons \( \tilde{U}_c \) is typically smaller than the original \( U_c \) due to hybridization with the delocalized \( |s_{\alpha}\rangle \) orbitals, and \( \Delta_{\alpha \sigma} \) plays an important role. For cuprates, this downfolding is achieved by invoking the “Zhang-Rice singlet” picture [19], and the effective correlation strength entering (Eq. 2) is reduced from the Coulomb repulsion of the Cu d-electron (\( \sim 10 \) eV) to the p-d charge-transfer gap (\( \sim 2 \) eV) [30].

Recall that in 1T-TaS\textsubscript{2}, \( \Delta_{\alpha \sigma} \) is a CCDW-induced variable, so the amplitude and fluctuation of CCDW will ultimately modify \( \tilde{U}_c \). Given that CCDW is essentially a periodic lattice distortion, this immediately leads to a striking speculation - the effective correlation strength of low-energy electrons in 1T-TaS\textsubscript{2} should strongly depend on the lattice temperature.

We mention that a rigorous downfolding from Eq. (1) to Eq. (2) is complicated. For cuprates, a first-principles construction was achieved by exactly diagonalizing finite clusters within a three-band Hubbard model parameterized by the density functional theory (DFT) and then fitting the single-band Hubbard model to the low-energy spectra [30]. Such a treatment including lattice dynamics is impossible at this point.

Fortunately, the DFT+U method [31] provides an approximated but efficient way to describe the Mott-insulating ground state. The merit is that by enforcing a spin-polarized mean field \( n_{i \sigma} = \langle c_{i \sigma}^\dagger c_{i \sigma} \rangle \), the onsite Coulomb repulsion is reduced to a spin-(and orbital-) dependent potential. It is straightforward to verify that Eq. (2) under this treatment produces a band gap \( E_g = \tilde{U}_c - z t \), in which \( z \) is a constant dictated by the underlying lattice and the spin configuration. When \( \tilde{U}_c \gg \tilde{t} \), \( E_g \sim \tilde{U}_c \).

Although not as ideal as the dimensionless \( \tilde{t}/\tilde{U}_c \) ratio, it is fair to view the DFT+U band gap \( E_g \) as a measure of the correlation strength of the low-energy electrons associated with Eq. (2). The advantage of embedding the +U correction in DFT is that the organization of the low-energy orbitals and the downfolding of the atomic Coulomb repulsion to \( E_g \) is self-consistently achieved. Indeed, for cuprates, DFT+U calculation produces a \( E_g \sim 2 \) eV [31]. For 1T-TaS\textsubscript{2}, the previous DFT+U calculation obtains a \( E_g \sim 0.4 \) eV, which can be directly compared with energy splitting between the lower Hubbard peak and the upper Hubbard peak observed by low-temperature STS [18]. Throughout this work, the average Coulomb repulsion of the Ta 5d-electrons as used in Dudarev’s version of +U correction [32] is fixed to 2.27 eV, which was determined previously by linear-response
FIG. 2. (a-c) The temperature dependence of (a) the CCDW order parameter $\phi_{SD}$; (b) the static DFT+U ($=2.27$ eV) band gap $E_g^{\text{static}}$; and (c) the time-averaged Born-Oppenheimer band gap ($E_g^{\text{BO}}$). The error bar in (c) is calculated from the standard deviation of the instant $E_g^{\text{BO}}$. (d) Correlation between $E_g^{\text{BO}}$ and the single-electron parameters in Eq. 1 extracted by Wannerizing the DFT band structure. The numbers on top denote the seven time slices marked in Figs. 3(e-g).

calculation [33].

On the other hand, CCDW as a lattice property can be nicely described by ab initio molecular dynamics (MD). Under equilibrium, ensemble average is calculable from the MD time average. We will focus on the lattice dynamics first. The calculation details are described in the SM, wherein the equilibrium structures and the behavior of lattice dynamics at several typical temperatures are displayed.

