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Scanning tunneling microscopy of charge-density waves in $NbSe_3$

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The charge-density-wave (CDW) structure in $NbSe_3$ due to the two independent CDW's has been imaged by scanning tunneling microscopy. As predicted by band-structure considerations, the CDW modulation is observed to be substantially localized on different chains for the separate CDW's. At 77 K where only the high-temperature CDW exists, a relatively weak modulation with a single component along the **b** axis is observed. At 4.2 K the low-temperature CDW contributes a much stronger $\sim 4\mathbf{b}_0 \times 2\mathbf{c}_0$ superlattice modulation.

$NbSe_3$ is a quasi-one-dimensional metal with two charge-density-wave (CDW) transitions,[1] one at $T_1 = 144$ K and one at $T_2 = 59$ K. These CDW's remain incommensurate and have wavelengths[2] of $4.115b_0$ (144 K) and $2.00a_0$, $3.802b_0$, $2.00c_0$ (59 K). The $NbSe_3$ crystals have been previously studied by scanning tunneling microscopy (STM) at 77 K[3] and at room temperature[4] with a reasonable resolution of the three chain structures of the unit cell in the **b**-**c** plane (see Fig. 1). Coleman and coworkers[3,5] have deduced from the STM profiles at 77 K that the atomic height and charge variations of the surface Se atoms dominate the STM scan images with only slight evidence of a CDW modulation from the high-temperature CDW.

In this paper we report the first conclusive observations of the CDW modulations in $NbSe_3$ at 77 and 4.2 K using STM. The STM scans have been made parallel to the **b**-**c** plane and resolve the atomic surface structure of Se atoms connected with three of the six parallel Nb chains per unit cell. This surface structure consists of three pairs of Se atom chains per unit cell. A unit cell cross section perpendicular to the **b** axis is shown in Fig. 1. The surface Se atoms in this chain structure have a height variation of 1.52 Å over the surface of the unit cell.

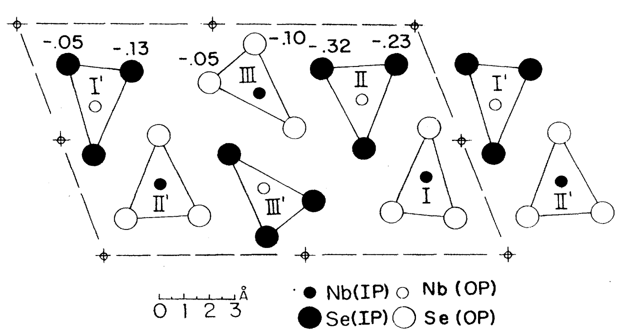

FIG. 1. Cross section of $NbSe_3$ unit cell perpendicular to chain axis (**b** axis). The black atoms lie in the plane of the figure and the white atoms are out of the plane. At the **b**-**c** plane surface there are three chains per unit cell; two are in-phase along the **b** axis and one is displaced by $b_0/2$ from the two in-phase chains. The height variation of the surface Se atoms is 1.52 Å. The numbers indicate the negative charges on the Se atoms. The chain designation as type I, II, and III is the nomenclature used in Ref. 6.

At 77 K a weak CDW modulation of wavelength $\sim 4b_0$ is observed in the STM scans made with the scan direction parallel to the **b** axis. At 4.2 K a much stronger CDW modulation is observed reflecting the increased gapping of the Fermi surface (FS) by the second CDW. The modulation along the chain axis again shows the expected modulation wavelength of $\sim 4b_0$ while the two-dimensional CDW superlattice shows the clear presence of the $2c_0$ component of the low-temperature CDW.

The band-structure calculations of Shima and Kamimura[6] and analysis of the bonding by Wilson[7] have associated the high-temperature CDW with FS sheets and wave functions derived from orbitals connected with the chain pairs of type III and III' which are identified in Fig. 1. The low-temperature CDW is identified with FS sheets and wave functions derived from orbitals connected with the chain pairs designated as I, I', II, and II'.

