

Charge-ordered phases in the hole-doped triangular Mott insulator $4Hb$ -TaS₂

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$4Hb$ -TaS₂ has been proposed to possess unconventional superconductivity with broken time-reversal symmetry due to distinctive layered structure, featuring a heterojunction between a 2D triangular Mott insulator and a charge-density wave metal. However, since a frustrated spin state in the correlated insulating layer is susceptible to charge ordering with carrier doping, it is required to investigate the charge distribution driven by interlayer charge transfer to understand its superconductivity. Here, we use scanning-tunneling microscopy and spectroscopy (STM/S) to investigate the charge-ordered phases of $1T$ -TaS₂ layers within $4Hb$ -TaS₂, explicitly focusing on the non-half-filled regime. Our STS results show an energy gap which exhibits an out-of-phase relation with the charge density. We ascribe the competition between onsite and nonlocal Coulomb repulsion as the driving force for the charge-ordered insulating phase of a doped triangular Mott insulator. In addition, we discuss the role of the insulating layer in the enhanced superconductivity of $4Hb$ -TaS₂.

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I. INTRODUCTION

Charge-ordered phases are primarily observed in strongly correlated electron systems. These phases arise due to strong onsite and nonlocal Coulomb interactions, which redistribute charges and lead to the formation of superstructures. Exploring these phenomena is motivated by their competitive relationship with superconductivity when carrier doping is introduced [1–4]. Significant progress has been made in the field due to intense interest in cuprate high-temperature superconductors, which have complex phase diagrams featuring magnetic ordering, checkerboard charge ordering, pseudogap, and other quantum phenomena. However, a comprehensive understanding of the impact of Coulomb interactions and lattice geometries other than square lattice on charge ordering and superconductivity in frustrated correlated electron systems is still incomplete. These systems are hypothesized to support a gapless spin-liquid phase [5–7] and chiral superconductivity [8,9].

TaS₂, a transition metal dichalcogenides-layered material, undergoes a charge-density wave (CDW) transition at low temperatures. It is known to exhibit metallic behavior at higher temperatures due to the presence of a single valence electron in its $5d$ orbital that stems from the covalent bonding between Ta and S atoms; conducting properties of CDW phases are differentiated according to the coordination of Ta and S atoms. In the monolayer, the $1H$ polymorph remains as a metal, whereas the $1T$ polymorph becomes a Mott insulator. $1T$ -TaS₂, with octahedral coordination [Fig. 1(a)], forms Star of David (SD) clusters consisting of 13 Ta atoms, in which

12 nonbonding orbitals pair up and one nonbonding orbital resides at the center of the SD [Fig. 1(b)] [10]. Each SD cluster can be regarded as a unit cell where a pair of electrons can reside within. In the following we denote the number of electrons per nonbonding orbital at the center of the SD cluster as n_{SD} ($n_{SD} = 0$: unoccupied, $n_{SD} = 1$: half-filled, $n_{SD} = 2$: fully occupied). This configuration significantly enhances the onsite Coulomb repulsion, opening an energy gap near the Fermi level (E_F) [11]. With the Mott insulating character, a triangular lattice adds more dimension of complexity of the $1T$ -TaS₂, accounting for spin frustration in nonbonding orbital sites [6].

At its surface, bulk $1T$ -TaS₂ can host two different insulating phases, a Mott and a band insulating phase, depending on distinct stacking orders of the surface-terminating layers [12–14]. In the monolayer limit, it becomes a two-dimensional triangular Mott insulator [11], whose electronic structure can significantly depend on the substrate. Indeed, scanning-tunneling spectroscopy (STS) measurements reveal distinct electronic structures of $1T$ -TaS₂ surfaces deposited onto different substrates. A monolayer $1T$ -TaS₂ grown on highly oriented pyrolytic graphite (HOPG) substrates shows electronic properties consistent with those of a correlated insulator [Fig. 1(c)], which is characterized by two spectral peaks called upper and lower Hubbard bands [15]. Meanwhile, a $1T/1H$ bilayered heterostructure of TaS₂ on HOPG hosts an electron in the center orbital of the SD ($n_{SD} = 1$), thus localized spins in the $1T$ layer are screened by itinerant electrons in the $1H$ layer. This Kondo screening gives rise to the sharp zero-bias peak in the tunneling spectrum [Fig. 1(d)] [15,16]. However on $4Hb$ -TaS₂, a $1T/1H$ heterostructure with the two polymorph layers stacked in an alternate sequence, the measurement exhibits a peak above E_F which corresponds to an unfilled narrow band centered at the SD ($n_{SD} = 0$). This

