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Abstract. – The transition metal dichalcogenides 1T-TaSe₂ and 1T-TaS₂ have been examined at room temperature by atomic force microscopy (AFM) and scanning tunnelling microscopy (STM). STM images are dominated by the charge density wave modulation. In some experiments the underlying atomic lattice can be revealed simultaneously. The AFM operated with a loading in the range of \(10^{-9} \text{ to } 10^{-7}\) N showed only the atomic surface structure. This experimental result shed new light on the relationship between the electronic surface structure and the force response. However, at present we cannot rule out a pressure dependence of the charge density wave state on the AFM results.

1. Introduction.

Collective phenomena in solids are one of the most challenging topics in condensed-matter physics. Among these the formation of charge density waves (CDW) has been of considerable interest in the seventies and eighties [1, 2]. The static structure of CDW systems has been determined by diffraction experiments with X-rays, neutrons and electrons [3]. They reveal the superstructures related to the periodic lattice distortion (PLD) of the arrangement of the ions which is accompanied by the charge modulation of the conduction electrons. While these diffraction experiments are sensitive to the CDW formation in the bulk, He scattering experiments have shown that CDWs propagate up to the topmost atom layer of the crystal [4, 5]. Additionally, the relatively strong superstructure reflections in the He scattering experiments were explained by assuming at least a contribution from the spatial modulation of the density of the conduction electrons. A large periodic deformation of the surface was concluded from these experiments. The invention of the scanning tunnelling microscope (STM) [6, 7] made it possible to probe the charge
modulation directly on a local scale [8-11], whereas the small lateral displacements of the ions due to the PLD (of the order of (0.1 ÷ 0.3) Å) seem to be below the lateral resolution capability of present STMs. The large corrugation heights ((2 ÷ 3) Å) of the $\sqrt{13} \times \sqrt{13}$ superstructure of the 1T-TaX$_2$ (X = S, Se) measured by STM have been explained by Tersoff [12].

Since the successful application of the atomic force microscope (AFM) [13] to the study of the atomic surface structure of highly oriented pyrolytic graphite (HOPG) [14-17] and the first insulator, highly oriented pyrolytic boron nitride (HOPBN) [15], there is considerable interest in the still open question to what AFM is sensitive to and how one can relate the electronic surface structure with the images obtained by the force interaction. CDW systems are one of the most instructive samples for the AFM. In addition, AFM is well suited for studying the effect of local pressure on the CDW state. One can hope to determine the degree of local lattice distortion necessary to depress the long range PLD associated with the CDW formation.

In this letter we report the first successful application of AFM operated in air at room temperature to CDW systems. We were able to resolve the atomic lattice of the transition metal dichalcogenides 1T-TaS$_2$ and 1T-TaSe$_2$ by AFM. No indication of a superstructure due to the CDW state was found by AFM operated with a loading in the range of $(10^{-8} \div 10^{-7})$ N, although it was possible to image both the CDWs and the underlying atomic lattices by using the same instrument in the STM mode of operation. Measurements of the interaction force as a function of tip-sample distance will be presented. In addition some large-area scans will be shown which will give further information about the imaging mechanism in AFM.

2. Experimental.

The instrument is operated in air and mounted on a commercial antivibration table. The design of this instrument has been described in a previous paper [17]. We use electron tunnelling to monitor the deflections of the cantilever-type spring. The tunnelling microscope and the cantilever act together as the force sensor. The instrument works as a simple STM by removing the cantilever. The x-y-movement is achieved by the sample piezo scanner. We used Si$_3$N$_4$ cantilevers produced by microfabrication techniques [14, 18] with typical spring constants $c_B$ between 0.3 and 1 N/m. For our AFM experiments it is important to know the forces acting between the probing tip and the sample. As reported earlier [17, 19, 20], this force can be evaluated out of $z_t(z_s)$-plots, where $z_t$ is the movement of the tip and $z_s$ the movement of the sample both perpendicular to the sample surface. Figure 1a) shows a $z_t(z_s)$-plot on 1T-TaS$_2$. The scale on the right-hand side indicates the force between the probing tip and sample, the so-called loading (equals $c_B \cdot z_t$). Figure 1b) represents a schematic diagram of the corresponding force as a function of distance. As the sample moves towards the tip, the gradient of the attractive force surpasses the spring constant at point 1, which leads to the first instability. Afterwards the zero force line is passed, which means that the attractive and repulsive force cancel each other. In the repulsive regime the tip follows closely the movement of the sample. Retracting again, the tip passes point 2 and reaches the maximal adhesive force. At point 3 the second instability occurs and finally the free lever (no measurable interaction between tip and sample) is reached again. We suppose that the difference in the slope of the $z_t(z_s)$-plot between approach and retraction direction is due to piezo creep. All the following measurements have been performed with repulsive forces in the range of $(10^{-8} \div 10^{-7})$ N. Although the stability was good enough to acquire images with attractive forces we could not detect any atomic structures in this force regime.
Fig. 1. - Experimental $z_t(z_s)$-plot of 1T-TaS$_2$. We used a SiO$_2$ lever with a spring constant of $c_B = 1$ N/m. The approach and retraction velocity was $|z_t| = 3$ nm/s. Before retraction a short wait cycle of 2 s was introduced. The maximum adhesive force $F_{\text{max}}$ is 18 nN. The force $F_2$ at point 2 is 2 nN. The peak of the attractive force is about 20 Å wide. Point 4 is 180 Å apart from the surface. b) Schematic diagram of the force as a function of distance. The main features like instability points, the forces $F_{\text{max}}, F_2$ are included. The shape of the curve is arbitrary.

