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Charge-density waves observed at 4.2 K by scanning-tunneling microscopy

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Scanning-tunneling-microscope images of layer structure dichalcogenides exhibiting charge-density-waves (CDW's) have been studied at 4.2 K. CDW amplitudes in the $2H$, $1T$, and $4Hb$ phases of $TaSe_2$ have been measured with the strongest CDW phase showing only the superlattice modulation while the weaker CDW phases show simultaneous CDW and surface-atom modulations. In $2H$-$NbSe_2$ a well-resolved hexagonal CDW superlattice superimposed on the dominant surface-atom pattern is observed.

Scanning-tunneling microscopy (STM) has been used with considerable success[1,2] to detect the superlattice charge modulation created by the charge-density-wave (CDW) formation in the layer-structure transition-metal dichalcogenides.[3] The amplitude of the charge modulation and the associated Fermi-surface gapping varies over a wide range depending on the compound, the crystal phase, and the temperature. The previous STM measurements have been carried out at 77 K on crystals exhibiting relatively high-temperature CDW transitions, all above 77 K.

In this paper we report results on observations of CDW structure using an STM operating at 4.2 K. We show that the STM images reflect the amplitude of the CDW charge modulation in great detail and that the resolution of atomic structure is directly related to the strength of the CDW. In the case of $2H$-$NbSe_2$ a weak incommensurate CDW forms below ~ 35 K and the STM scans at 4.2 K show good resolution of both atoms and CDW's with the atom pattern dominant. In $1T$-$TaSe_2$ an extremely strong CDW modulation forms below ~ 600 K and becomes commensurate below 473 K. The STM scans at 4.2 K show a surface charge density totally dominated by the CDW in a symmetric hexagonal pattern with $\lambda_{CDW} = \sqrt{13}a_0$. No atomic modulation can be detected, but atomic defects can strongly perturb the charge maxima of the CDW. An intermediate case is represented by the mixed coordination phase $4Hb$-$TaSe_2$. In this case, two essentially independent CDW's form below 600 and 75 K, respectively, in each of the alternating sandwiches of octahedral and trigonal prismatic coordination. Below 410 K the high-temperature CDW becomes commensurate and is very similar to the CDW formed in the $1T$ phase but of weaker amplitude. The STM scans at 4.2 K show a strong CDW modulation at $\lambda_{CDW} = \sqrt{13}a_0$, but a superimposed pattern from the surface Se atoms is also well resolved. In all cases, where both the CDW pattern and the atom pattern are simultaneously observed, the STM scans show an overall charge asymmetry at the superlattice maxima. This reflects the superposition of the CDW charge modulation centered on the transition-metal layer and the modulation of the conduction-electron wave functions by the potential of the surface Se atom layer. In the trigonal prismatic or the octahedral sandwiches these two layers are displaced by $a_0/\sqrt{3}$.

The liquid-helium STM operates immersed in a storage can of liquid helium with vibration isolation provided by inflated rubber innertubes. It is a smaller more compact version of the liquid-nitrogen microscope previously described.[4] At 4.2 K the piezoelectric coefficients are reduced by a factor of 3 compared to 77 K and higher-voltage ranges are required for a comparable scan range. This introduces some degree of nonorthogonality in the x-y translator and at the highest voltages a nonlinear response is also observed under some conditions. Corrections for these factors have been made in the drive electronics and the general performance gives excellent atomic resolution equivalent to the best performance obtained at 77 K. All of the STM scans were recorded in the constant current mode with the tip at positive bias. Voltage and current values are given in the figure captions.

A large area scan (94×94 Å^2) of $2H$-$NbSe_2$ at 4.2 K is shown in Fig. 1(a) and indicates a perfect atomic pattern over the entire surface area scanned. A high-magnification STM scan plotted as a charge-density contour map is shown in Fig. 1(c). Figure 1(c) is a black and white photo of a color contour map in which the Se atom positions of the surface layer appear as large white plateaus. The charge contours in the interstitial regions show three equivalent deep minima and three equivalent saddle points reflecting the atomic positions of the Nb atoms in the middle layer of the three-layer sandwich. The multiple concentric contours represent the deep minima at positions between the Nb atoms while the saddle points occur at the three interstitial positions which lie over the Nb atoms in the middle layer of the trigonal prismatic sandwich structure.[3]