We can define an CCDW order parameter $\phi_{SD} = \bar{d}_{\text{inter}} - \bar{d}_{\text{intra}}$, where $\bar{d}_{\text{inter}}$ ($\bar{d}_{\text{intra}}$) is the time-averaged Ta-Ta distance between SDs (within a SD). The definition of inter- (intra-)SD bonds is ambiguous in the high-T phase, so we always refer to the SD positions in the CCDW phase. Both $\bar{d}_{\text{inter}}$ and $\bar{d}_{\text{intra}}$ are determined from the time-averaged lattice structure as a function of T. In general when SDs melt, $\phi_{SD}$ vanishes.

Figure 2(a) plots $\phi_{SD}$ versus temperature. A sharp first-order transition can be observed. The loop shows hysteresis, indicating that there are two competing phases and the atoms have not fully relaxed to the low free-energy phase within the simulation duration. The transition temperature $T_C$ is 250 K $\sim$ 300 K.

It is usually challenging to reliably simulate the first-order phase transition, because the equilibrium time might be too long for MD. The good agreement obtained here should be attributed to a relatively shallow energy barrier between the two phases. Given that the simulation is performed for a 2D layer, one natural question is how to reconcile with the Mermin-Wagner theorem. The answer lies in the imposed periodic boundary condition, which cuts off any thermal fluctuation with a wave vector larger than the cell vectors. On the other hand, the most important thermal fluctuation that melts the SDs has the $\sqrt{3}\times\sqrt{3}$ wave vector, which is fully accommodated in our simulation cell. The transition occurs when the kinetic energy of the atoms becomes large enough to escape the $\sqrt{3}\times\sqrt{3}$ potential well. This physics is faithfully characterized by MD. Therefore, it is not surprising that our 2D simulation is able to predict a finite transition temperature.

We should also note that our simulation supercell [see Fig. 1(a)] is still not large enough to describe phase separation and long-wave incommensurate CDW. Experimentally, between $T_{CCDW}$ (the SDs start to melt) and $T_{NC}$ (the SDs completely melt), there is a wide range in which the CCDW domains and the discommensurate regions coexist [17]. It is understandable that our simulated transition temperature falls between the experimental $T_{CCDW}$ and $T_{NC}$.

Based on the lattice dynamics data, we proceed to evaluate how the DFT+U band gap gets renormalized by the lattice dynamics. We evaluate the gap within the static approximation and the Born-Oppenheimer (BO) approximation respectively. Under the former approximation, the time average is performed for the lattice structure first, and then the DFT+U band structure is obtained with respect to the time-averaged lattice, from which we read the band gap $E_g^{\text{static}}$. Under the latter approximation, the instant DFT+U gap size $E_g^{\text{BO}}$ is recorded at each MD step, and time averaged afterwards to obtain $\langle E_g^{\text{BO}} \rangle$.

Within the static approximation, the renormalization arises from the variation of the CCDW amplitude. Fig. 2(b) plots $E_g^{\text{static}}$ versus T. A sharp metal-to-insulator transition takes place in accompany with the CCDW transition. Figs. 3(a-d) show the band structure at four typical lattice temperatures, which only show marginal dependence on the lattice temperature below $T_C$. If we carefully examine Figs. 3(a-c), we can observe a slight reduction of $E_g^{\text{static}}$. Above $T_C$, the Mott gap collapses abruptly [Fig. 3(d)].

Going beyond the static approximation, Figs. 3(e-h) plot the instant energy levels at the $\Gamma$ point at each MD step. At 5 K, the gap size agrees well with the static band structure, despite slight temporal fluctuations. At higher temperatures, the temporal fluctuations significantly reduce the static gap size. At 275 K, instant level crossings can be observed, indicating that the system is close to the phase transition. The time-averaged $\langle E_g^{\text{BO}} \rangle$ as a function of lattice temperature is plotted in Fig. 2(c). The gap size decreases from around 0.4 eV at 5 K to around 0.2 eV at $T_C$.