Figure 2 shows a (48 × 48) Å$^2$ area on 1T-TaSe$_2$ measured by AFM with a loading of $3 \cdot 10^{-8}$ N. The atomic lattice is clearly resolved. The lattice constant was determined to be $(3.5 \pm 0.1)$ Å which agrees well with the bulk value of 3.477 Å. The image has been obtained in the variable deflection mode, where the tunnelling current is digitized. Assuming a local barrier height of $(1 \pm 0.1)$ eV on the fold surface, being evaporated on the backside of the lever, we can estimate the corrugation height on 1T-TaSe$_2$ to be $(0.2 \pm 0.4)$ Å. The $\sqrt{13} \times \sqrt{13}$ superstructure could not be resolved in our AFM experiments. According to these measurements the CDW amplitude is at least an order of magnitude smaller than the atomic corrugation, which means that it is smaller than 0.01 Å. For comparison we have performed STM measurements on the same single crystal. Figure 3 shows a typical example. This image has been taken shortly after the acquisition of fig. 2 by removing the lever. The period was determined to be $(12.6 \pm 0.1)$ Å which agrees well with the $\sqrt{13} \times \sqrt{13}$ superstructure.
superstructure being 12.54 Å. The CDW structure is dominating and the atomic lattice can hardly be seen. Only in a few experiments the CDW and the atomic lattice could be imaged simultaneously by STM, as shown in fig. 4. The corrugation height of the CDW is about $(2.7 \pm 0.3) \text{Å}$, whereas the atomic lattice corrugation is about $(0.8 \pm 0.1) \text{Å}$. These STM results agree well with the measurements of other groups [8, 9]. Other AFM experiments, where the loading was varied between $(10^{-8} \div 10^{-7}) \text{N}$ reproduced the same result. The atomic lattice was clearly resolved as well on 1T-TaS$_2$ as on 1T-TaSe$_2$.

![Fig. 4.](image)

Fig. 4. – (33 x 39) Å STM grey scale image on 1T-TaSe$_2$ taken in the constant current mode. The tunnelling current was $1 \text{nA}$ and sample bias voltage $+450 \text{mV}$. The atomic lattice and the CDW superstructure can be seen simultaneously.

![Fig. 5.](image)

Fig. 5. – AFM image of a $(3400 \times 3400) \text{Å}^2$ area of 1T-TaS$_2$. Steps which are multiples $(1, 3$ and $3)$ of the height of the unit cell $(5.86 \text{Å})$ can be observed.

In addition to these high-resolution images we also mapped some larger areas. Figure 5 shows an AFM image of $(3400 \times 3400) \text{Å}^2$ area on 1T-TaS$_2$, where steps could be detected being multiples of the height of the unit cell $(5.86 \text{Å})$. Such images give an indication of the sharpness of the probing tip. Closer examination of the step profile gives an upper limit of $500 \text{Å}$ for the radius of tip curvature.