At 77 K, with only the high-temperature CDW present, the STM scans show a weak CDW modulation of $\sim 4b_0$ localized on chains of type III. At 4.2 K the CDW intensity is greatly enhanced and a strong STM deflection due to a two-dimensional CDW superlattice is observed. The CDW maxima are observed to be localized on the two Nb chains of type I and III. The gray-scale images and scan profiles demonstrating these results are presented below.

The scans at 77 K have been made with the scan direction both parallel and perpendicular to the chain direction. The gray-scale image obtained with the scan direction perpendicular to the chain direction is shown in Fig. 2(a). The atoms in the pairs of surface Se atoms associated with each chain are resolved and by comparing profiles of parallel scans displaced along **b** by $b_0/2$ we can unambiguously identify which chains are of the types I, II, and III.

As indicated in Fig. 1 the chains of type I and II are in phase along the **b** axis while chain III is displaced by $b_0/2$ from chains I and II. Two profiles are shown in Fig. 2(b) and these were recorded along the tracks indicated in Fig. 2(a). One chain remains high in both profiles and one remains low while the third moves in an intermediate range. In the upper profile the scan passes over the Se atoms of the intermediate chain and gives a strong atomic deflection. This scan passes between the Se atoms of the

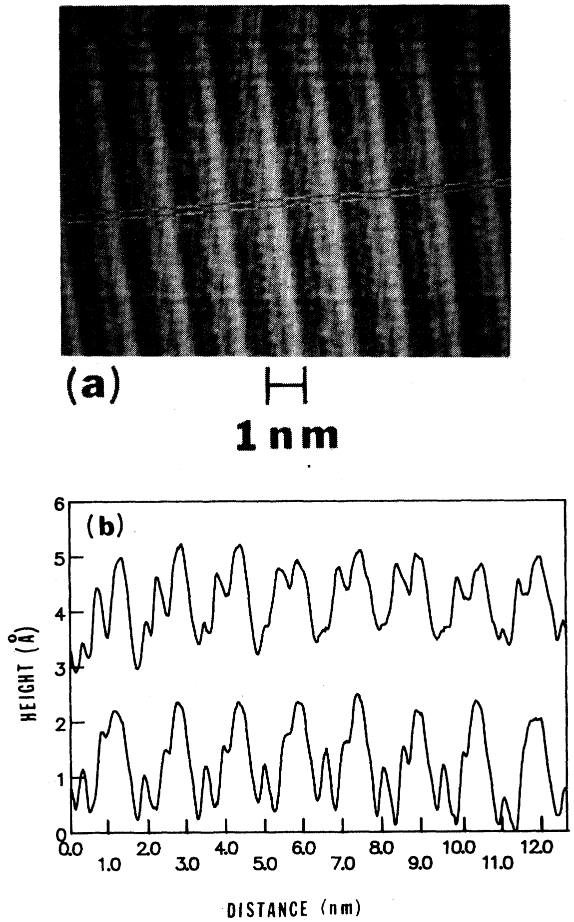

FIG. 2. (a) STM gray-scale image obtained at 77 K by scanning approximately perpendicular to the chain direction in the **b-c** plane. The image shows one high chain, one low chain, and one intermediate chain. The two tracks represent scans separated by $b_0/2$. (b) Scan profiles corresponding to the two scan tracks separated by $b_0/2$ in the gray-scale image of (a).

high and low chains and only small atomic structure is detected. In the lower profile, which is displaced by $b_0/2$ from the upper profile, the scan passes over the atoms of the low and high chains giving a relatively strong atomic deflection while the intermediate chain shows only a small blip. The high chain remains high in both profiles and we attribute this to a type-II chain where the Se atoms have a large negative charge as indicated by the numbers in Fig. 1. Both profiles exhibit a total z deflection of ~ 2 Å.

As discussed below in reference to Fig. 3, the CDW modulation is observed to be localized on the chain of intermediate height. The only possible identification consistent with all of the above observations is the following. Chain type I is low, chain type II is high, and chain type III, which supports the CDW, ranges from intermediate to high.

