Roles of the Narrow Electronic Band near the Fermi Level in 1T-TaS₂-Related Layered Materials

Chenhaoping Wen, Jingjing Gao, Yuan Xie, Qing Zhang, Pengfei Kong, Jinghui Wang, Yilan Jiang, Xuan Luo, and Shichao Yan

1School of Physical Science and Technology, ShanghaiTech University, Shanghai 201210, China
2Key Laboratory of Materials Physics, Institute of Solid State Physics, Chinese Academy of Sciences, Hefei 230031, China
3University of Science and Technology of China, Hefei 230026, China
4ShanghaiTech Laboratory for Topological Physics, ShanghaiTech University, Shanghai 201210, China
5High Magnetic Field Laboratory, Chinese Academy of Sciences, Hefei 230031, China
6Collaborative Innovation Centre of Advanced Microstructures, Nanjing University, Nanjing 210093, China

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Here we use low-temperature scanning tunneling microscopy and spectroscopy to reveal the roles of the narrow electronic band in two 1T-TaS₂ related materials (bulk 1T-TaS₂ and 4H₆-TaS₂). 4H₆-TaS₂ is a superconducting compound with alternating 1T-TaS₂ and 1H-TaS₂ layers, where the 1H-TaS₂ layer has weak charge density wave (CDW) pattern and reduces the CDW coupling between the adjacent 1T-TaS₂ layers. In the 1T-TaS₂ layer of 4H₆-TaS₂, we observe a narrow electronic band located near Fermi level, and its spatial distribution is consistent with the tight-binding calculations for two-dimensional 1T-TaS₂ layers. The weak electronic hybridization between the 1T-TaS₂ and 1H-TaS₂ layers in 4H₆-TaS₂ shifts the narrow electronic band to be slightly above the Fermi level, which suppresses the electronic correlation induced band splitting. In contrast, in bulk 1T-TaS₂, there is an interlayer CDW coupling induced insulating gap. In comparison with the spatial distributions of the electronic states in bulk 1T-TaS₂ and 4H₆-TaS₂, the insulating gap in bulk 1T-TaS₂ results from the formation of a bonding band and an antibonding band due to the overlap of the narrow electronic bands in the dimerized 1T-TaS₂ layers.

Atomic layers with narrow electronic band near Fermi level offer unique platforms for the emergence of unconventional superconducting or magnetic phases [13]. In the narrow electronic band, the kinetic energy of the electrons is strongly reduced. When the Fermi level of the electronic system lies within the narrow band, the Coulomb interactions between electrons can significantly exceed their kinetic energy and drives the system into correlated electronic phases. When the atomic layers with narrow electronic band stack together, the interlayer coupling between the adjacent stacking layers can also strongly modify their narrow electronic bands [4, 6]. The interplay between in-plane electron-electron interactions and interlayer coupling makes the electronic properties of layered materials with narrow electronic band near Fermi level extremely complicated.

One prominent example about the important and complicated roles of the narrow electronic band near Fermi level is the origin of the low-temperature insulating phase in bulk 1T-TaS₂ which has been debated over the past 40 years [5–11]. Below 350 K, the in-plane lattice distortion leads to the formation of Star-of-David (SD) cluster which consists of 13 Ta atoms [12]. There is a single Ta-5d electron in each Ta site and each SD cluster has an odd number of electrons. Below 180 K, the SD clusters become long-range ordered and the bulk 1T-TaS₂ enters the commensurate $\sqrt{13} \times \sqrt{13}$ charge density wave (CDW) state with an insulating ground state [13]. Without considering interlayer CDW coupling, the tight-binding simulations for two-dimensional 1T-TaS₂ indicate there is a very narrow electronic band near Fermi level in the commensurate CDW state of 1T-TaS₂ and it may be susceptible to Mott-Hubbard transition [14, 15]. The measured low-temperature insulating gap in bulk 1T-TaS₂ is first interpreted as a Mott-insulating gap due to the strong electron-electron interactions [Fig. 1(a)] [16, 17]. However, the recent scanning tunneling microscopy (STM) and angle-resolved photoemission spectroscopy (ARPES) studies demonstrate that the interlayer CDW dimerization doubles the unit cell to contain even number of Ta-5d-orbital electrons, and the insulating gap in bulk 1T-TaS₂ is a band insulating gap [Fig. 1(a)] [5, 6, 9–11, 18]. In this scenario, studying the electronic properties of the 1T-TaS₂ layers with strongly reduced interlayer CDW coupling would be very helpful to further reveal the roles of the narrow electronic band in the 1T-TaS₂ layer.

