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Waves and Atoms in 1T-TaSe₂ and 1T-TaS₂

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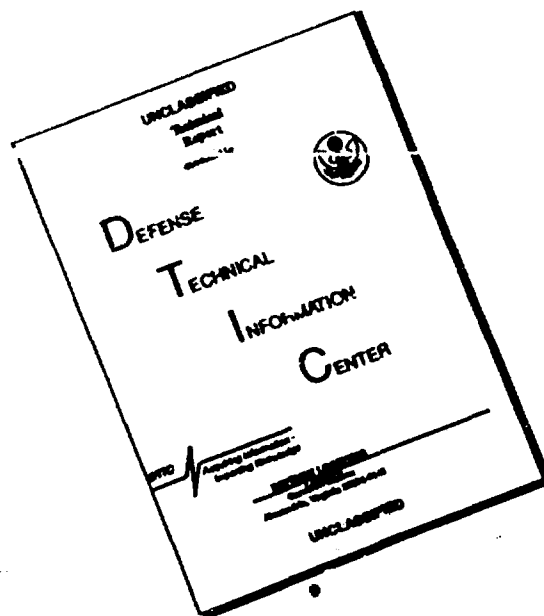
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Atomic force microscopy (AFM) and scanning tunneling microscopy (STM) images of 1T-TaSe₂ and 1T-TaS₂ at room temperature reveal both atoms and charge-density waves (CDW's). In AFM the atoms and CDW's have comparable amplitudes. In contrast, in STM the CDW's have amplitudes up to an order of magnitude larger than the atoms. Both AFM and STM images show that the CDW structure of 1T-TaS₂ is continuously incommensurate while 1T-TaSe₂ is commensurate.

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Atomic force microscopy and scanning tunneling microscopy of charge-density waves in $1T$ -TaSe₂ and $1T$ -TaS₂

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Atomic force microscopy (AFM) and scanning tunneling microscopy (STM) images of $1T$ -TaSe₂ and $1T$ -TaS₂ at room temperature reveal both atoms and charge-density waves (CDW's). In AFM the atoms and CDW's have comparable amplitudes. In contrast, in STM the CDW's have amplitudes up to an order of magnitude larger than the atoms. Both AFM and STM images show that the CDW structure of $1T$ -TaS₂ is continuously incommensurate while $1T$ -TaSe₂ is commensurate.

The charge-density wave (CDW) structure and the atomic structure in $1T$ -TaSe₂ and $1T$ -TaS₂ have been imaged using both the scanning tunneling microscope¹ (STM) and the atomic force microscope (AFM). The scans have been carried out at room temperature using freshly cleaved crystals in air and in helium gas. The long-range electronic charge modulation induced by the CDW below ~ 600 K is clearly resolved by both types of instruments, but the relative ratios of the atomic to CDW modulation amplitudes show major differences in the images obtained using the two types of instruments.

In this paper we present the first complete comparison of the commensurate CDW structure in $1T$ -TaSe₂ and the incommensurate CDW structure in $1T$ -TaS₂ as measured by both STM and AFM methods at room temperature. The AFM results along with the recent results of Barrett, Nogami, and Quate² represent the first successful detection of the CDW modulation with the AFM. In addition, the equal amplitudes of the CDW's and atoms in the AFM scans allow high-quality Fourier transforms (FT's) to be obtained. These along with accurate profiles show that the CDW structure in $1T$ -TaS₂ at room temperature is continuously incommensurate rather than forming commensurate regions separated by localized discommensurations as suggested by Wu and Lieber.³ The STM used for these experiments was a custom designed instrument which operates at all temperatures down to 4.2 K and has been previously described in Ref. 1. The AFM was a commercial instrument built by Digital Instruments⁴ of Santa Barbara, California. The STM uses a Pt_{0.8}Ir_{0.2} tip and the AFM a Si₃N₄ tip.⁵

In the case of $1T$ -TaSe₂ the CDW has a wavelength of $\sqrt{13} a_0$ and remains commensurate up to 473 K. A STM scan on $1T$ -TaSe₂ at room temperature in helium gas is shown in Fig. 1(a) and shows an extremely strong CDW modulation with a superimposed pattern of atoms that remains identical over the entire scan. As shown in the profile of Fig. 1(b) taken along the track indicated in Fig. 1(a) the z deflection is completely dominated by the CDW amplitude and the atoms contribute a very small