The above identification is a change from the original chain order deduced from a line scan profile by Coleman *et al.*[3] That scan did not resolve atoms or the CDW and it was assumed that the highest chain in the STM scan was the type-III chain since one of its Se atom rows is the highest on the surface. The present identification reverses the heights of chains II and III. This is clearly confirmed by observing the CDW on the intermediate height chain and assigning the large z deflection of chain II to the effect of the charged Se atoms on the conduction-electron density at the surface.

Figure 3(a) shows a gray scale STM image with the scan direction approximately parallel to the chains. The scan resolves the chains of surface Se atoms and careful examination shows the CDW modulation to be dominantly on the chains of intermediate height, i.e., chain III. A profile recorded along one of the intermediate height chains is shown in Fig. 3(b). The minima and maxima occur at the CDW wavelength of $\sim 4b_0$ and four surface Se atoms are resolved between the minima. The z deflection of ~ 1.2 Å is evenly divided between the atomic deflection and the CDW modulation.

At 4.2 K the superimposed CDW modulation is much stronger and a clear two-dimensional superlattice is resolved, as shown in Fig. 4(a). The surface two-

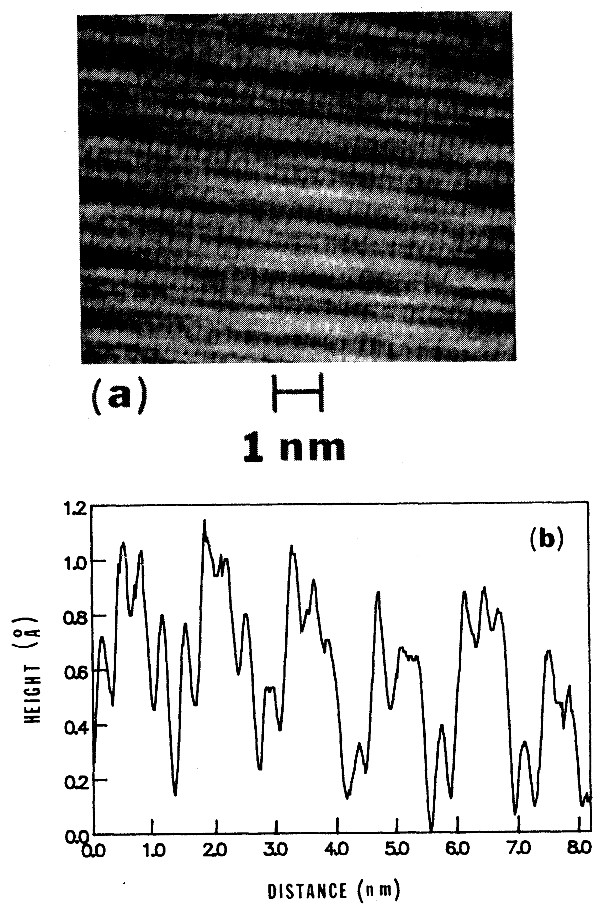

FIG. 3. (a) Gray-scale image obtained at 77 K by scanning approximately parallel to the chain direction. High, low, and intermediate z deflection are again observed. (b) Profile obtained by scanning along a chain of intermediate height. A modulation by the CDW is clearly observed with a wavelength of $\sim 4b_0$.