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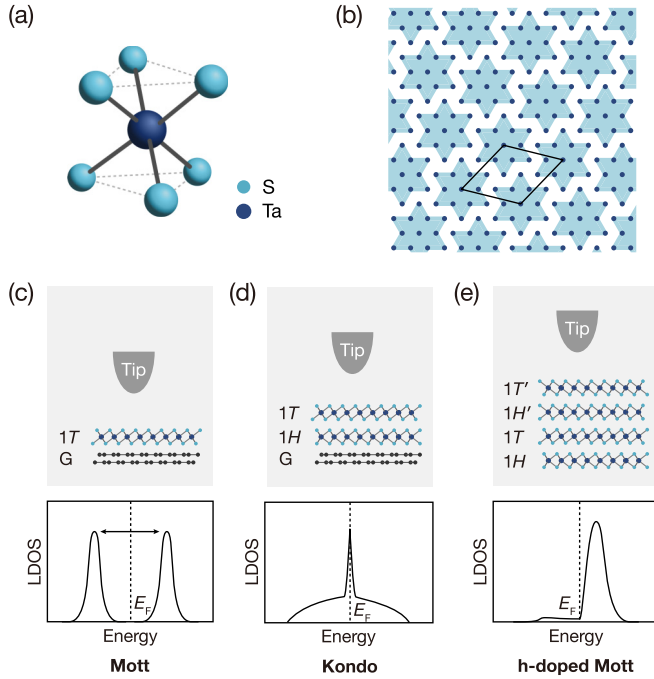


FIG. 1. Exotic quantum states arising from different layer stacking combinations of 1T-TaS₂. (a) Schematics of the atomic structure of 1T-TaS₂. A Ta atom (dark blue) is coordinated with six S atoms (bright blue) in an octahedral arrangement in the unit cell. (b) $\sqrt{13} \times \sqrt{13}$ CDW pattern with Star of David reconstruction in 1T-TaS₂. (c)–(e) Various quantum states and their corresponding spectral characteristics according to different stacking configurations of 1T and 1H layers. A Mott insulator (c), Kondo resonance (d), and hole-doped Mott insulator (e) observed on 1T/Graphene, 1T/1H/Graphene, and 1T/1H/1T/1H vertical heterostructures, respectively.

feature can be attributed to either spectral weight transfer in a hole-doped Mott insulator [17,18] or pseudodoping induced by weak hybridization between the 1T and 1H layer. [Fig. 1(e)] [19]. These diverse electronic states emerging from different structure configurations indicate the interlayer coupling as a pivotal factor in the complexity of TaS₂-based heterostructures, and establish their potential for investigating novel quantum states of matter.

The difference in spectroscopic results between the Kondo-resonated 1T/1H bilayer and the hole-doped Mott insulator 4Hb-TaS₂, despite the structural similarity, implies that doping levels in the Mott insulating 1T layer can be modulated through the interlayer coupling. Controlling the carrier concentration leading to the transition from a Mott insulator to a superconducting phase is a widely utilized approach [2]. It is also notable that intermediate fillings, between one and zero (or two) electron(s) per atomic site, give rise to metallic states characterized by unusual charge ordering and pseudogap features due to strong correlation [4]. With all conditions of the interlayer coupling and a frustrated structure, 1T layer in 4Hb-TaS₂ provides an ideal platform for investigating the effect of frustration on correlated phenomena.

In this study, we used scanning-tunneling microscopy and spectroscopy (STM/S) at a low temperature to investigate the electronic structure and charge distribution of 1T and 1H-TaS₂ layers within the 4Hb-TaS₂ compound, particularly focusing

on the triangular Mott insulator within the non-half-filled regime. A new $\sqrt{3} \times \sqrt{3}$ SD superstructure superimposed on the conventional $\sqrt{13} \times \sqrt{13}$ superstructure is observed on the cleaved 1T layer and the spatially resolved STS results show an energy gap with an out-of-phase relation with the local charge density. The observed charge-ordered insulating phase can be attributed to a bipolaronic insulating phase of the triangular Mott insulator in the intermediate hole-doping regime. Our results lead to a deeper understanding of the charge distribution and the emergent quantum phenomena in non-half-filled correlated electron systems with geometrically frustrated lattices.

