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Effect of Fe-doping on CDW state in 1*T*-TaS_2 investigated by STM/STS

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Abstract. 1*T*-TaS_2 has been known to undergo Mott transition from nearly commensurate charge density wave (CDW) state to commensurate CDW state at about 200 K. Recently, Fe doping was found to suppress the Mott transition and induce superconductivity. In this study, we report on the scanning tunneling microscopy (STM) and spectroscopy (STS) study on Fe doped 1*T*-TaS_2 with different Fe concentration. STM observations reveal that the CDW superlattice becomes irregular as increasing Fe concentration. STS measurements uncover the spatial change in the local density of state (LDOS). We find two types of David-star: one has symmetric LDOS with respect to Fermi energy, and the other has asymmetric one. We identify that the asymmetric spectrum is due to an Fe dopant.

1. Introduction

1*T*-TaS_2 is one of the transition metal dichalcogenides and is known to form charge density wave (CDW) states that originates from low dimensionality of the crystal structure. Below 200 K, it becomes commensurate CDW (CCDW) state. In the CCDW state, 13 Ta atoms form a "David-star" cluster and it forms triangular lattice with $\sqrt{13}a_0 \times \sqrt{13}a_0$ periodicity (where a_0 is in-plane lattice constant). This phase is the Mott state due to the strong correlation effect between Ta 5d electrons at the center of the David-star [1]. Above 200 K, the CCDW state melts into nearly commensurate CDW (NCCDW) state. In the NCCDW state, the hexagonal array of the CDW domains are separated by discommensurations. Accompanied with this structural change, the electronic structure changes from the Mott state to metallic one.

Not only the CDW order, but superconductivity has been realized by several methods, such as chemical doping or physical pressure [2-4]. Especially, Fe substitution influences on electronic properties of 1*T*-TaS_2 effectively. In $Ta_{1-x}Fe_xS_2$ system, only 1 % Fe doping suppresses the Mott transition, and 2 % doping induces superconductivity at about 3K [3]. Further doping reduces the electrical conductivity and $Ta_{0.95}Fe_{0.05}S_2$ shows insulating behavior at low temperature due to Anderson localization [3, 5]. Thus, this system is suitable for investigate the competition between superconductivity and CDW state. In order to disentangle the relation between CDW state and superconductivity, the role of Fe dopant should be important.

In this paper, we report on scanning tunneling microscopy and spectroscopy (STM/STS) measurements on 1*T*-$Ta_{1-x}Fe_xS_2$ with different Fe concentration. STM observation reveals that CDW

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superlattice becomes irregular as increasing Fe concentration. STS measurements on $Ta_{0.98}Fe_{0.02}S_2$ uncover the spatial change in the local density of state (LDOS). We find two types of David-star: one has symmetric LDOS with respect to Fermi energy (E_F), and the other has asymmetric one. Because the number of the David-star that has asymmetric LDOS increases as increasing Fe concentration, we conclude that asymmetric LDOS is due to the dopant Fe.

2. Experimental

Single crystals of $Ta_{1-x}Fe_xS_2$ (nominal x = 0, 0.02, and 0.05) were grown by chemical vapor transport method. For the pristine TaS_2, Mott transition was observed at about 220 K in heating process in the electrical resistivity measurements. For the sample with x = 0.02, Mott transition was not observed, but onset of superconducting transition was observed at 4 K. For x = 0.05, in contrast to the previous report [7, 9], the insulating behaviour was not observed. This seems to indicate that our samples have slightly less Fe concentration than the nominal one. The STM/STS measurements were performed by using a laboratory-build scanning tunneling microscope. All of the measurements were done at 4.2 K. Electrochemically polished Au wire was used as STM tip. Clean surface was obtained by cleavage at 4.2 K in a few torr He gas environment. STM images were obtained by constant-current mode. Tunneling spectra were obtained by the numerical differentiation of the I-V curves.

