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Scanning Tunneling Microscopy of Modulated Surface Structures

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Modulated structures are commonly found in transition-metal chalcogenides with compositions between MX_4 and M_3X_4. Their origin is in the low-dimensional character of these compounds, which supports phenomena like charge density waves (CDW). These can be further stabilized at surfaces, where the bulk dimensionality is additionally reduced. Modern surface methods, combined with calculations of the electronic properties, can give a new insight into such phenomena.

Two weak incommensurate modes, superimposed onto the main breathing mode, were discovered during the initial TEM studies of $Nb_{1-x}Ta_xTe_4$. They were detected at the $NbTe_4$ side of the phase diagram as weak and diffuse satellites in overexposed electron diffraction patterns [1]. Although a bulk phenomenon, these modes were for the first time successfully resolved by STM [2]. This was possible due to the preferential cleavage of the $NbTe_4$ crystals, which exposed complete tetragonal anti-prismatic columns. The weak transversal modes were observed as a surface phenomenon, superimposed onto the much stronger breathing mode (Fig.1).

The observed sliding of two apparently independent low-temperature CDWs in $NbSe_3$ was recently explained on basis of a new model [3], which took into account statistically distributed nano-domains of both CDW modes. The results of earlier low-temperature STM [4] and satellite dark field TEM studies [5] were shown to be in a good accord with the model. It was further shown that sub-monolayer gold deposits on the $NbSe_3$ van der Waals surface exhibit poorly correlated modulated regions, whose periodicities are comparable to those of the two CDWs in pure $NbSe_3$. In another trichalcogenide, $ZrTe_3$, a surface compositional modulation [6] was shown to be a result of ordered, surplus tellurium atoms, which occupied the interstitial positions on the (001) $ZrTe_3$ surface. Calculations within the extended Hückel tight binding (EHTB) approximation show that these tellurium atoms also account for the relatively high metallic conductivity of this compound.

CDW domains of two orientational variants were detected at the edges of disk-like surface defects in $NbSe_2$, which was an indication that the deformed regions of the Se-Nb-Se sandwiches assumed an octahedral rather than trigonal-prismatic coordination [7]. It was further shown that surface domain boundaries between orientational variants in the monoclinic $NbTe_2$ were often strongly modulated (Fig.2) with periodicities identical to those of the adjacent domains [8]. In contrast to the modulation in $NbSe_2$, the $NbTe_2$ modulation was interpreted on basis of a misfit between the domain boundaries across the van der Waals gaps.

Finally, the Nb_3X_4 (X = S, Se, Te) compounds, characterized by large hexagonal tunnels [9], were studied by means of TEM and STM. From the three compounds forming the family only Nb_3Te_4 shows bulk conductivity anomalies at 95 K, which were attributed to a CDW with a modulation vector $\mathbf{q} = \pm(1/3\mathbf{a}^* + 1/3\mathbf{b}^* + 3/7\mathbf{c}^*)$. Intercalation with indium and thallium raises the CDW onset temperature in Nb_3Te_4 and supports CDW formation in the other two compounds [10,11], without significantly deforming the host structure. The electronic properties, calculated within the EHTB method, confirmed that intercalation flattens the Fermi surfaces and consequently improves the one-dimensional character of these compounds. Poorly correlated modulation along the hexagonal columns was consistently observed in room-temperature STM images of these compounds, indicating that precursor effects to full CDW formation are surface supported phenomena.

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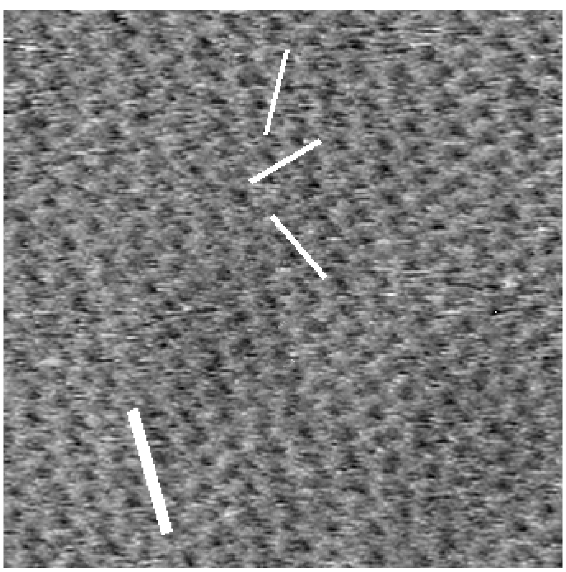

FIG.1. STM image of a {100} surface of $NbTe_4$, with the colums (thick) and the CDW modes (thin) indicated; $(10\ nm)^2$ area, constant height mode, $U_g = 1$ mV, $I_t = 2.5$ nA.

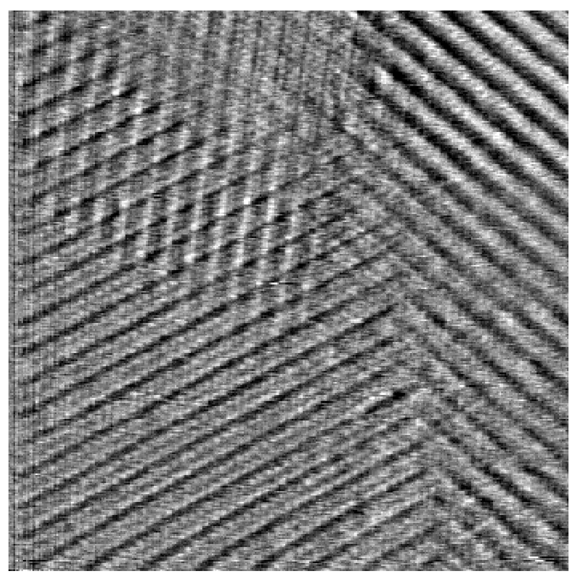

FIG.2. STM image of three domains in $NbTe_2$, separated by strongly modulated boundaries; $(20\ nm)^2$ area, constant height mode, $U_g = 0.2$ mV, $I_t = 2$ nA.

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