II. EXPERIMENTAL DETAILS

We used a commercial STM (UNISOKU-USM1200) for STM/S measurements. The experimental data were acquired at $T = 4.2$ K in an ultrahigh vacuum (UHV) environment with a pressure of 1×10^{-10} Torr. Commercial TaS₂ crystals (HQ graphene) were grown using the chemical vapor transport (CVT) method with iodine as a transport agent. Bulk TaS₂ was cleaved at room temperature and transferred to the STM head, which was cooled to 4.2 K. STM tips were fabricated through electrochemical etching of a tungsten wire and subsequently cleaned by electron beam heating under UHV conditions. The tip was subsequently characterized on a clean Au(111) surface [20]. The STM images were obtained in constant current mode by applying a bias voltage V_{set} to the sample. We employed a standard lock-in technique to obtain differential conductance dI/dV with ac voltage modulation $V_{\text{mod}} = 5$ mV and $f_{\text{mod}} = 613$ Hz added to the dc sample bias. Comparative Raman scattering measurements on single crystalline samples of 1T-TaS₂ and 4Hb-TaS₂ were carried out using a triple-stage spectrometer (Princeton Instruments TriVista) and a $\lambda = 561$ nm laser focused onto the sample with a spot diameter of 2 μm and a laser power of 0.1 mW. The samples were cooled via an open-flow He cryostat (Oxford MicroStat HR).

III. RESULTS

We confirm the 4Hb phase via temperature-dependent Raman spectroscopy. This technique allows us to clearly distinguish 4Hb from 1T polymorphs [21], as both feature their own characteristic phonon spectrum [Fig. 2(a)] as well as a distinct thermal evolution. Whereas 1T-TaS₂ is characterized by a series of successive CDW phase transitions (commensurate to nearly commensurate around $T = 225$ K, nearly commensurate to incommensurate around $T = 355$ K upon heating), 4Hb-TaS₂ only has one phase transition at $T = 315$ K [Fig. 2(b) and Fig. 2(c)].

On the surface of cleaved 4Hb-TaS₂, two different polymorphs can be seen across a monolayer step, as shown in Fig. 2(d). The step height is approximately 5.3 Å, corresponding to the thickness of a TaS₂ monolayer [22]. We identify the polymorphic structure of each surface by examining the CDW phases [23]. A zoomed-in STM topographic image of the upper terrace [Fig. 2(e)] exhibits a triangular lattice made up of triangular-shaped protrusions. On the other hand, on the lower terrace, we observe the typical threefold stripe patterns of 1H-TaS₂ [Fig. 2(f)]. The wavevectors of the typical CDWs