4H₆-TaS₂ is another 1T-TaS₂ related layered material in which the unit cell consists of alternating layers of 1T-TaS₂ and 1H-TaS₂ (half of 2H-TaS₂) [Fig. 1(c)]. The alternate stacking of the 1T-TaS₂ and 1H-TaS₂ layers can be clearly seen in the high-resolution transmission electron microscopy image [Fig. 1(d)]. In contrast to the low-temperature insulating phase in bulk 1T-TaS₂, 4H₆-TaS₂ is a superconductor with transition temperature $T_c \sim 3$ K (see Supplemental Materials Fig.S1, 19). Although the $\sqrt{13} \times \sqrt{13}$ CDW order exists in the 1T-TaS₂ layer of 4H₆-TaS₂ (1T₄H₆), the CDW order in the 1H-TaS₂ layer of 4H₆-TaS₂ (1H₄H₆) is very weak [20, 22]. The 1H₄H₆ can greatly reduce the interlayer CDW coupling between adjacent 1T₄H₆, and the previous ARPES measurements indicate 1T₄H₆ and 1H₄H₆ still retain their original electronic dispersion [23]. This makes 4H₆-TaS₂ an interesting platform to investigate the electronic properties of the 1T-TaS₂ layers with strongly reduced interlayer CDW coupling.

In this letter, we use low-temperature STM to probe and reveal the roles of the narrow electronic band in the low-temperature electronic states of 4H₆-TaS₂ and bulk 1T-TaS₂. We find that the narrow electronic band near Fermi level exists in the 1T₄H₆ and it is localized near the center of the
We show that the correlation effect in the 1T-4Hb depends on the filling factor of the narrow electronic band. We also demonstrate the relationship between the narrow electronic band in 1T-TaS₂ layer and the low-temperature insulating gap in bulk 1T-TaS₂.

Bulk 1T-TaS₂ and 4Hb-TaS₂ single crystals were synthesized by chemical vapor transport method with iodine as a transport agent and the detailed growth conditions were described elsewhere. STM experiments were performed with a home-built low-temperature STM. Bulk 1T-TaS₂ and 4Hb-TaS₂ samples were cleaved at 77 K and then transferred into the low-temperature STM head for measurements at 4.3 K which is slightly above the superconducting transition temperature of 4Hb-TaS₂. Chemically etched tungsten tips were flashed by electron-beam bombardment for several minutes before use. Scanning tunneling spectroscopy (STS) measurements were done by using standard lock-in technique with 3 mV modulation at the frequency of 914 Hz.

Figure 1(a) and (f) are the negative-bias-voltage STM topographies taken on the bulk 1T-TaS₂ and the 1T-4Hb, respectively. The √3 × √3 CDW pattern can be clearly seen on both these surfaces. In the negative-bias-voltage STM topography taken on the 1H-4Hb, the intrinsic 3 × 3 CDW pattern can be barely seen [Fig. 1(g)]. Due to the CDW order in the underneath 1T-4Hb, there is a modulation pattern with the √3 × √3 periodicity in the positive-bias-voltage STM topography taken on the 1H-4Hb (Supplemental Materials Figs.S2 and S3). Our STM topographies indicate that the CDW pattern in the 1H-4Hb is weak, which makes it behaves as a buffer layer between the adjacent 1T-4Hb.

We next perform STS to study and compare the local electronic structures in bulk 1T-TaS₂ and 1T-4Hb. Figure 2(a) is the STM topography taken on the most typical cleave plane of bulk 1T-TaS₂. Figure 2(b) shows the line cut differential conductance (dI/dV) spectra along the red arrow shown in Fig. 2(a), where the ~150 mV insulating gap induced by the interlayer dimerization effect can be clearly seen [9]. In comparison, Figure 2(d) shows the line cut dI/dV spectra taken on the 1T-4Hb along the red arrow shown in Fig. 2(c). As shown in Fig. 2(d), there is a sharp peak feature located just above the Fermi level, and the peak width at half height is ~50 mV. Another clear feature in Fig. 2(d) is a gap-like feature between ~200 mV and the Fermi level. Figure 2(e) shows the typical dI/dV spectra taken on the 1H-4Hb, 1T-4Hb and the bulk 1T-TaS₂. The overall feature of the dI/dV spectrum on 1H-4Hb is V-shaped without clear electronic peaks and gaps (Supplemental Materials Figs.S4 and S5).