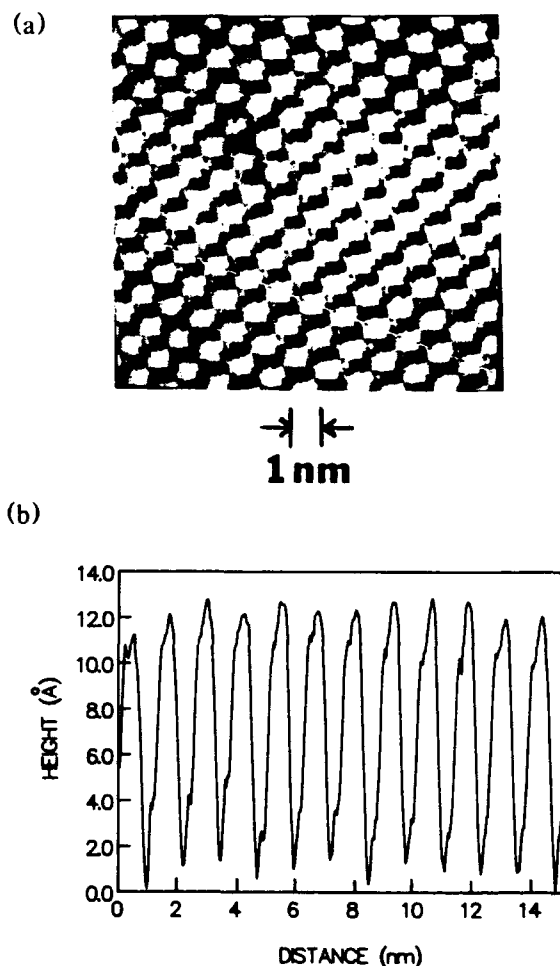


FIG. 1. (a) Grey-scale STM image of $1T$ -TaSe₂ taken at room temperature showing a uniform pattern of atoms and CDW's which maintain a constant phase relation characteristic of a commensurate structure ($I = 2$ nA, $V = 25$ mV). (b) Profile of the z deflection taken along the line indicated in (a). The CDW amplitude is constant also indicating a commensurate structure and the atoms contribute a very small fraction of the total z deflection.

fraction to the total amplitude. The CDW amplitude also remains constant over the entire profile and this, along with the constant phase observed in the grey scale of Fig. 1(a), indicates a completely commensurate structure with the CDW superlattice making an angle of 13.9° with the atomic lattice.

The corresponding AFM scan of $1T\text{-TaSe}_2$ at room temperature is shown in Fig. 2(a). The CDW maxima remain in phase with the atoms and the profile as shown in Fig. 2(b) shows a constant amplitude for the CDW modulation again indicating a completely commensurate structure. The Fourier transform of the grey-scale image of Fig. 2(a) gives a rotation angle between the atomic lattice and CDW superlattice of $14.2^\circ \pm 0.5^\circ$ consistent with a commensurate structure. In contrast to the STM scans the AFM scans show the atomic modulation amplitude to be as large or larger than the CDW modulation, both lying in the range $0.5\text{--}1 \text{ \AA}$. In general the total AFM modulation amplitude is observed to be relatively stable in the range $1\text{--}2 \text{ \AA}$ while the STM shows a variable range of $2\text{--}10 \text{ \AA}$.

In contrast to $1T\text{-TaSe}_2$ the CDW in $1T\text{-TaS}_2$ at room temperature is incommensurate with the lattice and exhibits a long-range modulation of the CDW amplitude as a result. This long-range modulation of the CDW ampli-

tude is detected in both the STM and AFM scans and leads to a two-dimensional domain-like structure. This has been previously studied using STM by a number of groups including Thomson *et al.*,⁶ Wu and Lieber,³ and Giambattista *et al.*⁷ This two-dimensional modulated structure is demonstrated in the processed grey-scale STM scan of Fig. 3(a) where the look-up table has been adjusted to accentuate the regions of different CDW amplitude. The profiles obtained from the original grey-scale scans show a continuous CDW amplitude modulation as demonstrated in Fig. 3(b) where the maximum CDW amplitude occurs at the center of the domain.

