The Research on the Complexity of 1T-TaS2 at Ultra-low Temperatures

Han Tianxue
School Of Physics, Northeast Normal University, Changchun, Jilin, 130024, China
418612572@qq.com

Abstract. Graphene, as a successfully industrialized two-dimensional material, has greatly promoted the development of other two-dimensional materials, such as transition metal dichalcogenide (TMDs). 1T-TaS2 is a classical TMDs material, which presents metallicity at high temperature. It undergoes a variety of charge density wave (CDW) phase transitions during the temperature declining process, and presents insulating properties at low temperature. During the temperature rise period, 1T-TaS2 goes through a phase transition, from an energy band insulator to Mott insulator, followed by an insulation-metal phase transition. The complexity of 1T-TaS2 phase diagram encourages researchers to conduct extensive research on it. This paper, via means of resistance, magnetic susceptibility and other technical methods, finds out that the ultra-low temperature of 1T-TaS2 suggests additional complexity. In addition, with the angle resolved photoemission spectroscopy (ARPES) technique of in-situ alkali metal evaporation, this paper proposes that the 1T-TaS2 ultra-low temperature ground state may exist a combination of state and surface state. Our findings provide more experimental evidence for the physical mechanism of this system.

Keywords: 1T-TaS2, transition metal dichalcogenide (TMDs), phase transition, ARPES.

1. Introduction
Graphite is a material that is familiar to everyone. The conductive material of the TV Imaging tube coating and the main component of the pencils for the child are graphite, and the graphite is also widely used in military, aerospace and electrical industries. Graphite is featured in its layered structure, which is stacked by layers of carbon atom. The single layer of graphite is graphene, and it has long been acknowledged to be mechanically or thermodynamically unstable. But in 2004, British physicist Geim A. K. and Novoselov K. S. successfully separated graphene from graphite in their laboratory by mechanical stripping methods [1]. This landmark discovery completely unlocked the door to the two-dimensional material and opened up a new field of graphene, and also lead to their 2010 Nobel Physics Award.

As a successfully industrialized two-dimensional material, graphene has greatly promoted the study of other two-dimensional materials, such as the transition metal dichalcogenides (TMDS). TMDS materials share some similar characteristics with graphene, such as it can be torn into thin layers, and the structure is flexible. According to the conductive property, TMDS material can also be divided into metal, semimetal, semiconductor, and superconductor junction. TMDS materials also display characteristics such as adjustable intricate band gap and valley freedom, which presents promising application prospects in the field of optoelectronic devices and self-propelled electronic devices, arousing the interest of researchers [2].
1T-TaS2 is a very classical TMDs material. The complexity and diversity of a series of charge density wave (CDW) phases and lattice structure in the process of temperature change have aroused strong research interest in the physical mechanism. At present, the explanation of CDW origin tends to be the result of electron phonon interaction and Fermi surface nesting mechanism, but further research is still in need. At the same time, the ground state of 1T-TaS2 also attracts a lot of attention. The ground state of this material is very sensitive to the external environment, and it is easily regulated by physical pressure, carrier regulation and other ways to produce more abundant physical properties such as superconductivity, which has a wide range of application prospect in device applications. In the process of exploring its insulating ground state, there are obvious differences between theoretical predictions and experimental observations, indicating that other physical factors should be explored as well as the tightly bound state model and spin-orbit coupling. Disagreements exist on whether 1T-TaS2 is Mott insulator or energy band insulator, and no conclusion has been reached yet. The existence of these unsolved mysteries also adds to higher research value of 1T-TaS2.

In the lattice structure of 1T-TaS2, one Ta atom in each center is surrounded by six S atoms in a regular octahedral configuration, forming a space point group of p-3ml structure. In a single layer of TaS2, Ta atoms in hexagonal arrangement are wrapped into a sandwich shape by two layers of S atoms in regular hexagonal arrangement, and then every two layers of TaS2 are coupled together by van der waals force, which is a quasi-two-dimensional material. The in-plane Ta atom layer of 1T-TaS2 will undergo periodic lattice distortion at low temperature. At low temperature, every 13 adjacent Ta atoms converge toward the center and transfer charges, forming a new protocell of the Star of David (SD) structure (Figure 1). Hence, the volume of the protocell expands 13 times as the original, and the in-plane lattice direction rotates by 13.9 degrees, resulting in \( p(\sqrt{13} \times \sqrt{13}) \) \( R \)\( ^{13.9\text{o}} \) periodic lattice distortion.