The atomic pattern in Fig. 1(c) is similar to that observed at room temperature by Bando *et al.*[5] and at 77 K by Coleman *et al.*,[6] except that the maximum z deflection is less at 4.2 K. At 4.2 K the minimum to maximum deflection is 0.6 ± 0.1 Å, substantially less than the 2.0 to 3.4 Å reported by Bando *et al.*[5] at room temperature and $\sim 30\%$ less than the 0.9 ± 0.1 Å reported by Coleman

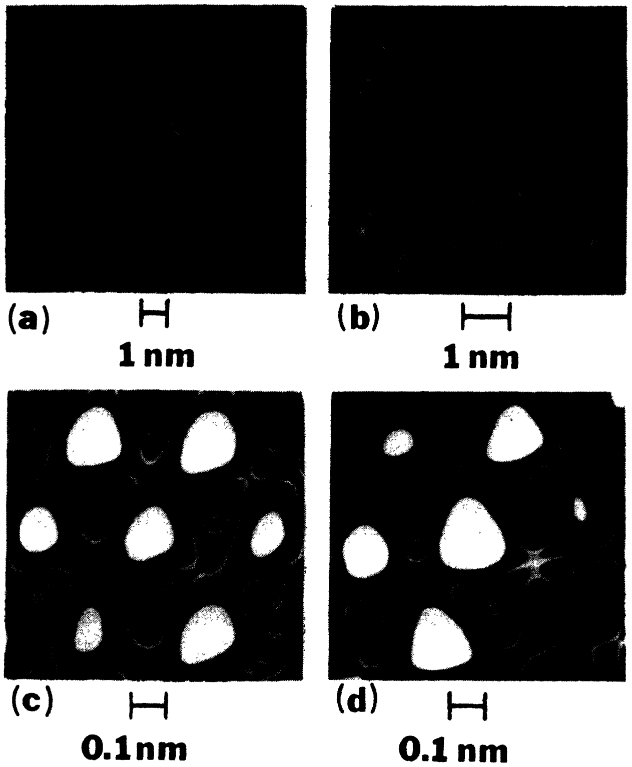

FIG. 1. STM images of atoms and CDW's on a $2H$-$NbSe_2$ surface at 4.2 K (2.0 nA, 25 mV). (a) Low-magnification gray scale image of atoms. (b) Gray scale image showing the CDW modulation superimposed on the atomic pattern. The asymmetry near the charge maxima is due to the displacement of the atomic and CDW modulations. (c) High-magnification computer-generated contour plot. The white islands indicate the atom positions. (d) High-magnification contour plot showing the charge asymmetry on the atoms surrounding a CDW maximum.

et al.[6] at 77 K. The data suggest a strong temperature dependence of the z deflection which decreases at low temperature. Superconductivity and CDW's exist simultaneously in $2H$-$NbSe_2$ below 7 K. The superconducting gaps have been measured at $\Delta = 1.07$ meV parallel[7] to the layers and $\Delta = 0.62$ meV perpendicular[8] to the layers. The STM images shown in Fig. 1 were recorded with the bias voltage at 25 meV. For bias voltages below 1 meV the atomic modulation could not be resolved. This may reflect the instrument response as well as the presence of a superconducting energy gap, but further study is required. The experimental atomic spacing calculated from the STM scans using the calibration of the translator at 4.2 K gives $a_0 = 3.45 \pm 0.05$ Å in good agreement with the electron diffraction value of 3.449 Å.

In Figs. 1(a) and 1(c) the CDW modulation although present is difficult to detect. Careful adjustment of the microscope when operating under conditions of high stability can enhance the extra modulation due to the CDW. The structure is a triple CDW with a wavelength of $\sim 3a_0$ and with incommensurate wave vectors given by $\mathbf{q}_\delta = (1-\delta)\mathbf{a}^*/3$ with $\delta \sim 0.025$ at 33 K and decreasing to $\delta \sim 0.011$ at 5 K as determined by neutron diffraction.[9] This should give rise to a charge-density enhancement on approximately every third row of Nb atoms which should appear as an overall charge modulation with period $\sim 3a_0$ as is clearly observed in the STM scan of Fig. 1(b). The vertices of the superlattice form a hexagonal pattern of charge maxima, but these maxima exhibit an asymmetry with respect to the superimposed surface Se atom pattern. This is evident from the unequal intensity of the atom cluster surrounding the charge maxima and shown in more detail in the high magnification scan of Fig. 1(d). The center atom shows the strongest z deflection, but the six surrounding atoms show unequal intensity corresponding to a total height variation of ~ 0.2 Å. The atom scan in Fig. 1(c) taken at the same magnification was centered between charge maxima and shows less asymmetry than Fig. 1(d), but asymmetry introduced by the adjacent charge maxima is still evident. An intermediate magnification scan of less sensitivity emphasizes only the charge maxima of the CDW superlattice and gives a hexagonal pattern as shown in Fig. 2. The surface Se atoms are still resolved as many closed concentric charge-density contours, but the asymmetry of the charge surrounding the maxima is not resolved on this scale.