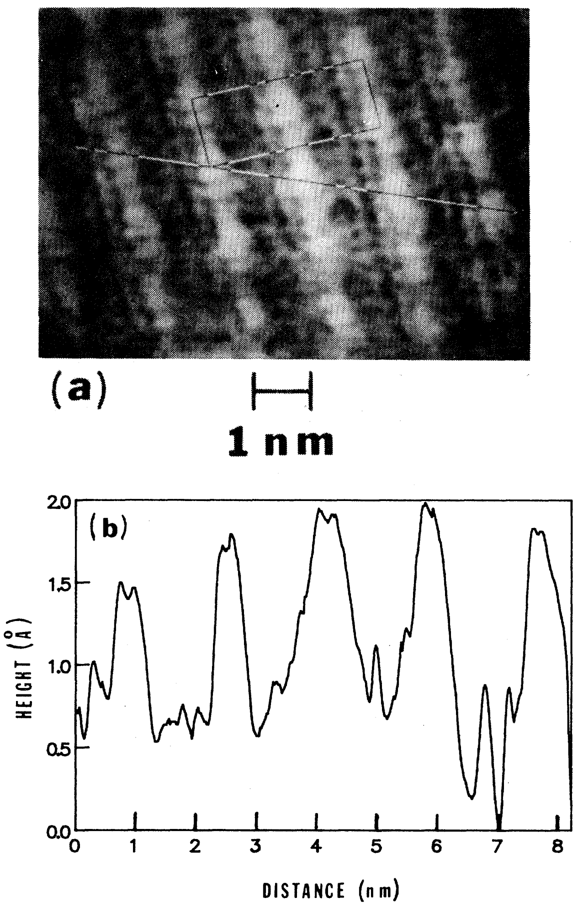

FIG. 4. (a) Gray-scale image obtained at 4.2 K by scanning approximately perpendicular to the chains in the **b**-**c** plane. A strong CDW superlattice with a unit cell $\sim 4b_0 \times 2c_0$ is observed and outlined by the rectangle. $b_0 = 3.478$ Å and $c_0 = 15.626$ Å. (b) Scan profile obtained along track shown in (a). One chain is low and two are high with the z deflection of the CDW modulation dominant.

dimensional superlattice unit cell is a rectangle with vectors of $\sim 4\mathbf{b}_0$ and $2\mathbf{c}_0$ as indicated by the superimposed traces in Fig. 4(a). The CDW maxima appear diffuse and overlap two of the parallel chains. The unit-cell pattern is clearly controlled by the $\sim 4\mathbf{b}_0 \times 2\mathbf{c}_0$ low-temperature CDW superlattice while the higher-temperature CDW with a single component of $\sim 4b_0$ also contributes along the chains to give the diffuse appearance. The suggested conclusion is that the large diffuse CDW maxima are largely localized on chains of type I and III and are responsible for the high STM z deflection, while the chains of type II are low, a major change from the profiles observed at 77 K.

The CDW maxima show a wider overlap of the chains at a regular spacing of $\sim 4b_0$ suggesting that the two CDW modulations along the chains are at least partially phase correlated, although the two CDW's will not be in phase over large distances due to the $\sim 7\%$ difference in the components along the **b** axis. The total z deflection observed for scans across the chains is ~ 2 Å, comparable to that observed at 77 K. A profile crossing the chains and centered on the CDW maxima is shown in Fig. 4(b) for the track designated by the transverse line in Fig. 4(a). Two of the chain structures are high while the third is low. The individual Se atom chains are only partially resolved and the profile is dominated by the CDW maxima. The profiles across the chains are therefore controlled by a combination of the atomic height variation and the CDW modulations. The presence of the low-temperature CDW localized on the chains of type I creates a large z deflection on this chain and offsets the lower height of this chain due to the atomic structure alone.

These observations and conclusions are consistent with the electronic modifications occurring at the two CDW transitions based on the existing band structure and FS analysis. Assuming that the conductivity changes are due only to the FS obliteration, $\sim 20\%$ of the FS is gapped by the high-temperature CDW. This CDW is associated with the almost perfect nesting of the FS sheets derived from the type-III wave functions. This will produce a refolding of the band structure into a reduced Brillouin zone but a reasonably good conductivity will remain. The localization of the CDW modulation will depend on the exact details of the band folding, the spatial extent of the wave function, and the possible presence of singularities[8] generated in the local density of states (LDOS) by the CDW. The STM scans show that both the modulation and localization from the high-temperature CDW are of intermediate strength suggesting that the FS changes make only a moderate modification of the LDOS.