The AFM results on $1T\text{-TaS}_2$ confirm the same long-range modulation structure as observed with the STM. Figure 4(a) shows a grey-scale AFM scan where the two-dimensional modulated structure is clearly present and the profile of Fig. 4(b) indicates a continuous variation of the CDW amplitude over ~ 6 CDW wavelengths in agreement with the STM results. Both measurements show an angle of rotation of $\sim 12^\circ$ between the CDW superlattice and the atomic lattice. As was the case in $1T\text{-TaSe}_2$ the atomic and CDW amplitudes in the AFM scans on $1T\text{-TaS}_2$ are again comparable with measured values in the range $0.5\text{--}1 \text{ \AA}$.

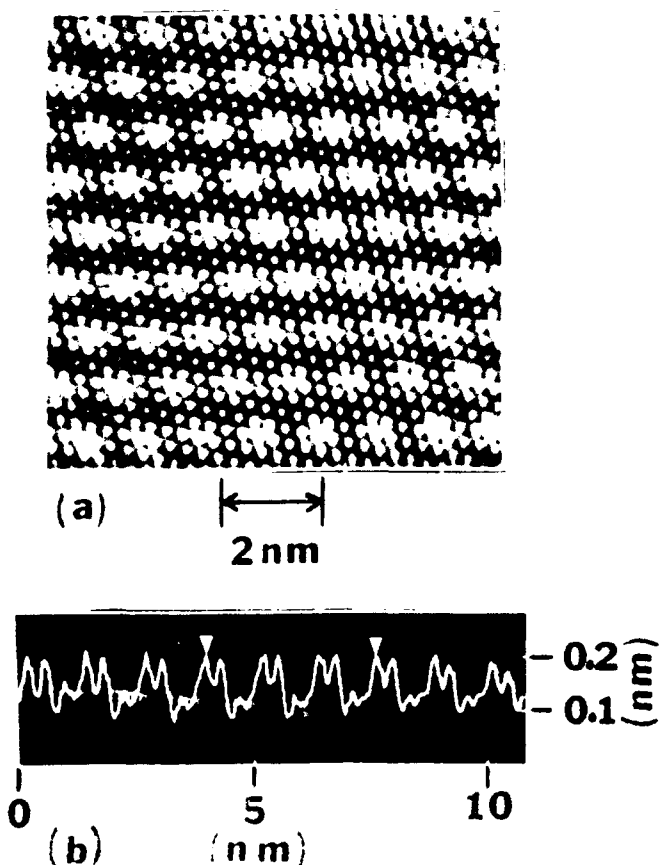


FIG. 2. (a) Grey-scale AFM image of $1T\text{-TaSe}_2$ taken at room temperature. A uniform pattern of atoms and CDW's maintaining a constant phase relation indicates a commensurate structure as observed in the STM images (constant force mode with force $\approx 10^{-10}$ newton). (b) Profile of z deflection showing a constant amplitude consistent with a commensurate structure.