The CDW modulation in $2H$-$NbSe_2$ should provide an overall charge-density pattern very similar to that produced by the $3a_0 \times 3a_0$ commensurate CDW structure occurring below 90 K in $2H$-$TaSe_2$. In fact the intermediate magnification STM scans of $2H$-$TaSe_2$ at 4.2 K show a very similar pattern as shown in Fig. 3. A triple CDW modulation of $3a_0$ is superimposed on the surface pattern of Se atoms and the charge asymmetry near the CDW maxima enhances a three-atom cluster similar to that obseved for $2H$-$NbSe_2$ in Fig. 1(d). $2H$-$TaSe_2$ has been studied and analyzed in more detail than $2H$-$NbSe_2$ and calculations[10] show three inequivalent Ta atoms with the number of Ta d electrons on each site given by

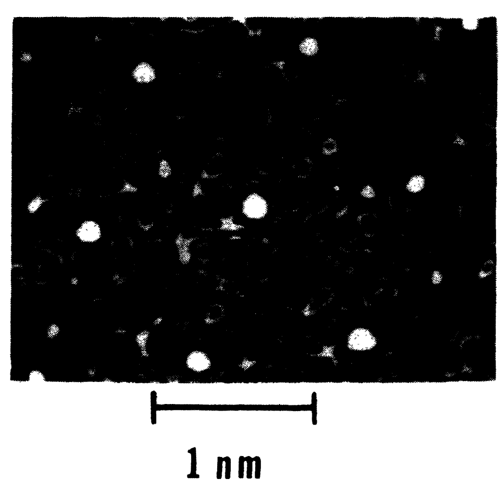

FIG. 2. Computer generated contour plot of $2H$-$NbSe_2$ showing the CDW superlattice superimposed on the atomic pattern (2.0 nA, 25 mV). The charge maxima appear as a hexagon of white islands with a $3a_0$ spacing.

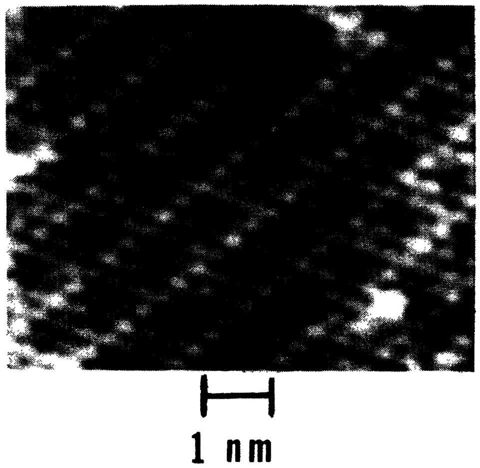

FIG. 3. Gray scale image of $2H$-$TaSe_2$ at 4.2 K showing the CDW modulation superimposed on the atomic pattern (2.2 nA, 25 mV). The displacement of the CDW and atomic modulations gives an asymmetric enhancement of a three-atom cluster near the CDW maximum.

