Superposition of $\sqrt{13} \times \sqrt{13}$ and $3 \times 3$ supermodulations in TaS$_2$ probed by scanning tunneling microscopy

Y Fujisawa, T Iwasaki, D Fujii, S Ohta, J Iwashita, T Fujita, M Nakata, K Kishimoto, S Demura, and H Sakata

Department of Physics, Tokyo University of Science, Shinjuku-ku, Tokyo 162-8601, Japan

1215702@ed.tus.ac.jp

Abstract. We report on a scanning tunnelling microscopy study of TaS$_2$ at 4.2 K. A surface prepared by cleavage showed a superimposed pattern of two types of charge density waves with $3a_0 \times 3a_0$ and $\sqrt{13}a_0 \times \sqrt{13}a_0$ periodicity, which had never been observed previously. We attribute the superposition to regular stacking of $4H_b$ polytypes or irregular stacking of $2H$ and $4H_b$ layers.

1. Introduction

Scanning tunneling microscopy (STM) is a technique for investigating the surface structure of materials with atomic resolution. STM can generally probe the topmost layer. However, it occasionally probes not only the topmost layer, but also the effect of the underlying layer. A Moiré pattern is an example of such effects and results from supermodulation due to two atomic layers that are stacked at an angle [1]. For example, a Moiré pattern is observed on the surface of highly ordered pyrolytic graphite, bilayer graphene, and graphene on transition metal substrates [2, 3]. On the other hand, there are few reports of such phenomena in other layered materials, such as transition metal dichalcogenides (TMDCs) [4].

One of the TMDCs, TaS$_2$, has several polytypes, such as $1T$, $2H$, and $4H_b$, and shows various charge density wave (CDW) states depending on the polytype. In $1T$-TaS$_2$, a layer is composed of edge sharing TaS$_6$ octahedra. It undergoes a phase transition from a nearly commensurate CDW state to the Mott insulating commensurate state with a period of $\sqrt{13}a_0 \times \sqrt{13}a_0$ at about 200 K [5, 6]. In $2H$-TaS$_2$, a layer is composed of edge shared TaS$_6$ prisms. It undergoes a phase transition to a commensurate CDW state with a period of $3a_0 \times 3a_0$ at 75 K. The electronic state is metallic and superconducting below 1 K [7, 8]. In $4H_b$-TaS$_2$, the structure consists of stacks of alternating $1T$ and $1H$ layers. Further, $4H_b$-TaS$_2$ undergoes CDW transitions and shows $\sqrt{13}a_0 \times \sqrt{13}a_0$ and $3a_0 \times 3a_0$ CDWs within each layer at 4.2 K. It also shows superconductivity at a transition temperature $T_c$ of 3.5 K, which is three times higher than that of $2H$-TaS$_2$ [9, 10]. Because $4H_b$-TaS$_2$ consists of alternating stacks of two different CDW layers, this material is expected to show superposition of the CDWs. However, previous reports presented STM images that showed both CDWs depending on the bias voltage but did not show superposition of the CDWs [11, 12]. In this study, we performed an STM study of a single crystal of TaS$_2$ and revealed a superimposed pattern composed of two types of CDWs with $\sqrt{13}a_0 \times \sqrt{13}a_0$ and $3a_0 \times 3a_0$ periodicity on the surface.
2. Experimental details

2.1. Crystal growth and characterization
The single crystal used in this study is grown by the chemical vapor transport method with iodine as a transport agent. First, Ta and S powders are mixed at chemical stoichiometry, heated at 1000 °C for 4 days in an evacuated silica tube, and then quenched in water. Second, polycrystalline TaS₂ and iodine (5 mg/cm³) are sealed in another quartz tube and heated for 7 days, where the source zone and the growth zone are fixed at 1000 and 850 °C, respectively. The obtained single crystal is evaluated by X-ray diffraction (XRD) using Cu Kα radiation and resistivity measurements. The XRD patterns are shown in Fig. 1(a) and (b). Figure 1(a) shows clear (00l) peaks without extra peaks. However, closer examination of the (008) peak [Fig. 1(b)] shows split peaks. Although the two peaks labeled as A' and B' are due to diffraction by Cu Kα₂, peaks A and B are associated with two different lattice constants, which are estimated to be 6.05n and 5.97n Å, where n is the number of stacks. Because these lattice constants coincide with those of 4Hₘ and 2H, we conclude that our crystal consists of two polytypes; the major one is 4Hₘ and the minor one is 2H. Figure 1(c) shows the temperature dependence of the resistivity of the single crystal. The resistivity decreases monotonically with decreasing temperature. This also indicates that our sample consists of metallic 2H and 4Hₘ polytypes. The inset shows the resistivity from 5 to 2 K. A rapid decrease due to superconductivity appears at about 3.5 K, which corresponds to the Tc value of the 4Hₘ polytype.

2.2. Experimental setup for the STM/STS measurements
STM/scanning tunnelling spectroscopy (STS) measurements are performed by a laboratory-made scanning tunneling microscope. All results are obtained at 4.2 K under a He gas environment at a few torr. Electrochemically polished Au wire is used as an STM tip. STM images are taken in the constant current mode. Tunneling spectra are obtained by numerical differentiation of the I-V characteristics. The sample surface is prepared by cleavage at 4.2 K. Because our sample consists of 2H and 4Hₘ polytypes, which have alternating stacks of 1T and 1H layers, the top most surface obtained by cleavage cannot be selected in a controlled manner.