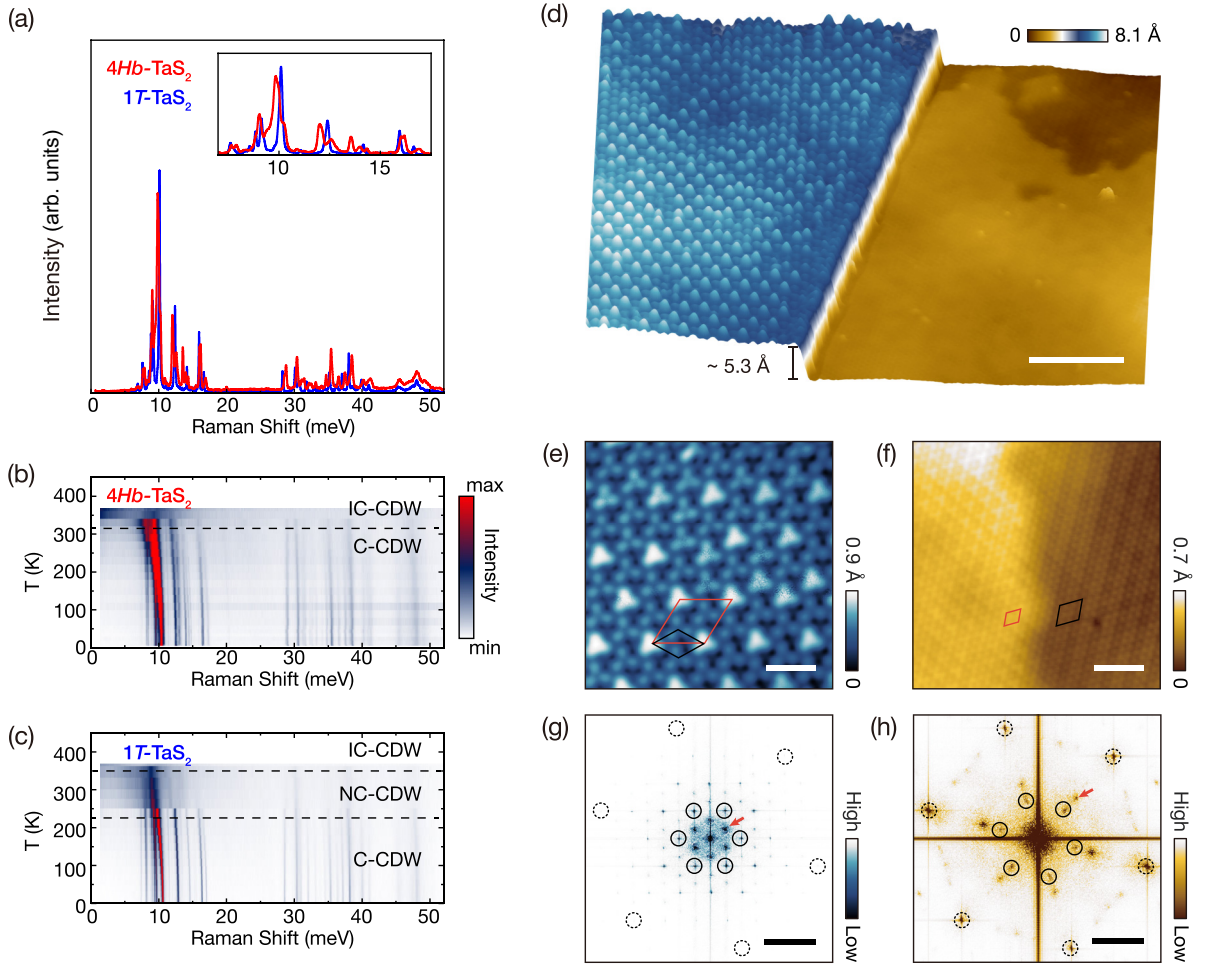


FIG. 2. Characterization and two distinct CDWs in 1T- and 1H-TaS₂. (a) Raman spectra of the 4Hb- and 1T polymorphs of TaS₂ measured in the CDW phase at $T = 4$ K. The inset zooms into the spectral range of CDW amplitude modes. (b), (c) Thermal evolution of Raman-active excitations in 4Hb- and 1T-TaS₂, respectively, through various CDW transitions. (d) A 3D-rendered STM image of 4Hb-TaS₂ with a monolayer step ($V_{\text{set}} = -0.8$ V, $I_{\text{set}} = 50$ pA). The upper and lower terraces correspond to the typical surfaces of 1T and 1H-TaS₂ layers, respectively. Scale bar, 10 nm. (e), (f) Zoomed-in STM images of the upper (e) and the lower (f) terrace. [$V_{\text{set}} = -0.4$ V, $I_{\text{set}} = 100(50)$ pA]. Scale bars for (e) and (f), 2 nm. (g), (h) FFT of STM images of the upper (g) and lower (h) terrace. The dashed circles indicate the Bragg peaks of the pristine crystal lattice. The black circles correspond to the $\sqrt{13} \times \sqrt{13}$ and 3×3 CDW typically observed in bulk 1T and 2H-TaS₂, respectively. The red arrows highlight the peak of $\sqrt{3} \times \sqrt{3}$ of SD and 2×2 CDW that are not present in the bulk. Scale bars for (g) and (h), 1 nm^{-1} .

of each polymorph are marked by black circles in the Fourier-transformed images of Figs. 2(g) and 2(h), well consistent with the $\sqrt{13} \times \sqrt{13}$ CDWs and the 3×3 CDWs of 1T-TaS₂ and 1H-TaS₂ [24], respectively.

In the two-dimensional (2D) fast Fourier transform (FFT) of STM images of both the 1T and 1H layers, additional superstructures are present, highlighted by red arrows in Figs. 2(g) and 2(h), which are associated with the ground state of each polymorph. In particular, in the topographic image of the upper terrace [Fig. 2(e)], two distinguished types of protrusions, one brighter and one darker, are regularly arranged in a $\sqrt{3} \times \sqrt{3}$ pattern on the SD lattice ($\sqrt{3}_{\text{SD}} \times \sqrt{3}_{\text{SD}}$). This $\sqrt{3}_{\text{SD}} \times \sqrt{3}_{\text{SD}}$ ordering is not fully commensurate due to the domain walls or random charge distribution, resulting in somewhat blurry peaks in Fig. 2(g). Notably, the $\sqrt{3}_{\text{SD}} \times \sqrt{3}_{\text{SD}}$ order in 1T-TaS₂ is absent when each SD is half-filled ($n_{\text{SD}} = 1$) [15] or fully unoccupied ($n_{\text{SD}} = 0$) [17]. The lower terrace shown in Fig. 2(f) is divided into two distinct CDW regions of a 2×2 order with a brighter contrast and a 3×3

order with a darker contrast. A 3×3 order mainly appears on 2H-TaS₂ as well as on the 1H layer of 4Hb-TaS₂, while a 2×2 order has been reported for the electron-doped [25] or strained [26] 2H-TaS₂. As shown in Fig. 2(d), our sample appears to be more corrugated than a typical sample [19]. The strain might be critical in letting our sample host heterogeneous charge distribution [20].