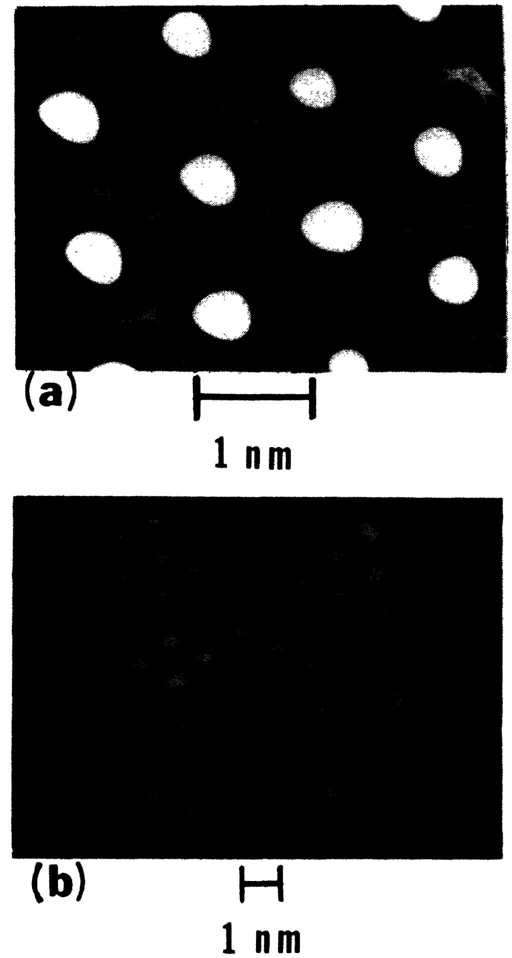

FIG. 4. STM images of CDW's on a $1T$-$TaSe_2$ surface at 4.2 K (2.2 nA, 30 mV). (a) Computer generated contour plot showing the charge maxima as white islands. (b) Low-magnification gray scale image showing a defect in the charge pattern.

$n_a = 1.014$, $n_b = 1.005$, and $n_c = 0.977$. The charge maxima occur on the center atom of a seven-atom cluster and represent a relatively small electron transfer of ~ 0.02 electron. In the trigonal prismatic structure the CDW charge maxima therefore occur at the center of a seven-atom transition-metal cluster and this will be displaced by $a_0/\sqrt{3}$ from the seven-atom cluster of surface Se atoms located in the surface layer above. The relative displacement of the two modulations and the dominant role of the surface Se atoms produces the observed asymmetry. The result of simply adding the two modulations is an asymmetrical enhancement of the seven-atom Se cluster such that the three-atom group shows a larger z deflection as observed in both the $2H$-$TaSe_2$ and $2H$-$NbSe_2$ STM scans.

In contrast to the STM images obtained from the $2H$ phases the CDW charge modulation in the $1T$ phases completely dominates the STM scans. An STM scan of $1T$-$TaSe_2$ at 4.2 K is shown in Fig. 4(a) where the CDW charge maxima appear as white plateaus centered on a $\sqrt{13}\mathbf{a}_0 \times \sqrt{13}\mathbf{a}_0$ superlattice. $1T$-$TaSe_2$ exhibits the initial onset of a triple incommensurate CDW above 600 K and becomes commensurate below 473 K where the CDW superlattice is rotated by 13.9° relative to the underlying atomic lattice. The charge density contours show no evidence of the surface Se atoms and the interstitial positions between the charge maxima show three deep minima and three saddle points symmetrically located relative to the maxima of the CDW superlattice.

The charge maxima in the $1T$ phase crystals are centered on a 13 Ta atom cluster arranged on a star-of-David pattern. Smith, Kevan, and DiSalvo[10] have carried out a model calculation for $1T$-TaS_2 and find three inequivalent Ta atoms with occupied d electrons per atom of $n_a = 1.455$, $n_b = 1.311$, and $n_c = 0.611$. This large electron transfer toward the center atom in the star-of-David cluster is certainly consistent with the large STM deflection produced by the CDW charge modulations in both $1T$-$TaSe_2$ and $1T$-TaS_2. However, the measured average value of 3.5 ± 1.4 Å for the z deflection of $1T$-$TaSe_2$ at 4.2 K is anomalously large. For different runs the z deflection shows substantial variation in the range 2.5 to 4.5 Å, but is relatively constant for any given cool down and scanning sequence. In the regions of both the CDW maxima and the minima the charge-density contours show no evidence of modulation by the surface Se atom potentials. However, crystal defects can strongly perturb the CDW maxima as shown in Fig. 4(b) where an isolated charge maximum has been completely quenched by a possible Ta-atom vacancy. This produces a very localized perturbation of the CDW maximum and the surrounding charge-density contours show very little distortion.