**Figure 1.** Resistance and phase diagram of 1T-TaS2. (a) Interior surface resistance data of 1T-TaS2. The temperature warming and cooling resistor curve are red and blue solid lines, respectively. The black arrows mark the first-order phase change points on the curve. Bars of different colors below the curve represent various electronic states. (b) Phase diagram of 1T-TaS2, the longitudinal axis is temperature, and the horizontal axis is doped or pressurized. The upper right corner is the structure of the Star of David at the C-CDW state, and the patterns in the area of each phase is the corresponding in plane lattice distortion of this phase [3].
2. Literature Review

1T-TaS$_2$ experiences a very complex phase transition during the temperature change (Figure 1). At high temperature ($T > 550$ K), the 1T-TaS$_2$ lattice structure has not changed. The 5d orbit of the Ta atom contributes to the half-filled charge energy band through the fermi surface, so that the system exhibits metallicity. As the cooling process continues, 1T-TaS$_2$ has undergone a series of first-order phase transition, producing varieties of CDW phases and the commensuration of CDW gradually increases (Figure 1.13). 1T-TaS$_2$ below 550 K is in the in-Commensurate CDW (IC-CDW) state. 1T-TaS$_2$ below 350 K displays Nearly-Commensurate CDW (NC-CDW, also known as the Quasi-CDW). Eventually, 1T-TaS$_2$ below 180 K is in Commensurate CDW state (C-CDW). Interestingly, 1T-TaS$_2$ first enters the Triclinic CDW state (T-CDW) in 220 K. The T-CDW state only appears during the temperature rise, then at 280 K, it enters the NC-CDW state. If we compare the resistance curve of cooling and warming, it can be observed that there is a significant hysteresis when it is around 200 K. The phase transition point of cooling process is 180 K, while the phase change point of warming process is 220 K. The temperature difference of warming and cooling at first-order phase change point is about 40 K, which is relatively rare in TMDS materials.

In different CDW states, the arrangement behavior of Ta atoms in 1T-TaS$_2$ interior surface is inconsistent (Figure 1). At the low temperature C-CDW ground state, the Star of David atomic group bespreads the entire Ta atomic plane, forming a $p(\sqrt{13} \times \sqrt{13})R13.9^\circ$ periodic lattice structure. In the T-CDW state, Star of David forms stripe-like structures. There is no reconstructed Ta atomic conductive channel between the stripes. In the NC-CDW state, the Star of David group forms a hexagonal area (Domain) structure, there is no Star of David structure between different domains, forming a metallic conductive channel. In IC-CDW state, there is sporadic Star of David dispersed in plane. Whereas in the normal metal state, there is no Star of David structure [4].

Renowned physicist Phil Anderson had a famous saying in the field of condensed state, that is, more is different. The complexity and diversity of the phase diagram and lattice structure of 1T-TaS$_2$ displayed during the temperature change have aroused much research enthusiasm to this system, which stimulates public interest in studying the mechanism, exploring the potential possibilities of device application.

![Figure 2](image_url) Figure 2. Flat electronic structure of different electron states during heating process of 1T-TaS$_2$. (a) Second derivative spectrum of the electronic structure of 1T-TaS$_2$ under different electron states along the Γ-M direction. (b) Schematic diagram of the corresponding electronic structure under different electronics state, the red circle represents the extreme point of data in (a), and the black line depicts the dispersion curve of the flat band. Brown thick lines represent the band of higher energy.
In 2020, Zhang Wei, affiliated in PKU Quartz Material Center, plotted detailed temperature-modified data of 1T-TaS2 (Figure 2), and discovered a new electron phase at around 217 K ~ 233K in the heating process [5]. As is shown in Figure 2, the 5d energy band of Ta atoms strips through the Fermi surface in the IC-CDW state. At the NC-CDW state and the T-CDW state, the 5d energy band of Ta atoms opens the CDW energy gap. At the same time, flat band is formed in the vicinity of Fermi energy band. The bandwidth of the flat band is very narrow, which is about 100 meV, and it is consistent with the spatial size of the Star of David. In the I-state, the flat band is translated from the Fermi surface to -170 meV, and opens up the energy gap. In the C-CDW state, the flat band is further translated to -200 meV, with more dispersion. Meanwhile, in the C-CDW state, the flat band appears to widen in energy. The shadow energy band can be seen from the vicinity of Fermi energy band, which is consistent with the broadened FWHM of the EDCs in Figure 2. Since ARPES is a surface-sensitive technique, the momentum resolution in the kz direction is very unsatisfactory. If an energy band had a strong dispersion in the kz direction, its ARPES spectrum would be broadened in energy. This study observes the flat band energy broadening in C-CDW state, which may imply reconstruction occurs in the C-CDW state flat band in kz direction. Zhang et al. successfully confirmed that ground state of 1T-TaS2 is a band insulator with dimeric inter-layer polymerization, with the use of poikilothermal X-ray diffraction technology and the ARPES technology of the variable photon energy. 1T-TaS2 at 217 K ~ 233 K during the heating process is a single-layer, high energy gap Mott insulator.

