Different response of atomic force microscopy and scanning tunneling microscopy to charge density waves

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We have studied the transition metal dichalcogenides 1T-TaS₂ and 1T-TaSe₂ exhibiting charge density waves (CDW) at room temperature by scanning tunneling microscopy (STM) and atomic force microscopy (AFM) with atomic resolution. STM images are dominated by the charge density wave modulation, while the AFM operated with an applied loading in the range of 10⁻⁸⁻¹₀⁻⁷ N responds only to the atomic surface structure. Several possible explanations for this experimental result are discussed, including differences in what STM and AFM are sensitive to, as well as a possible local pressure dependence of the CDW state.

I. INTRODUCTION

The investigation of charge density wave phenomena in solids is still of considerable interest, particularly the dynamics of charge density waves¹ and the possible close relationship between the charge and spin density wave state and high Tc superconductivity.² The static structure of low dimensional materials exhibiting CDWs has been studied extensively in the seventies by using x-ray, neutron, and electron diffraction.³ These experimental techniques are sensitive to the CDW formation in the bulk and reveal the superlattice structures related to the periodic lattice distortion (PLD) which is accompanied by the change modulation of the conduction electrons. Helium scattering as an extremely surface sensitive technique first proved that CDWs propagate up to the topmost layer of the crystal.⁴ The intensity of the superstructure peaks, e.g., for 1T-TaS₂ at 80 K was found to be as large as that of the main Bragg peaks indicating a strong deformation of the surface. The CDW corrugation, which was determined to be of the same order of magnitude as the atomic corrugation, was attributed to both a displacement of the ions and a change in the ionic radii as a direct consequence of the local charge modulation at each metal ion. Recently, scanning tunneling microscopy (STM)⁵ has proved to be a powerful technique to study charge density waves at surfaces in real space and on a local scale.⁶ In contrast to the diffraction experiments, STM is directly sensitive to the charge modulation of the conduction electrons, whereas the small displacements of the ions due to the PLD (typically of the order of 0.01 nm) are difficult to detect by STM. The question which we want to address here is how the atomic force microscopy (AFM)⁷ responds to the charge density wave state. This question is of interest from two points of view: (1) Concerning the AFM technique, the investigation of CDW systems may provide further insight into the relationship between the electronic surface structure and the force response. This will hopefully lead to a better understanding of what AFM is sensitive to. (2) Concerning the CDW state, it may be interesting to investigate a possible local pressure dependence of the CDW state by using AFM.

In Table I we summarize the information provided by the different experimental techniques.

II. EXPERIMENTAL

Single crystals of the transition metal dichalcogenides 1T-TaS₂ and 1T-TaSe₂ have been chosen as samples since they exhibit a charge density wave state at room temperature. Freshly cleaved surfaces remain free of oxides even in air within the time needed for the AFM and STM experiments as checked independently by Auger electron spectroscopy.

The AFM instrument used for the investigation of the 1T-TaX₂ (X = S, Se) single crystals has already been described earlier.⁹ For the experiments reported here, we used SiO₂ cantilevers produced by microfabrication techniques¹⁰ with spring constants between 0.3 and 1.0 N/m. The deflection of the cantilever while scanning the sample is monitored by electron tunneling between the rear side of the cantilever and a STM tip. Therefore by removing the cantilever, the instrument can work as a STM. The forces acting between the probing tip and the sample in the AFM experiment can be evaluted from z₁(z₂) plots, where z₁ is the movement of the tip and z₂ is the movement of the sample both perpendicular to the sample surface. This is discussed in detail in a forthcoming publication.¹¹ All AFM measurements reported here have been performed with repulsive forces in the range of 10⁻⁸⁻¹₀⁻⁷ N.

In Figs. 1 (a) and 1 (b) we present an AFM overview image showing a 340 × 340 nm² area on the 1T-TaS₂ surface. Several terraces separated by steps of various heights (one and three times the unit cell height) can be identified. A similar morphology was also observed on the 1T-TaSe₂ surface as studied by AFM and STM. After zooming into the terraces, atomic resolution could be obtained by using both techniques. In Fig. 2 we present an AFM image of a 8 × 8 nm² surface area on 1T-TaSe₂ obtained in the variable deflection mode of operation where the tunneling current flowing between the rear side of the lever and the STM tip is digitized. The atomic lattice is clearly resolved, whereas a
superlattice structure due to the CDW state is totally absent. This experimental result was confirmed for other 1T-TaX$_2$ samples as well and was found to be independent of the applied loading in the range of $10^{-8}$ and $10^{-7}$ N. The lattice constant on the 1T-TaSe$_2$ surface was determined to be $0.35 \pm 0.01$ nm, in good agreement with the bulk value of 0.3477 nm. An atomic corrugation of $0.02-0.04$ nm could be estimated. The absence of a superlattice structure in Fig. 2

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<th>Experimental technique</th>
<th>Bulk sensitive</th>
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**Fig. 1.** AFM image of a $340 \times 340$ nm$^2$ surface area on 1T-TaS$_2$. Several steps can be observed with step heights being multiples of the unit cell height (0.586 nm). (a) Line-scan representation, (b) perspective view.
implies that a possible existent CDW corrugation is at least an order of magnitude smaller than the atomic corrugation, i.e., smaller than ~0.005 nm.