In $4Hb$-$TaSe_2$ a triple CDW forms in the octahedral sandwiches below 410 K. This gives rise to a fairly complex commensurate superlattice of $13\mathbf{a}_0 \times 13\mathbf{a}_0 \times \mathbf{c}_0$. Within one octahedral sandwich this is apparently identical to the superlattice observed in the $1T$ polytypes. In the trigonal prismatic sandwiches an incommensurate

CDW with a superlattice close to $3a_0 \times 3a_0$ forms below 75 K. At 4.2 K the STM scans show a strong superlattice pattern spaced at $\sqrt{13}a_0$ with a superimposed Se atom pattern as shown in Fig. 5. In this case the rotation of 13.9° between the CDW superlattice and the underlying atomic lattice can be clearly identified as indicated by arrows. The presence of the alternating trigonal prismatic sandwiches with a weak CDW has apparently reduced the octahedral CDW amplitude sufficiently that the modulation by the surface Se atoms is detectable. However, the maximum to minimum z deflection produced by the CDW superlattice is still anomalously large at an average measured value of 2.0 ± 1.2 Å. The superimposed atom pattern has a measured z deflection of 0.7 ± 0.4 Å. A charge asymmetry resulting from the superposition of the atom pattern and the CDW superlattice is also visible but has not been analyzed in detail. Evidence of the $\sim 3a_0 \times 3a_0$ CDW modulation in the trigonal prismatic sandwiches has not been observed, but more detailed work with the STM on $4Hb$-$TaSe_2$ is clearly possible and should result in improved resolution.

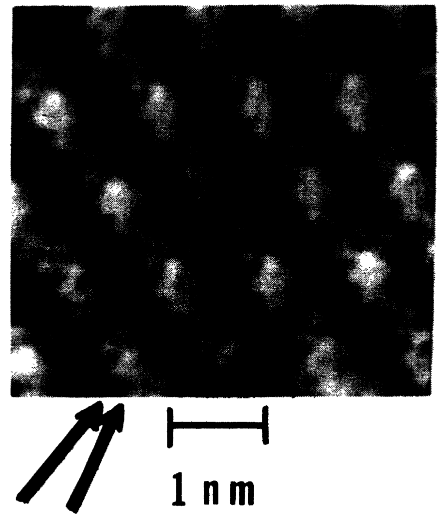

FIG. 5. Gray scale image of a $4Hb$-$TaSe_2$ surface at 4.2 K, showing both the CDW and atomic modulations (2.2 nA, 25 mV). (Left arrow points to atom rows, right arrow points to CDW maxima.)

The examples of STM scans shown in this paper demonstrate the high sensitivity of the liquid-helium STM to details of the charge-density contours at the crystal surface. The large range of CDW amplitudes allows a comparison of the relative roles of modulation by the surface atoms and the CDW superlattices in contributing to the z deflection of the STM. The extremely large z-deflection response of the STM to a strong CDW modulation in the $1T$ phases is largely unexplained. It is systematically observed and in $4Hb$-$TaSe_2$ occurs along with a much smaller deflection produced by the surface atom pattern. The excellent resolution obtained at 4.2 K and the reproducibility of the patterns can allow interpretation of very subtle changes in the symmetry and amplitudes of the charge density. Application to a wide range of similar problems should be possible.

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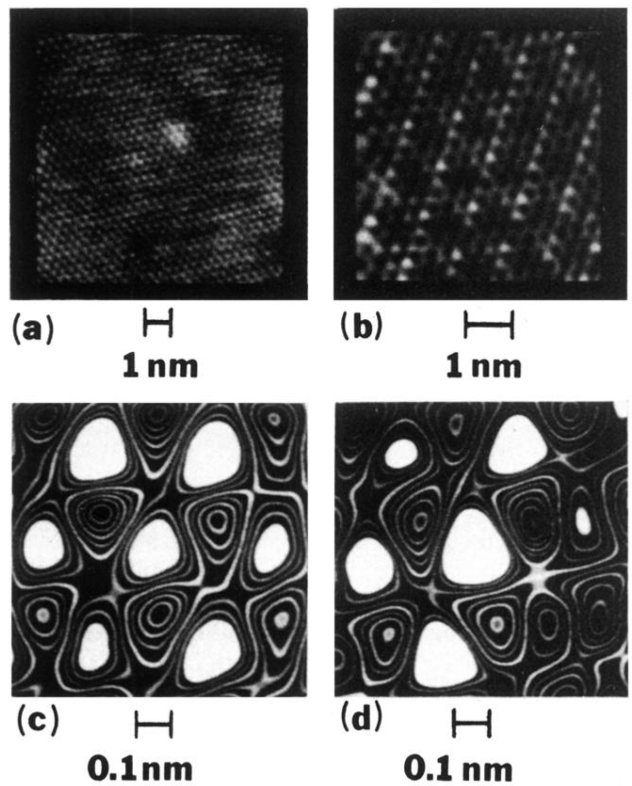