The temperature range in the research of Zhang et al., is 160 K ~ 300 K [5]. In this study, we set out to explore whether there is abnormal physical behavior at a temperature below 160 K?

3. Experiments and Results

With this question, we observed the transport data (resistivity, susceptibility) of 1T-TaS2. As shown in Figure 3, it is obvious that below about 100 K, resistivity and susceptibility curves of 1T-TaS2 appear “upwarped” as the temperature decreases, and the resistance near the ultra-low temperature of 2 K increases by 3 orders of magnitude, relative to 100 K. The abnormal behavior of the resistivity and susceptibility curves below 100 K is inconsistent with that above 100 K, suggesting the complexity of the ultra-low temperature phase of 1T-TaS2.

Consequently, will the electronic structure of 1T-TaS2 at ultra-low temperature appear to be special? As is demonstrated in Figure 4, the energy spectra of 50 K and 150 K of 1T-TaS2 have slight differences near point M. The energy spectrum at 50 K shows that M energy band has obvious splitting behavior, but the energy spectrum at 150 K does not indicate it, suggesting that the energy band structures of 1T-TaS2 at 50 K and 150 K are inconsistent, and the ultra-low temperature electronic structure demonstrates more complexity.

Figure 3. Resistivity and susceptibility data of T-TaS2
In order to explore the temperature at which energy band splitting behavior disappears at ultra-low temperature, this study also conducted a detailed temperature change. Figure 5(b) shows that the splitting behavior of M-band disappears at temperature above 120 K during the warming process of 1T-TaS2. Figure 5(c) also illustrates that phase transformation occurs near 120 K during the heating process of over-doped 1T-TaS2. As can be seen from Figure 5(c), energy band splitting occurs in P-band above 120 K. Based on the original two bands, a new P-band gradually emerges near -1.15 eV, and the distances between the three P-bands are all 130 meV, suggesting that there is a strong correlation between the three new energy bands. As the temperature continues to rise, 1T-TaS2...
undergoes a first-order phase transition at 217 K, which is reflected in the re-degeneration of three energy bands into two energy bands, and the energy band position is at the middle interval. In addition, the 217 K phase transition point corresponds to the energy band insulator-Mott insulator phase transformation point found in Chapter 3 of this article, which is also the first-order phase transformation point observed on resistance and XRD.

All the above signs indicate that 1T-TaS2 may have a potential phase transition at 120 K. During the heating process of over-doped 1T-TaS2, various electronic states are generated, while the ultralow temperature electronic states display more complexity.

This subject studied the precise alkali metal doping response of 1T-TaS2 at ultra-low temperature (20 K), and described the evolution of the three main energy bands (flat band, P-band, and M-band) of 1T-TaS2 with the amount of alkali metal doping (Fig. 6). The following section will analyze the results of alkali metal Rb atom doping for these three energy bands.

The first is the doping evolution of the flat band. In the whole doping process, it can be seen that the flat band gradually sinks in the first five doping processes, and energy band splitting appears at the sixth doping, in which the upper flat band remains stationary with an energy position of -0.24 eV. The lower flat band gradually submerges, then remains stationary with an energy position of -0.32 eV, and

![Figure 6](image.png)

**Figure 6.** Energy band evolution during the doping of 1T-TaS2 alkali metal Rb atoms at ultra-low temperature (20 K). (a) The evolution of the flat band (original spectrum EDC2) with the number of doping. (b) is the mosaic of EDC and the evolution of flat band position with doping in quantitative analysis. (c), (d) and (e), (f) are similar to (a) and (b), but correspond to the evolution of P-band (original spectrum EDC1) and M-band (original spectrum EDC2) with doping.
the maximum band splitting is 80 meV. After the 16th doping, the two flat bands remerge, with an energy position of -0.28 eV. Therefore, in the whole doping process, the flat bands split firstly, and then degenerate again at high doping.

