Scanning tunneling microscope study of charge-density-wave modulations in NbTe₄

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The room-temperature modulated structure of NbTe₄ was studied by means of scanning tunneling microscopy. In addition to a relatively weak image of the average structure and stronger contrast from the incommensurate modulation, contributions from domains of nanometer sizes were detected, which appeared with variable amplitudes. The existence of secondary modulation displacements associated with precursor effects of modulation phase transitions was suggested earlier on the basis of electron-diffraction results and their computer simulation. The current results are direct evidence of these fine-scale modulation phenomena.

I. INTRODUCTION

The average structure of NbTe₄ (Ref. 1) is formed of cages of interconnected Te antiprismatic columns hosting quasi-one-dimensional Nb chains (Fig. 1). It is isostructural with that of TaTe₄ (Ref. 2) and both are strongly modulated below and above room temperature (RT).³–⁵ This charge-density modulation is at RT incommensurate (IC) in NbTe₄ and commensurate in TaTe₄ and the two compounds are end members of a continuous solid solution NbₓTa₁₋ₓTe₄ (0 < x < 1) (Ref. 6) (Fig. 2) with a series of composition- and temperature-dependent modulation phases. For various reasons some regions in this phase diagram are not fully determined yet. First, the shaded areas depend on the exact composition, which was so far not determined with sufficient accuracy. Second, there are additional parameters to those shown, which influence the stability of a particular phase and which cannot be fully controlled in practice. For instance, the very sluggish lock-in transition in NbTe₄, which was observed in transmission electron diffraction (TED) patterns close to the liquid helium temperature, depends not only on the specimen composition but also on its size.⁷

The as determined RT modulated structure of NbTe₄ (Refs. 5 and 8) was found to be a first approximation only. Additional faint and diffuse satellites, which on cooling gradually develop into elongated streaks, were detected in overexposed TED patterns even well above RT.⁹,¹⁰ It was suggested on the basis of a computer simulation that the origin of these fine diffraction phenomena was in two weak additional modes, which modify the strong breathing mode and which in fact represent precursor effects to the low-temperature lock-in phase.¹¹

To our knowledge, there have been no reports so far on scanning tunneling microscopy (STM) of transition-metal tetra-chalcogenides, although the modulation in both NbTe₄ and TaTe₄ is strong and stable at RT, which is certainly in favor of such experiments. Thus, the scope of this work was to investigate the RT modulated structure of NbTe₄ and to look for additional phenomena that might be related to the weak and diffuse satellites detected earlier by TED.

II. EXPERIMENT

All crystals investigated were grown by iodine transport as described in previous papers on this subject.³–⁵ STM was performed in ultrahigh vacuum with an Omicron STM-1. Freshly cleaved surfaces were prepared by breaking the needlelike crystals between two glass slides immediately before their introduction into the STM chamber. Crystals preferentially cleave along the equivalent 〈010〉 planes located in the structure as shown by arrows in Fig. 1. As a rule the obtained surfaces are relatively rough on an atomic scale. Although such a cleavage involves breaking of the shortest Te-Te bonds (0.29 nm), it is the only one that leaves all
III. RESULTS

An unfiltered image of a relatively flat (010) surface of NbTe₄, with the corresponding Fourier transform in the inset, is shown in Fig. 3(a). The indicated a₀ and c₀ axes of the average structure are deduced from the orientation of the crystal with regard to the direction of scanning during the STM experiment. In addition to the spots, which correspond to the observed periodicities, the Fourier transform clearly reveals an enhanced diffuse contribution perpendicular to the direction of scanning. This was partially reduced by Fourier filtering, which improved the image as shown in Fig. 3(b).

As a rule the contribution of the average structure to the STM images is extremely weak and an atomic resolution along the antiprismatic Te columns was not achieved. Nevertheless, the columns as units are clearly discerned by viewing the images obliquely. These columns appear parallel to lines A in Fig. 3(b) in agreement with the crystal axes shown in Fig. 3(a).

Figures 3(a) and 3(b) reveal several additional contributions. The first is the superimposed RT IC modulation, which is known to involve a longitudinal modulation of the Nb positions accompanied by a breathing mode of the Te cages. In Fig. 3(b) this modulation is indicated by the lines D. By ignoring the somewhat weaker additional contributions discussed below, this modulation is out of phase along neighboring columns with 5.5 modulation periods fitting approximately 16 antiprismic heights (i.e., 8c₀). The lines D thus connect modulation maxima of the adjacent columns and do not appear perpendicularly to the antiprismic columns (i.e., to lines A). Due to this out-of-phase stacking the lines D reveal a more or less pronounced zigzag appearance as indicated at Z.

Two further sets of lines, marked B and C, can clearly be distinguished in Figs. 3(a) and 3(b). Their intersections are indicated in Fig. 3(b) by large open circles. Lines B are not equidistant throughout the image and there are minute regions of anything between equally spaced (e.g., region 1) and clearly paired lines (e.g., region 2). The latter are frequently interrupted by antiphase boundaries (APB) of two types. The first (I) are straight and simply interchange the narrow and wide spacings between lines B (e.g., the one shown by the arrow 3), while the second (II) are of no regular shape. These effects become more evident in case other contributions to the image are suppressed as in Figs. 4(a) and 4(b), which again show an unfiltered and a Fourier filtered image, respectively. Different domains of lines B only are visible, separated by both types of APB’s.