Below $T_2 = 59$ K an additional 60% of the FS is obliterated assuming a simple relation between conductivity and FS area. In this case the band refolding into a more complex reduced Brillouin zone can in general be expected to have a major effect on all sections of the FS and to produce a greater modification in the LDOS. A greater mixing of the states at $2k_F$ along with the greater FS obli-

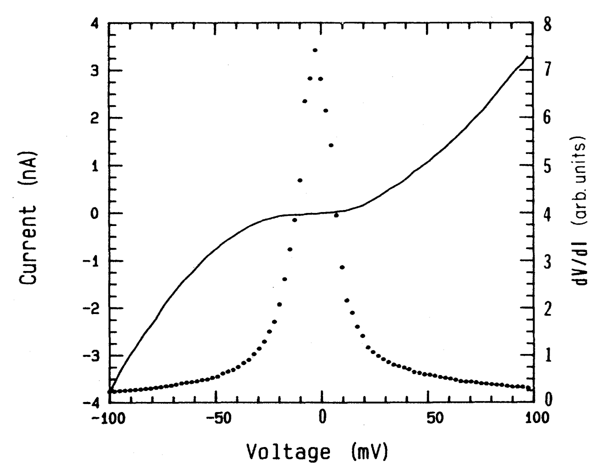

FIG. 5. I vs V (solid line) and dV/dI vs V (dotted line) measured at 4.2 K. The onset of a strong nonlinear region above ~ 20 mV indicates a charge-density-wave gap in the range 20–30 mV.

teration can also produce stronger singularities in the LDOS.

At 4.2 K the I vs V and dynamic resistance dV/dI vs V have been checked at a number of positions on the surface of the $NbSe_3$ crystal. Figure 5 shows the curves obtained at a position of a CDW maximum and indicates the onset of a strong nonlinear behavior at 20–30 mV bias. This can be interpreted as the onset of tunneling into states above the low-temperature CDW gap and an increase in the density of states available for tunneling. The dynamic resistance behaves similarly to a zero-bias anomaly as previously pointed out by Fournel *et al.*,[9] who measured a fixed Pb-NbO_x-$NbSe_3$ junction at 4.2 K and obtained $\Delta_{CDW} = 35 \pm 5$ meV. The low-temperature CDW gaps only part of the FS and arises from imperfectly nested FS sheets. Therefore the expected structure in the density of states as a function of energy is not expected to be sharp. Possible weak structure in the range 50–100 mV may be connected with the high-temperature CDW, but no clear data have yet been obtained on this point.

The STM scans presented in this paper were taken with a bias voltage of 75 and 70 mV at 4.2 and 77 K, respectively. At 4.2 K we have examined scans for a range of bias voltages from 20 to 100 mV and so far have not detected any major change in the STM image.

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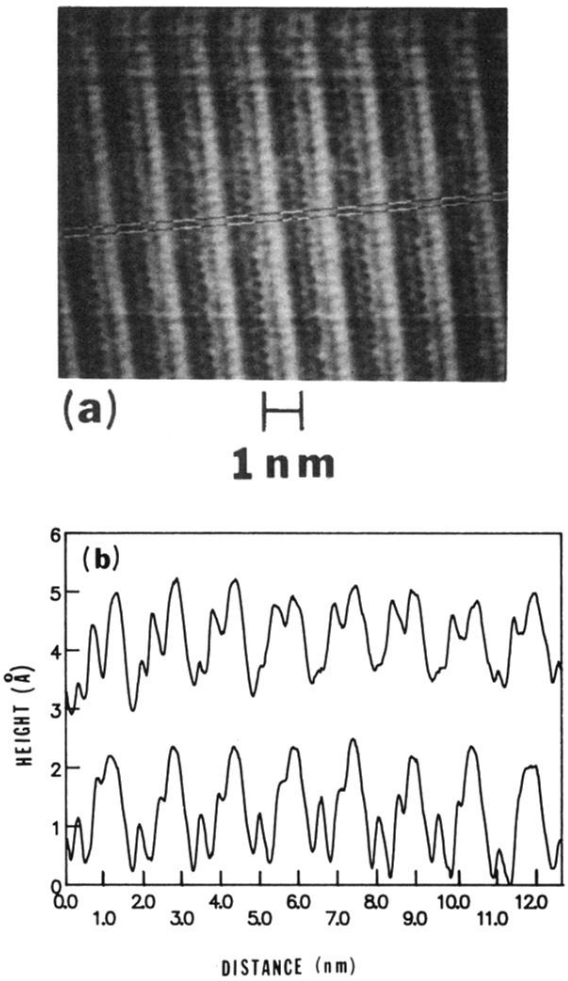