The comparison between $E_g^{\text{static}}$ and $\langle E_g^{\text{BO}} \rangle$ clearly indicates that the driving force is not the static CCDW amplitude but the fluctuations. The band gap size
FIG. 3. (a-d) Static DFT+U(=2.27 eV) band structures calculated from the time-averaged lattice structures at different temperatures. (e-h) Time evolution of the instant energy levels at the Γ point within the last 4 ps of the MD simulation. The vertical dashed lines mark seven time slices used to extract the data in Fig. 2(d). The pink and green bands indicate different spins.

shrinks by half when the temperature approaches $T_C$. $\Delta \langle E^{BO}_g \rangle / k_B \Delta T$ is of the order of $-10$. To the best of our knowledge, a continuous variation of the correlation strength of this magnitude is not known in any other Mott insulators.

We emphasize that $\langle E^{BO}_g \rangle$ should not be directly interpreted as the experimental Mott gap at finite temperature, because electronic temperature is absent in the DFT+U framework. Both spin fluctuation and charge excitation are known to significantly modify the gap beyond a plain band scenario [19]. The basic understanding is that electronic temperature also tends to reduce the gap size by transferring spectral weight from the Hubbard bands to Fermi surface [34]. Therefore, the real finite-temperature Mott gap observed in experiment is expected to have an even steeper slope with respect to temperature. More discussions on the possible consequences are given in the SM.

According to Eq. (1), the gap size reduction is mainly attributed to a strong coupling between $\Delta_{cs}$ and the lattice dynamics. Obviously, melting of $\varphi_{SD}$ will lead to a vanishing $\Delta_{cs}$. Similarly, dynamical vibrations of the CCDW should also weaken the differentiation between central and surrounding Wannier orbitals. To justify this scenario, seven instant structures are picked from Figs. 3 (e-g), and the single-electron parameters in Eq. (1) are extracted via a Fourier transformation of the DFT band structure to the $\{|c\rangle, |s_\alpha\rangle\}$ Wannier function basis [35] (See the SM for details). In Fig. 2(d), a clear correlation between $\Delta_{cs}$ and $E^{BO}_g$ can be observed as expected, while the hopping parameters do not play an active role.

Generally speaking, this effect is related to strong electron-phonon coupling (EPC) typically existing in a CDW material. However, the underlying mechanism of gap reduction is fundamentally different from that in conventional semiconductors, where the key is the EPC deformation potential at the band edge [36]. Here, EPC comes into play in a much more obscure way. The key is a reconstruction of the low-energy orbitals. Using the jargon of cuprates [19], we may say that EPC leverages $\tilde{U}_c$ through modifying the localization degree of the CCDW-induced counterpart of “Zhang-Rice singlets”.

In summary, our calculation demonstrates that the correlation strength of low-energy electrons in 1T-TaS$_2$ is reduced significantly by lattice entropy. Due to this giant lattice temperature effect, the Mott insulating phase in 1T-TaS$_2$ is predicted to be much more fragile than the common perception obtained from studying a Hubbard model with electronic temperature only, providing a highly tunable platform to investigate Mottness collapse. This newly identified effect is also expected to provide an important clue to understand the puzzling thermodynamics response observed in this material.

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COMPUTATIONAL DETAILS

Our calculations are performed using the Vienna \textit{ab} \textit{initio} Simulation Package (VASP) \cite{PhysRevB.68.195115, Kresse1996, Kresse1994, Kresse1993}. Nuclei are subject to the Newton’s equation of motion on the Born-Oppenheimer potential surface using a time step of 2 fs. To simulate a canonical ensemble with constant $T$, the Nose thermostat is used \cite{PhysRevA.39.355, PhysRevA.39.359, Nose1984}. For each $T$, the molecular dynamics (MD) simulation lasts for 20 ps, and the last 4 ps is used to calculate thermodynamic properties. The simulation cell contains a single layer of 52 Ta atoms sandwiched by 104 S atoms (in total $N_{\text{atom}} = 156$), which can accommodate up to 4 SDs. A 15 Å vacuum layer is included in the $z$-direction. The complexities of the stacking order of the single layer and the interlayer coupling are beyond the scope of the current calculation.