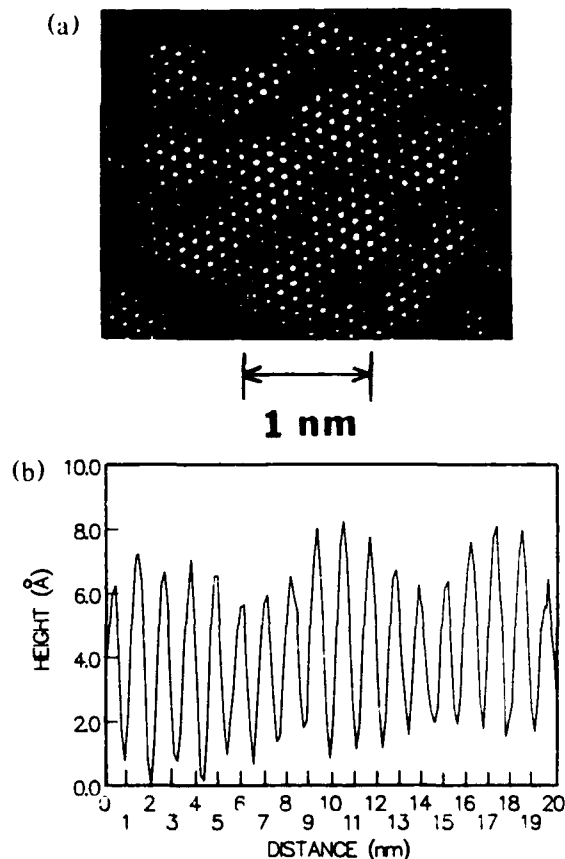


FIG. 3. (a) Grey-scale STM image of $1T\text{-TaS}_2$ taken at room temperature with a look-up table adjusted to emphasize the two-dimensional domain-like structure resulting from a variation of the CDW amplitude ($I = 2.2 \text{ nA}$, $V = 25 \text{ mV}$). (b) Profile of the z deflection measured along a row of CDW maxima in (a). The CDW amplitude undergoes a continuous modulation with a period of ~ 6 CDW wavelengths.

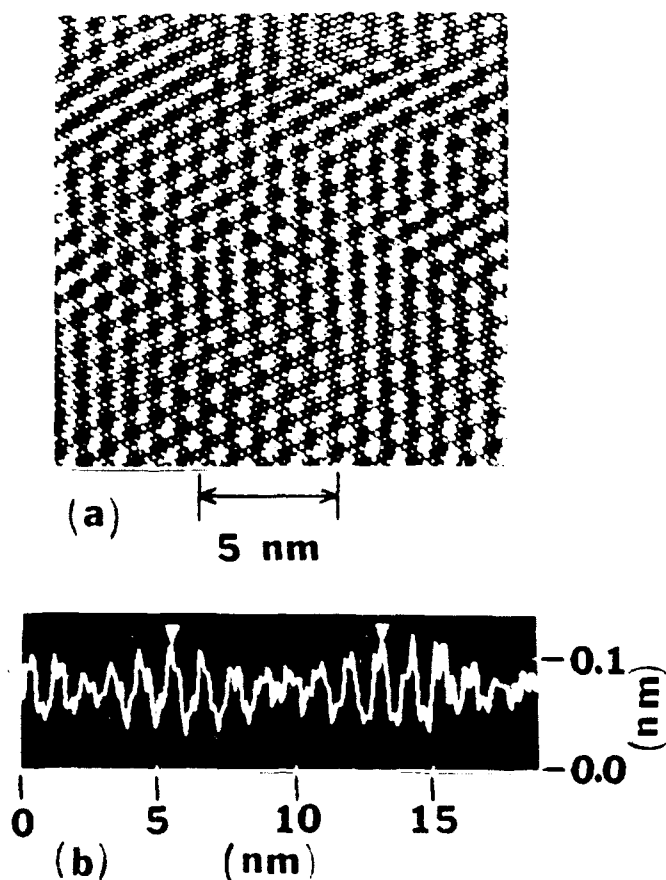


FIG. 4. (a) Grey-scale AFM image of $1T\text{-TaS}_2$ taken at room temperature. The incommensurate CDW produces a clearly visible modulated structure. The atoms and CDW's contribute approximately equal amplitudes to the AFM image (constant force mode with force $\approx 10^{-8}$ newtons). (b) Profile of the z deflection along a row of CDW maxima in (a). The profile exhibits a continuous amplitude modulation of the CDW with a period of ~ 6 CDW wavelengths.

The STM and AFM images of $1T\text{-TaSe}_2$ and $1T\text{-TaS}_2$ are in basic agreement with respect to the CDW structures in both materials at room temperature. The major difference between the two types of image is the relative amplitude of the atomic and CDW modulation. The STM responds to the local density of states (LDOS) at the Fermi level and many previous studies have indicated that the CDW in the $1T$ phases of TaSe_2 and TaS_2 involves a very strong charge transfer centered on thirteen-atom clusters of Ta. The resulting Fermi-surface annihilation and $\mathbf{k} + \mathbf{G}$ mixing can produce electronic singularities¹⁻⁸ in the LDOS. The AFM, on the other hand, samples the total electronic charge density at the surface which contributes to the atomic force measured by the AFM tip. The CDW occurs mainly in the d bands contributed by the Ta-atom layer and the associated static charge can be partially screened so that it makes a reduced contribution to the total force at the surface S or Se layer. In this respect the comparison of the STM and AFM results tends to confirm that the strong STM response to the CDW results from an electronic modification at the Fermi level.