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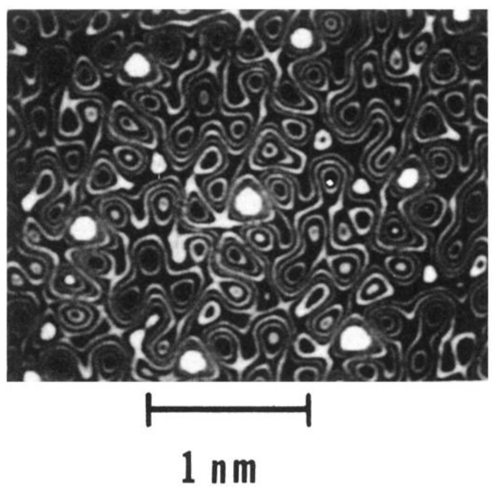

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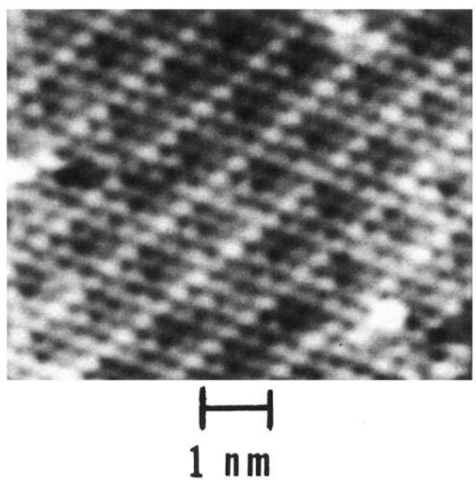

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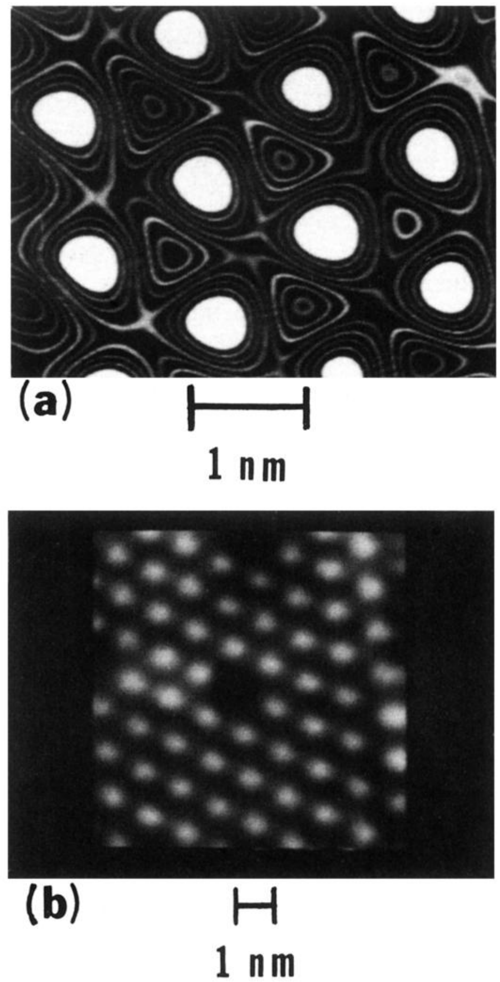

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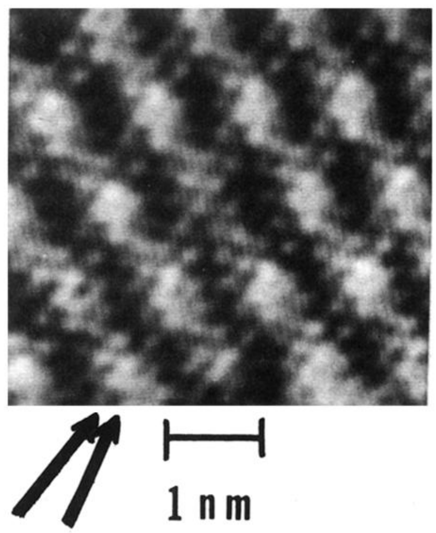

FIG. 5. Gray scale image of a $4Hb$-$TaSe_2$ surface at 4.2 K, showing both the CDW and atomic modulations (2.2 nA, 25 mV). (Left arrow points to atom rows, right arrow points to CDW maxima.)