Numerically, it is important to guarantee that the last 4 ps has already achieved thermal equilibrium. For a better convergence, we start from a low-$T$ structure, which is closest to the DFT relaxed static structure. Then, the structure of the final MD step is used as the initial structure of the next temperature, which is elevated progressively. When all the SDs melt, we reversely reduce the temperature progressively, using the equilibrium structure at the higher temperature as input. Finally, the simulation forms a complete heating-cooling cycle. Our criterion for thermal equilibrium are that (i) the temperature fluctuation has already converged to $\sqrt{2/(3N_{\text{atom}})} = 6.5\%$ as expected from a Boltzmann distribution, (ii) clear periodicity with constant amplitude can be observed from the atomic displacement, and (iii) the observables from the heating and cooling processes coincide when the temperature is away from the transition point.

At any instant of time, the ground state of electrons is calculated self-consistently within DFT+$U$. We employ the projector augmented wave method \cite{Blochl1994} and the exchange-correlation functional due to Perdew, Burke and Ernzerhof (PBE) \cite{Perdew1996}. The +$U$ correction is employed to capture the Coulomb interaction of Ta 5d orbitals on the Hartree-Fock level, following the simplified (rotational invariant) approach introduced by Dudarev \cite{Dudarev1998}. We employ an effective $U = 2.27$ eV as previously derived from the linear-response calculation \cite{Dudarev1998}. We use a plane-wave cutoff of 300 eV, and the Brillouin zone was sampled with the $\Gamma$ point only.

The obtained equilibrium lattice structure at 5 K and 300 K are shown in Fig. S1. The temperature effect on the CCDW order can be clearly observed. The animation files of the equilibrium lattice dynamics at four typical temperatures are uploaded separately.

![Figure S1. Equilibrium lattice structures obtained from MD at (a) 5K and (b) 300K. The black box indicates the simulation cell and $a_1$, $a_2$, $z$ are the three cell vectors. The colored surface gives the spin density isovalue contour, with an isosurface value of 0.003 $e/Å^3$. A Ta-Ta bond is drawn when the Ta-Ta distance is below 3.4 Å.](attachment:figure_s1.png)
MORE DISCUSSION ON THE ELECTRONIC TEMPERATURE EFFECT

It remains a theoretical challenge to quantitatively predict the electronic temperature effect in a real Mott insulator of such a complicated supercell as 1T-TaS2. Heuristically, we assume that the experimentally observed Mott gap $\Delta_{\text{Mott}}$ gradually deviates from the DFT+U band gap as temperature increases [12]. A schematic illustration of the possible consequences is presented in Fig. S2. In principle, the gap melting can be momentum dependent [13]. In an intermediate temperature range, the pseudogap state may emerge [14]. Accordingly, $\Delta_{\text{Mott}}$ is plotted with a finite width instead of a single-value curve.

The common perception is that the Mott transition of 1T-TaS2 is accompanied with the first-order CDW transition [Fig. S2(a)]. The giant reduction of $\langle E^\text{BO}_g \rangle$ induced by the lattice vibration was not known before. When both the electronic and the lattice effects kick in, it is not clear whether the Mott gap is still open at $T_{\text{CCDW}}$. The lower and upper bounds of $\Delta_{\text{Mott}}$ define two additional charateristic temperatures, respectively, which we term as $T_{\text{Mott}}$ and $T^*$. Depending on the positions of $T_{\text{Mott}}$ and $T^*$ with respect to $T_{\text{CCDW}}$, the phase diagram has different structures. Figure S2(b) shows a trivial outcome, where electronic temperature only quantitatively reduce the size of the gap. More exotic possibilities are Figs. S2(c) and (d), where the gap has already collapsed or partially collapsed at $T_{\text{CCDW}}$.