Next, we turn to spatially resolved STS measurements on the 1T surface to investigate the origin of the $\sqrt{3}_{\text{SD}} \times \sqrt{3}_{\text{SD}}$ charge ordering. Figure 3(a) illustrates a distinct pattern of alternating brighter and darker SDs, marked by solid and dashed yellow circles, respectively. These variations reflect the different electron fillings on the surface. The dI/dV spectra presented in Fig. 3(b) were obtained by spatially averaging each type of CDW protrusions. Contrary to the measured spectrum on the CDW protrusion in a monolayer 1T-TaS₂ on graphene, which typically shows a gap with peaks around -0.2 and $+0.2$ eV, our measurements reveal that both brighter and darker sites on the 1T surface exhibit distinct, single peaks

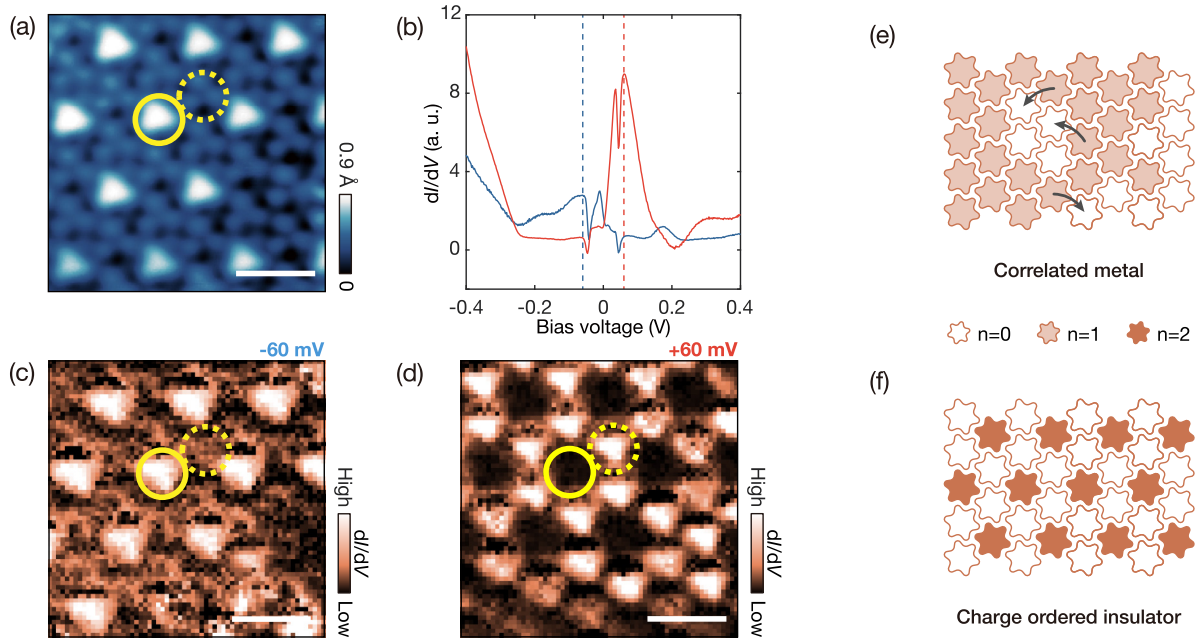


FIG. 3. Spectroscopic results and schematics of the charge-ordered phase. (a) STM image of the $\sqrt{3}\text{SD} \times \sqrt{3}\text{SD}$ charge-ordered phase at filled state ($V_{\text{set}} = -0.4$ V and $I_{\text{set}} = 50$ pA). (b) Spatially averaged differential conductance dI/dV spectra. Blue and red curves are acquired in brighter and darker sites in (a), respectively. ($V_{\text{set}} = -0.4$ V, $I_{\text{set}} = 200$ pA, and $V_{\text{mod}} = 5$ mV). (c) and (d) dI/dV maps at the energy of -60 mV (c) and $+60$ mV (d) which correspond to the dashed lines in (b), respectively. The solid and dashed yellow circles represent two types of CDW protrusions shown as brighter and darker sites in (a). Scale bars for (a), (c), and (d), 2 nm. (e) A schematic of randomly distributed half-filled ($n_{\text{SD}} = 1$) and fully empty ($n_{\text{SD}} = 0$) SD. The black arrows indicate the potential hopping processes driven by adding voids in the half-filled insulator, otherwise strongly suppressed. (f) Charge redistribution of a hole-doped triangular Mott insulator with average filling factor $n_{\text{avg}} = 2/3$, the same as in the case shown in (e).