The images in Figs. 3(a) and 3(b) are further complicated. First, the intersections of lines B and C do not coincide with the direction of the columns, but form with the latter an angle of about 4°, i.e., the angle between the directions Y and A. Second, while the intersections of lines A and D are properly spaced (5.5 modulation lengths fit about 8c₀ = 5.44 nm, the spacing shown between the two bold arrows marked with X), those between lines B and C evidently ex-
ceed that value for about 10%. By shifting the latter (indicated by large empty circles) along lines $C$, a coincidence with the intersections between lines $A$ and $D$ (large full circles) can be achieved. Alternatively, the described misfit between directions $A$ and $Y$ can be accounted for if lines $A$ are replaced by zigzag lines, as shown by the rightmost one. The intersections of lines $A$ and $D$, shown by full large circles, along lines $C$, a coincidence with the intersections between lines $A$ and $D$ (large full circles) can be achieved. Alternatively, the described misfit between directions $A$ and $Y$ can be accounted for if lines $A$ are replaced by zigzag lines, as shown by the rightmost one.

FIG. 3. (a) An unfiltered STM image ($U_t = -0.5$ mV, $I_t = 0.5$ nA, constant-current mode) of NbTe$_4$, with the crystal axes of the average structure indicated. The inset shows the Fourier transform with an enhanced scattering along the $y$ axis. (b) The same area after Fourier filtering. Shown are the average structure ($A$), the RT IC modulation zigzag lines ($Z$) with 11 modulation periods fitting $16c_0(D)$, and the contribution of additional modes ($B$ and $C$). Note the regions with approximately equidistant (1) and paired (2) lines $B$, as well as a type-I APB ($3$).

IV. DISCUSSION

Although atomic resolution of the average structure was not achieved, the observation of columns is important for calibration purposes, with regard to the directions as well as spacings in the images. First, their presence indicates that they do not coincide with the intersections of lines $B$ and $C$. 

FIG. 4. (a) An unfiltered STM image ($U_t = 0.3$ mV, $I_t = 0.5$ nA, constant-current mode) of NbTe$_4$ showing an enhanced contrast of lines $B$ only. The average structure axes are indicated. (b) The same area after Fourier filtering. Domains, separated by type-I and type-II APB’s, are indicated by broken lines. 

(modulation maxima) and small (minima) circles, show that the modulation along neighboring columns is out of phase, as indicated at the top of the columns (two thin crossed interrupted lines).
Second, their spacings as well as those of their intersections with lines $D$ fit very well with the calculated ones and clearly differ from those obtained by intersecting lines $B$ and $C$.

The observed lines $D$ have a periodicity of 11 spacings within a distance of $16c_0$, consistent with previous diffraction experiments. Being of a zigzag instead of a straight form they reveal the antiphase stacking of neighboring modulation columns.

Contrasting effects along sets of lines $B$ and $C$ in the STM images are interpreted in terms of the two additional modulation modes to the RT IC one, postulated to exist in RT NbTe$_4$ on the basis of electron diffraction evidence.$^{11}$ Since lines $B$ connect modulation maxima of one column with minima of the adjacent one, their pairing is first interpreted as an up and down displacement of adjacent modulation columns (LT1). Similarly, the small misfit between the lines connecting intersections of lines $B$ and $C$ with those of lines $A$ and $D$ strongly supports the previous predictions$^{11}$ that a second mode (LT2), representing a slight clockwise and anticlockwise rotation of the modulation maxima, is also present. Both modes cause the weak and diffuse satellites observed in the RT TED patterns.

Finally, there is an apparent discrepancy between the contributions of different modulation modes as observed by TED and STM. In the case of TED the contribution of the RT IC breathing mode is strong as compared to those of the superimposed modes LT1 and LT2, while the corresponding sets of lines in the STM images are of comparable intensity.

The reason for this discrepancy is in the way NbTe$_4$ crystals cleave along the $\{010\}$ planes. If the modulation columns remain intact during cleaving as suggested earlier, the terminating surfaces are composed of Te atoms only, which screen the strongly modulated subsurface Nb atoms. Thus, in STM only the response of the Te cages to the strong one-dimensional modulation of the Nb positions is observed and the RT IC breathing mode appears with a comparable intensity to those of the LT1 and LT2 modes.

V. CONCLUSIONS

By using STM as a surface method, charge modulation phenomena in NbTe$_4$ were investigated. The main result of this study is a direct visualization of a CDW modulation superstructure in NbTe$_4$. In addition, direct evidence of two modes superimposed onto the strong RT IC modulation is given. These modes, together with the observed two types of APB’s, account for the diffuse scattering effects in the corresponding TED patterns of this compound.

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