The doping process of P-band is rather complicated. When it is not doped, P-band has two band bands with an interval of 120 meV. In the first five doping processes, these two P-bands gradually begin to sink, and then splitting starts to occur in both adjacent energy bands in the 5th doping. During the splitting process, a total of four P-bands could be observed, among which the two P-bands of the intermediate energy level begin to degenerate with doping. The energy positions of the three P-bands are as follows, -1.53 eV, -1.42 eV, and -1.30 eV, while the size of the two energy gaps are respectively 113 eV and 118 meV. After the 16th time of excessive doping, three P-bands are recombined into two P-bands, with energy positions of -1.50 eV and -1.37 eV, while the energy gap size is 130 meV.

Finally, this article analyzes the doping evolution of the M-band. There are two energy bands at point M when it is undoped, and the energy gap is about 80 meV. With the doping, the two energy bands soon begin to merge, and they have been completely degenerated together at the third doping. As doping continues, the M-band sinks slightly and then moves upward.

4. Discussion

Based on the evolution of the doping process of flat band, P-band and M-band, this study proposes a possible explanation (Figure 7). At low temperature, 1T-TaS2 has inhomogeneous electronic state. Taking stacking order of 1T-TaS2 with interlayer dimerization into consideration, due to the randomness of sample dissociation in the ARPES experiment, there will be two planar structures, namely double layer and single layer coupling, respectively corresponding to surface 1 and surface 2. These two surfaces may correspond to different insulation states respectively. For example, surface 1 may be an energy-band insulator phase with interlayer dimerization, while surface 2 may be a single-layer Mott insulator state.

If the inhomogeneity of electronic states on the sample surface is considered, the two energy bands observed in the doping process can be understood to a certain extent. In the undoped sample, two electronic states, namely energy-band insulator phase and Mott insulator state, share similar band structures. As a result, only one set of energy bands can be seen on the ARPES spectrum of the flat band and the P-band. On the M-band, two sets of energy bands can be distinguished, and the splitting between them is about 80 meV, which may respectively correspond to the electronic states of the two surfaces. In the doping process, the two electronic states are extremely sensitive and insensitive to Rb atom doping. Therefore, with doping, one set of relatively sensitive energy bands sinks, while another set of relatively insensitive energy bands remains constant with the doping energy position. This can explain the splitting behavior of flat band and P-band with doping, as is observed in this paper. In the heavily doping region, due to the destruction of surface heterogeneity by doping, the energy difference between the two electronic states disappears, and all energy bands splitting disappear and degenerate again. Thus, only one energy band can be observed in the ARPES spectrum.

Although the data observed in this paper can be explained, to a certain extent, by the inhomogeneity of electronic states, there are still many problems in such interpretation. For instance, if these two electronic states correspond to a double-coupled energy band insulator and a single-layer Mott insulator state, then the temperature at which this inhomogeneity occurs should be below 217 K, not 120 K. In addition, if one of them corresponds to the Mott insulation state, it should be very sensitive to the change of doping concentration, and the study ought to be able to observe the closure of energy gap. However, the energy gap identified in this paper is not sensitive to doping response at low temperature, which is different from the results of high temperature electron doping regulation at 225 K to some degree.

5. Conclusion

To conclude, it can be noticed that 1T-TaS2 has a very complex electronic structure, which shows the possibility of realizing Mott insulators and spin liquids. Its ground state can be easily regulated by a
variety of physical control measures. Thus, it is a very promising material. At the same time, this paper discovers that the ultra-low temperature electronic state of 1T-TaS2 has additional complexity, and there is a potential physical phase transition near 120 K. The results of the ultra-low temperature alkali metal doping demonstrate that there is a combination of state and surface state. The complete phase diagram of 1T-TaS2 and the physical mechanism of ultra-low temperature still need to be further studied.

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