in the filled and empty states, as indicated by the red and blue dashed lines in Fig. 3(b). The red spectrum corresponds to that of a typical $4Hb\text{-TaS}_2$ [19], while the blue one is consistent with that of electron-doped $1T\text{-TaS}_2$ [13,27]. The coexistence of these two distinct spectra has not been reported in $4Hb\text{-TaS}_2$. This unique spectral characteristic suggests an energy gap opening, possibly linked to charge redistribution, significantly deviating from the electronic structure of monolayer $1T\text{-TaS}_2$. Meanwhile, there are dips at ± 50 mV in the spectra that exhibit slightly negative conductance. These could be due to resonant tunneling of localized states of tip and sample [20,28], or stem from electron tunneling coupled to the characteristic vibrational modes [29,30]. Note that they do not affect our interpretation of the relation between the filling factors and spectral features.

The dI/dV maps acquired on the same region corresponding to Fig. 3(a) unveil the origin of the charge redistribution. By comparing the dI/dV maps at the energy levels of -0.06 eV and $+0.06$ eV, indicated by dashed lines in Fig. 3(b), we observe a contrast inversion of the spatial $\sqrt{3}\text{SD} \times \sqrt{3}\text{SD}$ superstructure [Figs. 3(c) and 3(d)]. Furthermore, our two distinct spectra are consistent with the cases of fully empty ($n_{\text{SD}} = 0$) and fully filled ($n_{\text{SD}} = 2$) in the doped Mott-Hubbard systems, featured by spectral weight transfer into in-gap states with suppression of the Hubbard bands [17]. The electron doping forms the in-gap features below E_F , while the hole doping generates those above E_F . Our spectra show only a single peak, with no indications of any residual spectral

features from the Hubbard band. Taken together, we may estimate the overall electron filling in the $1T\text{-TaS}_2$ layer to be $n_{\text{avg}} = 2/3$, where n_{avg} is the average number of electrons per SD cluster in the layer. This electron occupation differs from the half-filled ($n_{\text{avg}} = 1$) state of monolayer $1T\text{-TaS}_2$ [15] and the fully empty ($n_{\text{avg}} = 0$) state of typical $1T$ layers in $4Hb\text{-TaS}_2$ [17] that exhibit a commensurate $\sqrt{13} \times \sqrt{13}$ CDW. In our case, the average amount of charge transfer to the adjacent $1H$ layer is not 1 but $1/3$ electron for each SD cluster. Such fractional charge filling can be susceptible to charge redistribution, forming fully occupied and unoccupied dangling bonds, due to onsite and nonlocal Coulomb interaction.

Band filling is intimately related to the various charge-ordered phases emerging from $1T\text{-TaS}_2$. A half-filled monolayer of $1T\text{-TaS}_2$ typically behaves as a correlated insulator [Fig. 1(c)]. However, the alternating stacking of $1T$ and $1H$ layers leads to an interlayer charge transfer due to the work function difference between the two polymorphs as the valence electrons of $1T$ layers flow to the $1H$ layers in $4Hb\text{-TaS}_2$ [31]. In line with this, a $1T\text{-TaS}_2$ layer in $4Hb\text{-TaS}_2$ shows a hole-doped Mott phase in which the spectral peak is formed just above E_F with very weak (almost absent) spectral intensity below E_F [Fig. 1(e)]. The strongly asymmetric spectral feature suggests that one electron per $\sqrt{13} \times \sqrt{13}$ SD cluster is transferred to the $1H$ -layer. Interestingly, even though the CDW is susceptible to band filling, the commensurate CDW in $1T\text{-TaS}_2$ is preserved in two different limits: half-filled ($n_{\text{avg}} = 1$) and fully empty ($n_{\text{avg}} = 0$).