Because of the 1H-4Hb, the interlayer CDW coupling between the adjacent 1T-4Hb is reduced. To understand the features in the dI/dV spectrum taken on the 1T-4Hb, we compare it with the previous empirical tight-binding simulations for two-dimensional 1T-TaS₂ without considering the interlayer coupling [Fig. 2(f)]. Surprisingly, the overall feature in the dI/dV spectrum of the 1T-4Hb matches with the calculated density of states shown in Fig. 2(f), including the narrow band near Fermi level and the gap between ~200 mV and the Fermi level. The difference is that the whole spectrum measured on the 1T-4Hb is shifted up by ~20 mV [Fig. 2(e)]. This is likely due to the weak electronic hybridization between the 1T-4Hb and the 1H-4Hb, which induces effective doping effect to the...
After characterizing the narrow electronic band in the 1T-4Hb, we try to explore the relationship between this narrow electronic band and the insulating gap in the bulk 1T-TaS2. We also use spatially resolved STS to measure the spatial distributions of the electronic states in bulk 1T-TaS2. As shown in Figs. 4(d) and (g), the spatial distributions of the electronic states at ∼320 mV and +460 mV are consistent with the corresponding electronic states in the 1T-4Hb [Figs. 3(d) and (g)] which prefer to locate at the rim the SD cluster. Interestingly, the spatial distributions of the electronic peaks below and above the insulating gap [Figs. 4(c) and (f)] agree with the spatial distribution of the narrow electronic band in the 1T-4Hb [Fig. 3(f)], which prefer to reside on the center of the SD cluster [28]. The recent STM work has demonstrated that the ∼150 meV insulating gap in bulk 1T-TaS2 [Fig. 4(b)] appears when the CDW patterns are vertical aligned in the dimerized 1T-TaS2 layers [Fig. 4(c)] [9]. Our data further indicates that in that stacking configuration, the narrow electronic bands in the dimerized 1T-TaS2 layers have strong spatial overlap and form the bonding and antibonding bands [Fig. 3(c)].

We next discuss why the narrow electronic band in the 1T-4Hb is not splitted by the in-plane electron-electron interactions. This is likely because of the weak electronic hybridization between the 1T-4Hb and 1H-4Hb which shifts the narrow electronic band to be slightly above the Fermi level. This makes the narrow electronic band in the 1T-4Hb almost unfilled, and suppresses the correlation induced electronic gap. The filling-factor-dependent correlation gap has been reported in twisted-bilayer graphene, where the correlation induced band splitting strongly depends on the filling factor of the flat electronic band [29]. However, the electronic hybridization is usually sensitive to the interlayer distances between the two layers. In the 4Hb-TaS2 sample, we find that in a few regions the narrow electronic band is located slightly closer to the Fermi level, and a ∼30 meV electronic gap can be detected (see Supplemental Materials Fig.9, [19]). This ∼30 meV gap may be due to the electronic-correlation-induced gap in the 1T-4Hb. This also agrees with the size of the possible correlation gap (∼50 meV) in the undimerized 1T-TaS2 layer of bulk 1T-TaS2 [9]. For the further experiments, it would be interesting to investigate correlation effect in the 1T-4Hb by moving the narrow electronic band closer to Fermi level with electron doping.

In summary, our data not only shows the existence of the narrow electronic band near Fermi level in 1T-TaS2 layer, but also demonstrates it plays a crucial role in the low-temperature electronic properties of 1T-TaS2 related materials. When the narrow electronic band in the 1T-4Hb is located slightly...
FIG. 3. (a) Constant-current STM topography taken on 1T_4Hb (V_s = 500 mV, I = 1 nA). Size: 6 nm × 6 nm. (b) The typical dI/dV spectrum taken on 1T_4Hb (left panel). The right panel shows the previously calculated atom-projected density of states on the ‘a’, ‘b’ and ‘c’ Ta atoms shown in (c) [14]. (c) Unit-cell of the √13 × √13 reconstruction in the 1T-TaS2 layer. The green, blue and red dots denote the inequivalent Ta atoms in the SD clusters. (d)-(g) dI/dV maps taken on the same region as shown in (a) with −320 mV (d), −140 mV (e), +20 mV (f) and +460 mV (g) bias voltages.

FIG. 4. (a) Constant-current STM topography taken on bulk 1T-TaS2 (V_s = 500 mV, I = 1 nA). Size: 6 nm × 6 nm. (b) The typical dI/dV spectrum taken on bulk 1T-TaS2. (c) Schematic showing the interlayer CDW dimerization induced band insulating gap in bulk 1T-TaS2. (d)-(g) dI/dV maps taken on the same region as shown in (a) with −320 mV (d), −200 mV (e), +250 mV (f) and +460 mV (g) bias voltages.

above the Fermi level, the electronic correlation induced narrow band splitting is suppressed. The insulating gap in bulk 1T-TaS2 originates from the interlayer CDW dimerization induced bonding and antibonding bands of the narrow electronic band. Our work also paves the way for further understanding the novel electronic phases in 1T-TaS2 related materials, such as the possible chiral superconductivity in 4Hb-TaS2 [23] and the electronic states in single layer 1T-TaS2 [30, 31].

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