3. Results and Discussion

Figures 1(a) to (c) show typical STM images of $Ta_{1-x}Fe_xS_2$ (nominal x = 0, 0.02, and 0.05), respectively. In all images, bright points, which correspond to David-stars can be seen. Figure 1(a) shows almost perfect triangular lattice composed of David-stars. On the other hand, in the sample with x = 0.02, the CDW superlattice distorts. Furthermore, in the sample with x = 0.05, the distortion becomes significant. Here, it should be noted that the defects of David-star lattice that can be seen as dark points in figures 1(b) and (c) do not correspond to Fe site, because such defect exists even in the pristine sample (not shown) and its concentration is not proportional to the nominal Fe concentration.

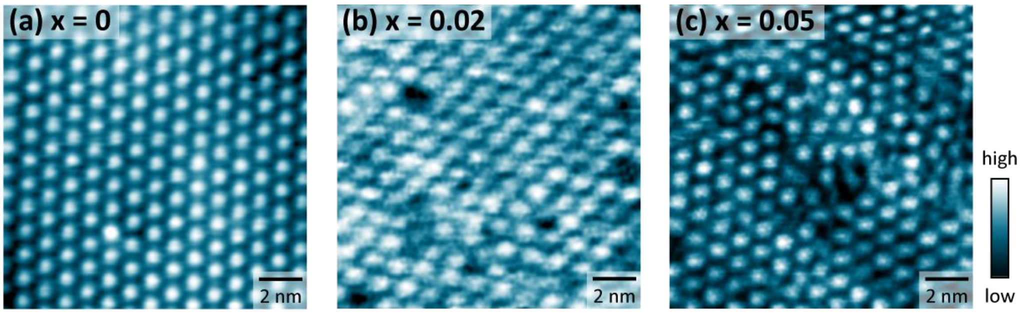

Figure. 1. (a)-(c) STM images of $Ta_{1-x}Fe_xS_2$ (nominal x = 0, 0.02, and 0.05) obtained at 4.2 K on a 14 × 14 nm^2 field of view, respectively. The sample bias voltage is 500 mV and the tunneling current is 200 pA.