In the intermediate doping regime, we can expect a charge rearrangement in a Mott insulator due to a strong correlation effect. For example, when a Mott insulator is charge depleted and thus its overall charge density approaches $n_{\text{avg}} = 2/3$, one can expect the half-filled ($n_{\text{SD}} = 1$) and the fully-empty ($n_{\text{SD}} = 0$) SD to coexist with a commensurate CDW within $1T$ layers [Fig. 3(e)]. These voids allow for sequential electron hopping, which is strongly suppressed in the half-filled condition [17]. However, this correlated metallic state was not observed in our measurements. Instead, we suggest that electrons can be redistributed to form one SD cluster occupied by two electrons with its nearest-neighbor clusters in the $\sqrt{3}_{\text{SD}} \times \sqrt{3}_{\text{SD}}$ unit cell remaining unoccupied [Fig. 3(f)]. Therefore, this demonstrates that a doped Mott insulator undergoes a CDW transition rather than becoming a correlated metal within a certain doping concentration range.

It is evident from Fig. 4(a) that the heterogeneous charge-ordered phase in the upper $1T$ -TaS₂ layer is affected by the different CDW domains of the $1H$ -TaS₂ below. Although we cannot explicitly determine whether the charge ordering observed in the exposed part of the $1H$ -TaS₂ layer persists below the $1T$ -TaS₂ layer, we can clearly observe that the domain walls separating the CDW phases in each layer overlap with each other. We can distinguish three domains. The first one is composed of fully empty SDs with $\sqrt{13} \times \sqrt{13}$ ordering that are aligned with the 3×3 CDW domain in the $1H$ layer below [upper region of Fig. 4(a)]. The second one exhibits a $\sqrt{3}_{\text{SD}} \times \sqrt{3}_{\text{SD}}$ reconstruction on top of a 2×2 CDW domain in the $1H$ layer [lower region of Fig. 4(a)]. On occasion, domain walls are present between $\sqrt{3}_{\text{SD}} \times \sqrt{3}_{\text{SD}}$ domains with fluctuations [Fig. 4(b)]. The third domain consists of randomly distributed fully filled SDs with a low concentration above a disordered 3×3 CDW domain in the $1H$ layer [middle region of Fig. 4(a)]. We can argue that a 2×2 CDW has a higher work function than the 3×3 CDW, and thus attracts fewer electrons from the $1T$ layer, assuming the absence of intercalation. These observations imply that interlayer charge transfer can be modulated by the heterogeneous CDW substrate, and the band filling is crucial to determining the charge order in a triangular Mott insulator.

IV. DISCUSSION

A similar charge-ordered phase has been observed in triangular arrays of group-IV adatoms on semiconductor surfaces at low temperatures [32,33]. Each metallic atom passivates the dangling bonds of the semiconductor surface and hosts one valence electron. This metallic electron configuration makes the systems susceptible to onsite and nonlocal Coulomb repulsion [9]. In case of Pb on Si(111) and Ge(111) surfaces, charges are redistributed to form $\sqrt{3} \times \sqrt{3}$ superstructures at low temperatures [32,34]. The $n_{\text{Pb}} = 0, 1$, and 2 states alternately reside in atomic sites within the half-filled ($n_{\text{avg}} = 1$) regime [35]. On the other hand, Sn on Si(111) does not exhibit charge-ordered phase while it becomes superconducting upon increased doping concentration [36,37]. The insulator-to-metal transition accompanied by a spectral weight transfer and a putative unconventional superconductivity [38,39] are the aspects that remain ambiguous in the doped $1T$ -TaS₂.