Barrett *et al.*² have recently carried out AFM-STM measurements on $1T\text{-TaS}_2$ at room temperature and we confirm their results with respect to the relative atomic to CDW amplitudes. They report CDW amplitudes of $0.1\text{--}0.3 \text{ \AA}$ in approximate agreement with the periodic lattice distortion (PLD) perpendicular to the S layer as measured by helium atom scattering⁹ and x-ray diffraction.¹⁰

Our AFM results show CDW amplitudes of $0.3\text{--}1.0 \text{ \AA}$ which are larger than the measured PLD's. This indicates that the CDW charge may not be completely screened at the surface allowing the AFM to detect this unscreened charge in addition to the PLD associated with the CDW. Barrett *et al.*² also report some disorder in the CDW images of $1T\text{-TaS}_2$ when using an unmetallized cantilever. This was attributed to the effects of tip pressure and a similar argument was advanced by Meyer *et al.*^{11,12} as a possible explanation for their failure to detect PLD's with the AFM. Our AFM results with unmetallized cantilevers do not detect disorder in the CDW pattern.

The AFM and STM results on $1T\text{-TaS}_2$ at room temperature provide evidence that the CDW amplitude is continuously modulated rather than constant within commensurate regions which would then be separated by localized discommensurations and abrupt phase slips between the CDW and the lattice. Although a two-dimensional domain-like structure is observed as discussed originally by Nakanishi and Shiba,^{13,14} we do not see evidence of any substantial regions of commensurate CDW formation. Rather the domain-like structure is consistent with a continuous modulation of the CDW amplitude and a continuous phase shift of the CDW with respect to the

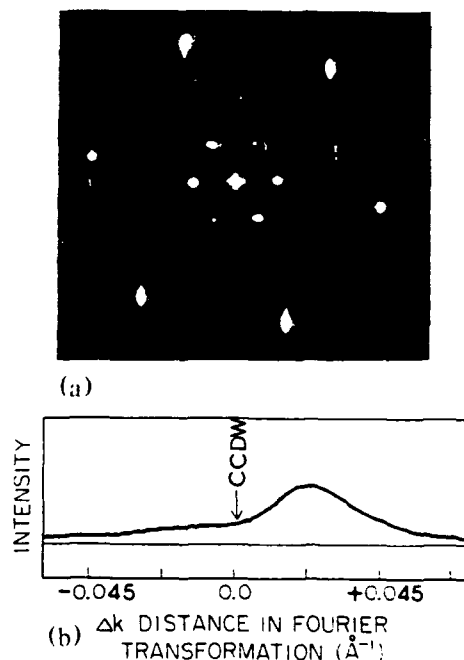


FIG. 5. (a) Fourier transform of the AFM image shown in Fig. 4(a). The two sets of spots in a hexagonal pattern represent the CDW superlattice and the atomic lattice. The relative angles of rotation measured using pairs of spots are in the range $11.7\text{--}12.2^\circ$ with an average value of $11.8^\circ \pm 0.4^\circ$ indicating continuous incommensurate CDW's. (b) Arrow on spot profile shows commensurate wave-vector position.

lattice. The FT of the $27 \times 27 \text{ nm}^2$ data set from which the AFM scan in Fig. 4(a) was taken is shown in Fig. 5(a) and gives a measured rotation angle of $11.8^\circ \pm 0.4^\circ$. A CDW spot profile from the FT is shown in Fig. 5(b) with an arrow marking the commensurate k -vector position. No evidence of enhanced intensity at the commensurate angle is observed.

The extent to which the CDW superlattice vector deviates from the average angle in local regions cannot be resolved in direct graphical measurement from the STM and AFM images. The continuous variation of the CDW amplitude with a superimposed atomic pattern running at an average angle of $\sim 12^\circ$ produces a combined local variation in the CDW and atomic pattern that does not allow a precise separation.

In conclusion the scans on $1T\text{-TaS}_2$ using both STM and AFM show patterns and profiles consistent with a continuously modulated CDW amplitude and a CDW structure predominantly incommensurate with the lattice. The main difference between the AFM and STM re-

sponses occurs in the relative atom to CDW amplitudes. In the AFM images the atom and CDW amplitudes are comparable while in the STM images the CDW amplitude dominates. This difference appears to reflect the expected intrinsic difference in the response of tunneling versus force measurements.

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