STM measurements have been performed on the same single crystal shortly after the data acquisition of the AFM image shown in Fig. 2 by just removing the cantilever. In Fig. 3 we present a STM image of a $8 \times 8$ nm$^2$ surface area on 1T-TaSe$_2$ obtained by current imaging with a mean tunneling current of $I = 1$ nA and a sample bias voltage of $U = +30$ mV. The image is dominated by the $\sqrt{13} \times \sqrt{13}$ superlattice due to the CDW state as reported earlier.$^{15}$ In another series of STM measurements on 1T-TaSe$_2$, the CDW superlattice structure and the atomic lattice could be imaged simultaneously as shown in Figs. 4(a) and 4(b). The CDW corrugation in this constant current STM image is $\sim 0.27 \pm 0.03$ nm, whereas the atomic corrugation is $\sim 0.08 \pm 0.01$ nm. The sample bias voltage was higher (0.45 V) than for the STM image presented in Fig. 3. However, the ability to resolve the atomic lattice in addition to the CDW superlattice by STM is believed to depend more on the state of the tip than on the tunneling parameters.

Finally, we present a STM image of a $12 \times 12$ nm$^2$ surface area on 1T-TaSe$_2$ (Fig. 5) demonstrating that the CDW superlattice persists right up to a step.

III. DISCUSSION

The different response of AFM to the CDW state in comparison to STM and He scattering is certainly remarkable. At present, we can give only qualitative arguments for this experimental result, whereas a profound understanding can be obtained only by a well elaborated theory which is hopefully motivated by the presentation of this work.

It is well known that CDW formation results from a Fermi surface instability leading to both a periodic lattice distortion (PLD) and a spatial modulation of the density of states near the Fermi level. The latter can be probed directly by STM which is therefore a highly sensitive technique for studying the CDW state although the PLD seems to be below the detection limit of present STMs. On the other hand, AFM is believed to respond to the total charge density at the sample surface and should therefore be less sensitive to the CDW state. Thus we can understand qualitatively the different response of STM and AFM. However, there remains the problem of understanding the different experimental results in AFM and He scattering experiments.

It has been shown$^{13}$ that the He–surface interaction energy is basically proportional to the substrate total electron density at the He site. The He scattering potential and the surface total electron density are therefore directly related. Thus we expect the corrugations derived from He scattering and AFM experiments to be comparable in size. The He diffraction pattern usually can be satisfactorily explained in terms of scattering from a rigid wall, whose corrugation is described by a shape function $z = \xi(R)$ having the periodicity of the surface lattice. For CDW systems one can write $\xi(R) = \xi_0(R) + \xi_{\text{CDW}}(R)$, where $\xi_0(R)$ describes the atomic lattice and $\xi_{\text{CDW}}(R)$ the deformation induced by the CDW state. From the He scattering experiments on 1T-TaS$_2$ at 80 K,$^7$ an atomic corrugation of 0.052 nm and a corrugation of 0.037 nm due to the CDW superlattice are derived. Even if one is concerned with the derivation of the absolute amount of corrugation from the He diffraction experiment, the results clearly indicate that the atomic and the CDW corrugation should be of the same order of magnitude. This is in strong contrast to the AFM results and can not simply be explained by a reduction of the order parameter at 300 K in comparison to 80 K since this reduction is only of a small amount due to the high transition temperature ($\sim 600$ K) between the normal state and...
and the CDW state for the $1T-TaX_2$ compounds. There might be several other explanations for the different response of AFM and He scattering to the CDW state. One possible reason might be the influence of local applied pressure in the AFM experiment. It is well known that transitions between different CDW phases in transition metal dichalcogenides are highly pressure sensitive since pressure leads to significant changes in the band shape for the layer compounds by reducing their two-dimensionality.\textsuperscript{14} For $1T-TaX_2$, the transition temperatures $T_{\text{trans}}$ between differ-
ent CDW phases usually decrease with increasing uniform applied pressure by an amount of \( |dT_{\text{trans}}/dp| \sim 3-5 \) K/kbar. The nonobservation of the CDW state by AFM could be explained if we assume that a reduction of the transition temperatures, or in general a depression of the CDW state, occurs when local pressure is applied such as in an AFM experiment where pressures of \( \sim 100 \) kbar can be estimated for reasonable values for the area of contact of \( \sim 1 \) nm² and a loading of \( 10^{-8} \) N. A further reduction of the applied loading would be highly desirable in order to investigate a possible local pressure dependence of the CDW state, but this has led to experimental difficulties so far. Instead we have performed tunneling experiments with a conducting cantilever where the tunneling image clearly showed the CDW superlattice. By varying the tunneling resistance between 30 MΩ and 300 kΩ, a force change of \( 10^{-9} \) N could be determined from the lever deflection. Although we cannot determine the absolute value of force by this method, we can give a lower limit for the force of about \( 10^{-9} \) N.

Finally, frictional forces may also play an important role for the imaging mechanism of 1T-TaX₂ by AFM and may lead to differences between AFM and He scattering results.

IV. SUMMARY

We have presented the first atomic resolution studies of the charge density wave systems 1T-TaS₂ and 1T-TaSe₂ by AFM showing the absence of a CDW modulation for an applied loading of \( 10^{-8}-10^{-7} \) N in contrast to STM and He scattering experiments. Possible reasons for this absence have been discussed, including the influence of local applied pressure in the AFM experiment. Other explanations may be given such as possible differences in the surface potential probed in AFM and He scattering experiments. This problem is left open for future theoretical work.

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1For a recent review, see G. Grüner, Rev. Mod. Phys. 60, 1129 (1988).