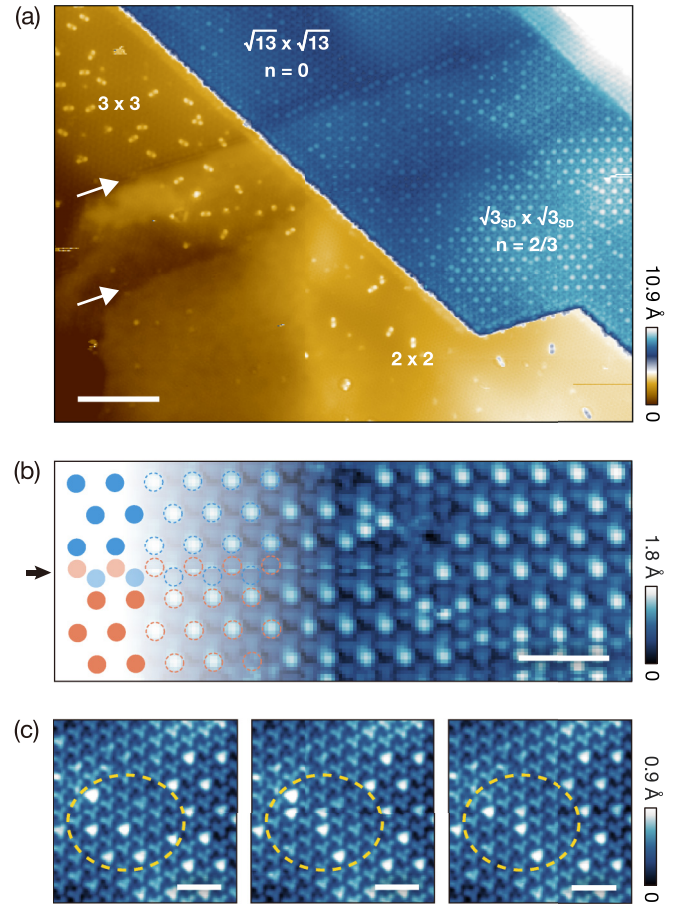


FIG. 4. Heterogeneous charge-ordered phase and its dynamical properties. (a) An STM image of $1T$ and $1H$ surfaces containing multiple phases. The white arrows highlight the boundaries of distinct phase domains of the $1H$ layer underneath the $1T$ layer. Scale bar, 10 nm. (b) An STM image of $\sqrt{3}_{\text{SD}} \times \sqrt{3}_{\text{SD}}$ charge ordering with distinct CDW domains $V_{\text{set}} = -0.8$ V and $I_{\text{set}} = 50$ pA. Brighter sites are highlighted with circles and the color of the circles (blue and orange) represents the CDW phase of each domain. The black arrow points to the CDW domain wall between two domains and its fluctuations. Scale bar, 5 nm. (c) A temporal-sequential STM image series of the same field of view ($V_{\text{set}} = -2.0$ V and $I_{\text{set}} = 100$ pA). The yellow dashed circles highlight areas showing current-induced fluctuations. The time interval between the STM images is about 40 min. Further investigations using high-frequency measurements with a local probe will be required to reveal the origin of the dynamic behavior and its temporal characteristics. Scale bar, 3 nm.

Deviations from the half-filled case also lead to charge redistributions governed by competition between onsite and nonlocal Coulomb repulsion [40–42]. Previous studies together with our observations on $4Hb$ -TaS₂ indicate that each SD strongly prefers only two discrete charged states, $n_{\text{SD}} = 0$ or 2 , while the half-filled SDs ($n_{\text{SD}} = 1$) and current-induced fluctuations [Fig. 4(c)] are only observed occasionally [16]. The absence of a half-filled SD also indicates that our charge-ordered state is bipolaronic rather than paramagnetic. Since the CDW gap is larger than the Mott gap in $1T$ -TaS₂, CDW is not altered even if an SD is fully empty or filled. Notably, all of the stable charge distributions result in insulating states rather than metallic states.

Due to the interlayer charge transfer, 1T-TaS₂ likely loses the exotic electronic properties expected in a half-filled triangular Mott insulator, which have been considered as a prerequisite for chiral superconductivity with broken time-reversal symmetry [43–46]. Instead, in 4Hb-TaS₂, a two-dimensional metallic 1H-TaS₂ layer is encapsulated by charge-ordered insulating 1T-TaS₂ layers. Note that 4Hb-TaS₂ ($T_c \sim 2.7$ K) [43] exhibits a higher critical temperature than 2H-TaS₂ ($T_c \sim 0.8$ K) [47]. The origin of this enhanced superconductivity has yet to be firmly established. Recalling the structural similarity of monolayer FeSe on insulators [48], our observation can turn one's attention to the interface between the two-dimensional superconducting layer and the charge-ordered insulating layer [31], the dimension-dependent pairing strength [47], and the suppressed CDW in 1H-TaS₂ [31] in order to understand the exotic superconductivity of 4Hb-TaS₂.

V. CONCLUSION

In conclusion, our STM measurements on 4Hb-TaS₂ reveal the emergence of charge-ordered phases in strongly correlated electron systems in the intermediate doping regime. Our findings indicate the presence of a $\sqrt{3} \times \sqrt{3}$ superstructure on the SD lattice in the 1T-TaS₂ layer, which is a triangular Mott insulator at half-filled condition. The spatially resolved STS measurement on the charge-ordered state reveals unique characteristics that point toward an out-of-phase charge distribution, providing evidence for a CDW insulating phase.

This suggests the presence of an intermediate state within the 1T-TaS₂ layer, between half-filled and fully empty states, which has a commensurate $\sqrt{13} \times \sqrt{13}$ CDW phase. This intermediate state is likely due to charge transfer modulated by the CDW phases of the sublayer. Our findings shed light on the charge-ordered insulating states in a geometrically frustrated Mott insulator. They also provide a route to control the electronic properties of layered materials by regulating interlayer couplings.

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