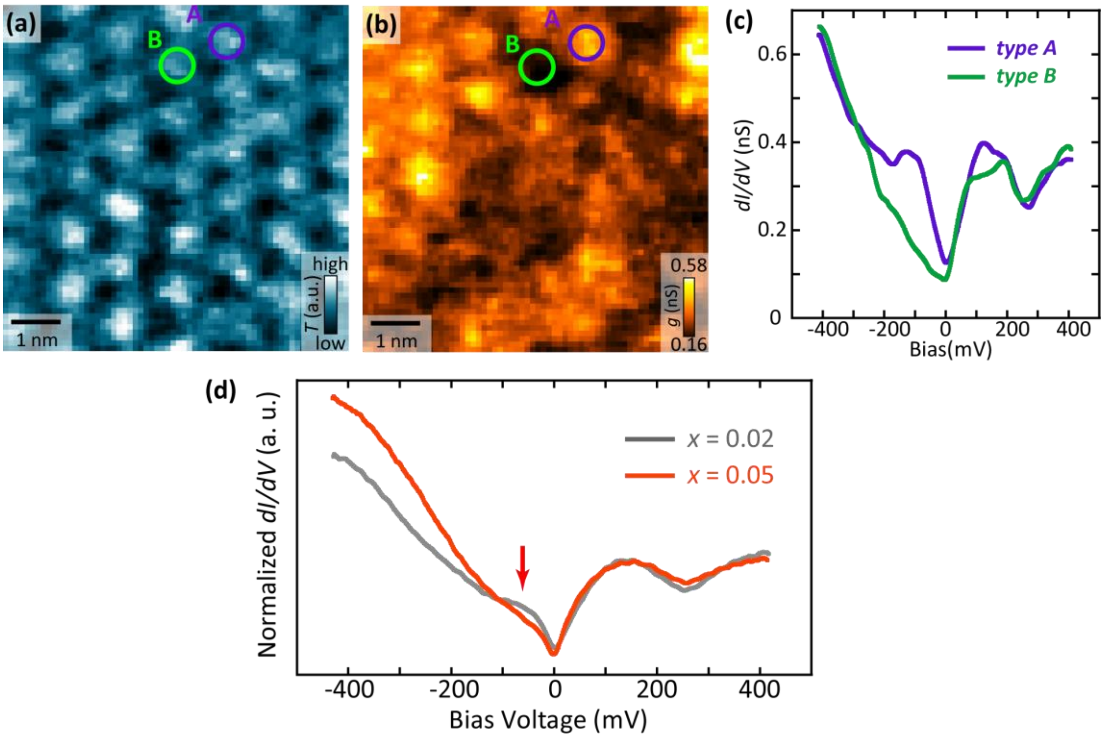

Figure. 2. (a); STM image of $Ta_{0.98}Fe_{0.02}S_2$ that is simultaneously obtained by STS measurements on a 7 × 7 nm^2 field of view. The sample bias voltage is 500 mV and the tunneling current is 200 pA. (b); The conductance (*g*) map at -120 mV on the same field of view as (a). (c); Tunneling spectra obtained in the circles shown in (a) and (b). (d); Spatially averaged tunneling spectra on a 14×14 nm^2 field of view. Gray and red lines indicate the spectra taken on the sample with x = 0.02 and 0.05, respectively. Each spectrum is normalized at +300 mV.

Figures 2(a) and (b) show a STM image and the simultaneously obtained conductance (*g*) map at -120 mV in x = 0.02 sample, respectively. The *g* map (figure 2(b)) indicates the existence of the spatial inhomogeneity of the LDOS while the STM image shows the periodic array of David-stars. This is in contrast to pristine 1*T*-TaS_2 [1, 6] where each David star shows the same tunneling spectrum. This implies that Fe dopant affects the LDOS. To investigate the effect of Fe doping, we examined the spatial change in LDOS at each David-star. Because the STM image shows the array of David-stars, we averaged the tunneling spectra at each David-star. We found the existence of two types of tunneling spectrum. Typical spectra are shown in figure 2 (c). These tunneling spectra were obtained in the regions indicated by circles shown in figure 2(c). These spectra have finite conductance at 0 mV. This is consistent with the metallic behavior in the electric conductivity. The spectrum averaged in purple circle shown in figure (type A) has two peak structures around -100 mV and 100 mV, and thus shows symmetry with respect to E_F. We think that this structure represents the Mott gap reduced by local structural strain or reduction of the coherency of the CDW [7]. On the other hand, the spectrum averaged in blue circle (type B) shows suppression of the peaks, especially at negative bias, and thus shows asymmetry with respect to E_F. It is plausible that type B spectrum is caused by the existence of Fe dopant because the peaks caused by Mott gap are reduced.

To investigate the Fe concentration dependence of the tunneling spectra, we spatially averaged on a 14×14 nm^2 field of view in x = 0.02 and 0.05 samples. Gray and red spectra in figure 2(d) represent the results taken on the sample with x = 0.02 and 0.05, respectively. Both spectra show peak structure at about 100 mV. This can be explained by the existence of the peak structure at the similar bias voltage in both type A and B spectrum. On the other hand, the peak structure at negative bias voltage becomes less conspicuous in the tunneling spectrum obtained in the sample with x = 0.05. This can be recognized as the ratio of type B spectrum to that of type A spectrum increased in the sample with x = 0.05. This result confirms that type B spectrum is caused by the existence of Fe dopant. Precise site where Fe is doped and the reason why Fe site shows type B spectrum are not clear at present. Further STM/STS and other experimental and theoretical investigations are required.

4. Summary

We have performed STM/STS measurements on $1T$-$Ta_{1-x}Fe_xS_2$ with different Fe concentration in order to clarify the effect of dopant Fe on $1T$-TaS_2. STM images show that the CDW superlattice becomes irregular as increasing Fe concentration. From the STS measurements, we found the spatial inhomogeneity of electronic state that is represented by two types of tunneling spectrum: symmetric spectrum with respect to E_F (type A), and asymmetric one (type B). Because the ratio of the David-star that has type B spectrum increases as increasing Fe concentration, we conclude that the type B tunneling spectrum is due to dopant Fe. The reason why Fe site shows such electronic feature is an open question.

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