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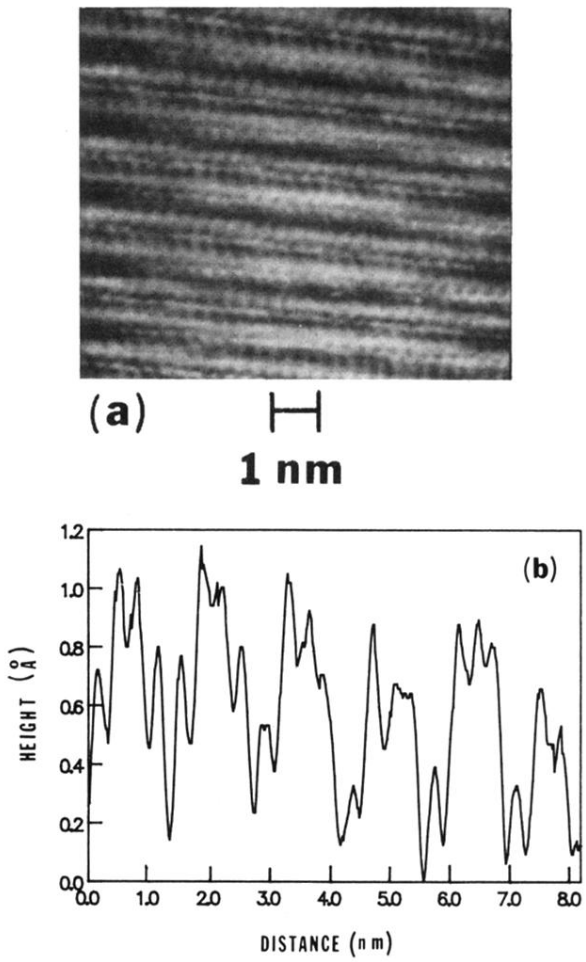

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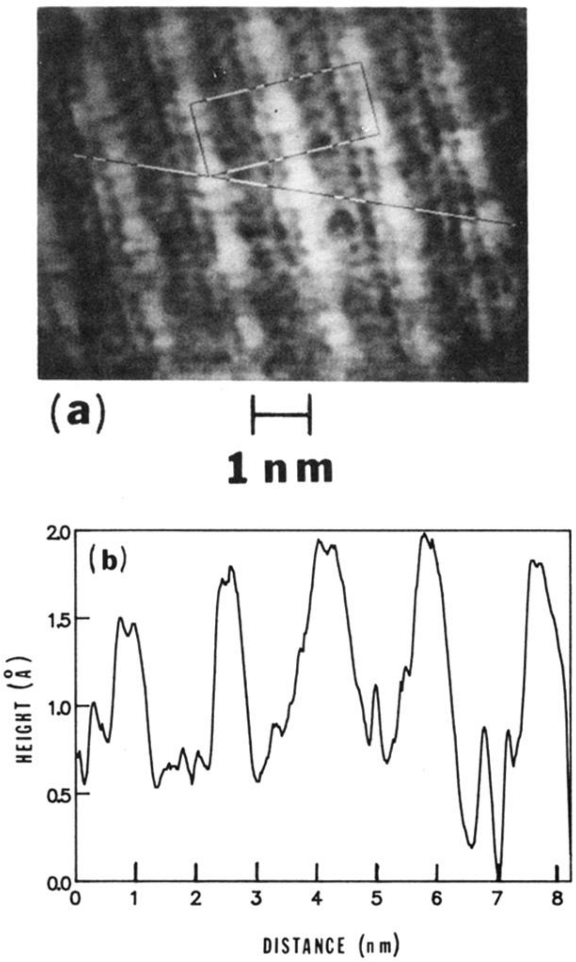

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