A revisit of the experimental data suggests that it deserves further investigations to address the question: is it proper to assign the whole regime below $T_{\text{CCDW}}$ as a Mott insulator or does additional transition temperatures exist? The scanning tunneling spectroscopy shows that while the energy splitting between the lower Hubbard peak and the upper Hubbard peak at 5 K [15] and 78 K [16] appear to fall on our $\langle E^\text{BO}_g (T) \rangle$ curve [Fig. 2(c)], some in-gap density of states has emerged at the elevated temperature. At 130 K [17], spatial inhomogeneity becomes evident, and the Hubbard peaks are broad, which hinders an accurate extraction of the peak-to-peak energy splitting. More peculiarly, the gap profile has transformed into the V shape. On the other hand, the recent nuclear quadruple resonance measurement [18] shows that below $T_{\text{CCDW}}$, the spin-lattice relaxation rate $1/T_1$ undergoes an anomalous transition from $T^2$ to a much steeper $T^4$ power law. The transition temperature is decided as 55 K. Around this temperature, the in-plane resistivity was long noticed to undergo a crossover from a metallic behavior to an insulator behavior [19].

WANNIER FUNCTION ANALYSIS

The Wannier function analysis is performed using the WANNIER90 code [20] in order to quantify the single-electron parameters in Eq.(1). Seven instant lattice structures are picked as marked in Figs. 3(e-g), and the single-electron band structures are calculated at the DFT-PBE level. Following the recipe in [15], the Bloch states of the seven highest occupied energy bands per star-of-David (SD) are chosen to construct the maximally localized Wannier functions (MLWFs), which can accommodate up to 14 electrons with the spin degree of freedom. Since the MD supercell contains four SDs in total, the total number of MLWFs is 28, including 4 $|c_i\rangle$ orbitals and 24 $|s_{i\alpha}\rangle$ orbitals, where $i$ labels the four SDs in the supercell, and $\alpha$ labels the six surrounding orbitals of each SD. For all the parameters, an average of $i$ is performed afterwards. In Tab. I, we list the onsite-energy difference $\Delta_{cs}$, the nearest-neighbor hopping parameter between the central and the surrounding orbitals $t_{cs}$ and the largest six hopping parameters between two surrounding orbitals $t_{ss}$. In Fig. 2(d), $t_{ss}$ is an average of the six largest $t_{ss}$.

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TABLE I. Single-electron parameters from MLWF analysis. The first column contains the previous data obtained from the fully-relaxed structure[15]. The other seven columns correspond to the seven instant MD lattice structures marked in Figs. 3(e-g).

| Unit(eV)          | [15] | 1   | 2   | 3   | 4   | 5   | 6   | 7   |
|-------------------|------|-----|-----|-----|-----|-----|-----|-----|
| $\Delta cs$       | 0.212| 0.215| 0.192| 0.117| 0.164| 0.140| 0.066|
| $t cs$            | 0.162| 0.153| 0.148| 0.142| 0.142| 0.154| 0.160| 0.156|
| $t ss_1$          | 0.150| 0.141| 0.155| 0.111| 0.183| 0.131| 0.118| 0.200|
| $t ss_2$          | 0.091| 0.093| 0.092| 0.092| 0.093| 0.081| 0.094| 0.094|
| $t ss_3$          | 0.072| 0.063| 0.064| 0.073| 0.071| 0.060| 0.065| 0.068|
| $t ss_4$          | 0.050| 0.052| 0.048| 0.052| 0.048| 0.043| 0.048| 0.045|
| $t ss_5$          | 0.042| 0.038| 0.035| 0.037| 0.032| 0.027| 0.032| 0.031|
| $t ss_6$          | 0.042| 0.030| 0.024| 0.026| 0.023| 0.018| 0.023| 0.023|

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