![Figure 1(a) XRD profile of the single crystal used in this study. (b) Magnified view of XRD profile in (a). (c) Temperature dependence of resistivity of the single crystal used in this study.](image)

3. Results and Discussion
Figure 2(a) shows an STM image obtained at a bias voltage of −50 mV. The observed pattern does not correspond to either √3a₀ × √3a₀ or 3a₀ × 3a₀ CDWs; although √3a₀ × √3a₀ and 3a₀ × 3a₀ CDWs have three fold symmetry, the observed image does not. To disentangle the complicated supermodulation, we performed fast Fourier transform (FFT) analysis. The inset of Fig. 2(b) shows the corresponding FFT image. One can see six Bragg peaks (black circles). This indicates that the top most S atoms form a regular triangular lattice. The main figure shows the magnified FFT image. This image captures two types of CDWs; the one marked by red circles corresponds to the 3a₀ × 3a₀ CDW, and the one marked by blue diamonds corresponds to the √3a₀ × √3a₀ CDW. Whereas the wave vector of the 3a₀ × 3a₀ CDW is aligned with the S atoms, the wave vector of the √3a₀ × √3a₀ CDW is rotated by 14° with respect to the S atoms. These results show that the STM image...
can be expressed as the superposition of the two types of CDWs with periods of $\sqrt{13} a_0 \times \sqrt{13} a_0$ and $3a_0 \times 3a_0$. Because each CDW comes from different layers, namely the $T$ and $H$ layers, respectively, the observed STM image is a result of the superposition of the effects of each layer. The lack of three-fold symmetry in the obtained STM image is due to the difference in the intensity of the FFT spots of the $3a_0 \times 3a_0$ CDW; the intensity of spots in one direction is much stronger than that of spots in the other two directions. This is not the effect of the tip shape, because there is no difference between the intensity of the FFT spots of the other CDW or atoms. It is reported that, in $2H$-NbSe$_2$, owing to the strain of one layer perpendicular to the other layer, the $3q$ state was suppressed, and the $1q$ state was realized [13]. The non-equivalence of the $3q$ state in this sample may result from strain caused by stacking of different types of layers.

Figure 2(a) STM image at bias voltage of $\sim 50$ mV and current of 200 pA. (b) Magnified FFT image of (a). Inset shows FFT image including Bragg peaks. (c) Possible model explaining the superposition pattern in (a). (d) STM image taken in almost the same area as (a). The set point is 500 mV and 200 pA. (e) Tunneling spectrum of the surface investigated by STM.

Figure 2(c) shows a schematic of the configuration of the two CDWs. Because one of the three components in the $3a_0 \times 3a_0$ CDW in the $H$ layer is stronger, the superposition of the star of David pattern and one $3a_0$ component causes one-dimensional supermodulation with a period of about $8.1a_0$, which is consistent with the observed STM image. This indicates that there is no misorientation or slight relative displacement of the atomic lattices, but that STM image can be described as the superposition of two types of CDWs.

The relative strength of the two CDWs changed depending on the bias voltage. Figure 2(d) shows an STM image taken at a bias voltage of $+500$ mV. At this bias voltage, the $\sqrt{13} a_0 \times \sqrt{13} a_0$ CDW is greatly enhanced compared to its appearance in the STM image at $-50$ mV. The same tendency has been reported in a $4H_b$ sample, although the superposition of two CDWs has not been observed [11, 12]. The tunneling spectrum of this surface is shown in Fig. 2(e). The observed spectrum has a finite local density of states (LDOS) at the Fermi level ($E_F$) with a shallow gap of approximately 100 meV. This feature does not coincide with either the $1T$ surface of $4H_b$-TaS$_2$, where a clear energy gap opens, or the $1H$ surface, where the spectrum is metallic and flat near $E_F$, but rather is rather intermediate
between the two. The shallow gap seems to come from the energy gap in the $1T$ layer, indicating a smaller LDOS contribution from the $1T$ layer at a low bias voltage. Thus, the low-bias STM would show the $3a_0 \times 3a_0$ CDW more strongly.

We found that the STM image shown in Fig. 2(a) is explained by the superposition of two CDWs. The superposition is due to stacking of $1T$ and $1H$ layers. One possible origin of this stacking is $4H_b$ structure, which consists of alternate stacks of $1T$ and $1H$ layers, although previous reports on $4H_b$ have not shown the superposition of two CDWs on both the $1T$ and $1H$ layers [11, 12]. Another possibility is irregular stacking. As shown in the XRD results in Fig. 1(b), our sample has a partial $2H$ polytype volume fraction, indicating possible irregular stacking of $2H$ and $4H_b$ layers, such as $H-H-H-T$. In this case, if cleavage revealed a $1T$ layer as the top most layer, the resultant structure below the top $1T$ layer is $2H$, which is different from $4H_b$ stacking. This stacking may produce superposition of two CDWs.

4. Summary

In conclusion, we report an STM study of TaS$_2$ that revealed the superposition of two types of CDWs with periods of $\sqrt{13}a_0 \times \sqrt{13}a_0$ and $3a_0 \times 3a_0$. We propose two possible explanations for the phenomenon. One is regular stacking of the $4H_b$ crystal structure. Another is some types of stacking fault such as $H-H-H-T$ stacking.

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