3. Discussion.

The different response of STM and AFM on CDW systems does not seem to be surprising at first sight. STM probes the density of states near the Fermi level and is therefore highly sensitive to the CDW-formation which results from a Fermi surface instability. On the other hand, AFM is believed to respond to the total charge density at the sample surface. Since only a small fraction of the total number of electrons is condensed in the CDW state, AFM should be less sensitive to the CDW formation. However, the absence of a superstructure in the AFM images of CDW systems is surprising if one compares with the results from He scattering experiments [5]. In these experiments the intensities due to the atomic lattice and the CDW superstructure were determined to be of the same size. At 80 K the corrugation height of the atomic lattice on 1T-TaS$_2$ was determined to be $0.52 \text{Å}$, and the
CDW corrugation was 0.37 Å. No room temperature data is known to the authors. Although a reduction of the order parameter at 300 K is expected, it is assumed to be of a small amount because of the high transition temperature ($\approx$ 600 K). Therefore, we conclude that either the corrugations measured with the AFM and in the He scattering experiments have not the same origin and may not be compared with each other as done previously or there are other mechanisms responsible for the nonobservation of the CDW state in the AFM experiments such as the pressure dependence of the CDW state, multiple-tip effects and the influence of frictional forces.

It is well known that the transition between different CDW phases in transition metal dichalcogenides are highly pressure sensitive [21, 22] since pressure leads to significant changes in the band shape for the layer compounds by reducing their two-dimensionality. The transition temperatures $T_{\text{trans}}$ between different CDW phases usually decrease with increasing pressure by an amount of $dT_{\text{trans}}/dp = (3 + 5)$ K/kbar for 1T-TaX$_2$ [1, 22]. No high-temperature data for the transition between the normal and the incommensurate phase in 1T-TaX$_2$ are currently known to the authors. Anyhow, one has to be careful in comparing the measured decrease in the transition temperatures with increasing uniform pressure with a possible reduction of the transition temperatures in a small volume with increasing local applied pressure as in an AFM experiment which may originate from a local destruction of the long-range PLD by a significant local lattice distortion. Keeping in mind a possible reduction of the transition temperature from the normal phase to the CDW phase below room temperature in 1T-TaX$_2$ by an effect of local pressure, we have varied the applied loading in our AFM experiment from $(0.0 - 10^{-4})$ N. Assuming a reasonable value for the area of contact in the AFM-experiment of about 100 Å$^2$ one can estimate the amount of local pressure which will be about 100 kbar. This pressure is high enough that a reduction of the transition temperature from the normal phase to a CDW phase below room temperature might occur. A final answer to this question can be given by performing low-temperature AFM experiments or by a further reduction of the applied loading.

To discuss the possibility of a pressure effect further we now want to focus on the STM results, which clearly show the CDW modulation. It is presently accepted that significant forces between tip and sample are also acting in a STM experiment which might have a different origin depending on both tip and sample. Particularly in the case of STM experiments on graphite in air it has been shown [23, 24] that forces in the range of $10^{-7}$ to $10^{-6}$ N are required between the STM tip and the sample to achieve tunnelling. Similar forces may also act in STM experiments in air on other layered materials like the transition metal dichalcogenides. Nevertheless the CDW modulation is clearly observed as shown in fig. 3-4 and also by several other STM groups before [8, 9]. However, the observed reduction of the order parameter (amplitude of the CDW modulation) with increasing tunnelling current [25] and therefore increasing local pressure on the CDW state may originate from an influence of pressure on the CDW state which has not been discussed previously. To clarify this point, we have performed AFM experiments with a conducting lever. By varying the tunnelling resistance between 30 MΩ to 300 kΩ a force change of $10^{-9}$ N is determined from the lever deflection. Although we cannot determine the absolute value of force by this method, we can give a lower limit of the force of about $10^{-8}$ N.

Besides the pressure effect as a possible reason for the nonobservation of the CDW modulation in the AFM experiment, there remain the problems of multiple tips and frictional forces. The good reproducibility of our result, the nonoccurrence of features like striped images and «every other atom» images and the imaging of steps (cf. fig. 5) exclude the multiple-tip effects.

Finally we must consider the influence of frictional forces, which play a significant role in the AFM experiments on graphite [17, 24]. If these frictional forces are important in the
imaging mechanism of 1T-TaX₂, the differences between He scattering and AFM probably could be explained. This point needs certainly clarification from the theoretical side.

In summary, we have presented the first atomic resolution AFM experiments on the CDW systems 1T-TaS₂ and 1T-TaSe₂ which show the absence of a CDW modulation for an applied loading of \((10^{-8}+10^{-7})\) N in contrast to STM and He scattering experiments. We have discussed an influence of pressure on the CDW state as a possible reason for the nonobservation of a CDW modulation in the AFM experiment which is currently investigated further by reducing the loading below \(10^{-8}\) N. Other explanations lead to possible differences in the surface potential probed in AFM and He scattering experiment—a challenging problem which is left open for future theoretical work.

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REFERENCES