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Periodic surface modulation of $(LaSe)_{1.14}(NbSe_2)$ observed by scanning tunneling microscopy.

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Fourier transformation of atomically resolved STM topography of $(LaSe)_{1.14}(NbSe_2)$ revealed a surface modulation along the triangular crystal lattice of $NbSe_2$ layer, but with a two times larger period. We compare it to the modified charge density wave found on plain $NbSe_2$under strain.

Keywords: scanning tunneling microscopy, misfit layer compound, Lanthanum niobium selenides, electronic properties

1. Introduction

The layered transition metal dichalcogenides (TMD), TX2, where T is the early transition metal and X is S, Se or Te, are remarkable compounds due to their fascinating physical properties. They can accommodate various physical phenomena, such as the charge density waves (CDWs) and superconductivity [1–3]. Though TMDs with 1T structure could be superconducting only by doping or external pressure [4,5],TMD materials with 2H structure, *e.g.* 2H-$NbSe_2$, exhibit intrinsic superconductivity [6,7]. Their two-dimensional structure is an important feature giving rise to *e.g.* Ising or topological superconductivity [8,9].

Transition-metal dichalcogenides (TMDs) are the promising candidates for tuning their properties by inducing strain. They can withstand up to 10 % of in-plane strain before breaking, thus providing enough space for engineering new strain induced properties [10]. Charge density wave (CDW) is one of the emergent states occurring in TMDs [10] often accompanied by other, possibly competing phases.

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In the case of 2H-$NbSe_2$ superconductivity (T_c = 7.2 K) meets triangular (3Q) charge density wave phase (T_{CDW} = 33 K) [2]. Exact mechanisms driving the choice of particular CDW wavevector remains unanswered even though various mechanisms have been proposed [11–16].

Small strain-induced changes in the electronic band structure and phonon dispersion can lead to dramatic change in CDW wavevector and geometry [17]. Single crystal attached to the silica plate at room temperature can be stretched while cooling down to 4 K because of mismatch between their thermal expansion coefficients. Shang Gao et al. induced strain in 2H-$NbSe_2$ via this method and observed change of CDW period. In addition to the well-known CDW ordering of ~ $3a_0$ period (below 33 K), where a_0 is the triangular $NbSe_2$ lattice constant, they observed two additional CDW phases, unidirectional "stripe" (1Q) CDW ordering with $4a_0$ period and a triangular (3Q) ordering with $2a_0$ period. The wavevectors of all observed CDWs were found to be oriented along Γ-M direction. Presence of various CDW phases in different regions of sample was attributed to inhomogeneous strain [17].

Misfit compounds are based on alternating hexagonal TMDs and square MX lattice, where M can be for example Sn, Pb or La. They have peculiar structure arising from stacking layers with different lattice types. Lattice mismatch results in variety of physical properties misfit compounds can have. There are misfit materials in which we can observe superconductivity and CDWs. The single-crystalline misfit compound $(LaSe)_{1.14}(NbSe_2)$ has been successfully synthesized in the 90s [18]. It is possible to grow very good superconductive (T_c = 1.2K) single crystals with RRR close to 6. It is expected that vertically stacked TMDs are strongly affected by strain [19,20].

Here we report the observation of surface modulation on $(LaSe)_{1.14}(NbSe_2)$with period ~ $2a_0$, commensurate with the crystal lattice. This observation correlates to the strain induced change of CDW order parameter in pure $NbSe_2$.

2. Preparation of experiment

Scanning tunneling microscopy (STM) experiments were carried out by means of the Specs JT STM system operated in ultra-high vacuum (10^{-10} mbar). Atomically sharp Au STM tips were formed *ex situ* by electrochemical etching followed by Ar^+ sputtering and annealing *in situ*.

$(LaSe)_{1.14}(NbSe_2)$ samples have layered structure with weak iono-covalent bonds between layers, which enables easy cleaving procedure. The sample was glued to a molybdenum sample holder, conductively connected by silver paste. We glued a thin metal stripe to the top layer of the sample. By removing the metal stripe *in situ* prior to the STM experiment, we exfoliated the upper layers, thus

achieving an atomically flat surface without contaminations. Moreover, during the cleavage, the sample was placed on the liquid nitrogen shield of the refrigerator. This way we were able to obtain larger atomically flat terraces compared to the cleaving procedure at room temperature.

Surface topography was acquired in the constant current mode with the set point current I_{set} = 50 pA. Bias voltage V_{bias}= 100 mV was applied to the sample while the tip was grounded. Both the STM head and sample were kept at 1.2 K.

3. Results

Although it is not clear in advance which of the two planes will terminate the surface of the $(LaSe)_{1.14}(NbSe_2)$ monocrystal after cleavage, STM topography (Fig. 1 left) reveals a triangular lattice. LaSe layer has square crystal structure; therefore, we assume that the surface is terminated by the $NbSe_2$ layer. In addition to the triangular lattice of individually resolved Nb atoms characteristic for the $NbSe_2$ surface, the topography reveals a plethora of elevated or depressed areas. To facilitate the analysis of these intricate patterns, we employed the two-dimensional Fourier transform (FT). The evident six atomic Bragg peaks of the FT, marked by the green circles in figure 1b, correspond to the triangular $NbSe_2$ lattice with period a_0. Notably, another distinct feature appears halfway along two of the three Bragg vectors, *i.e.* along the Γ- M directions. This surface modulation with period ~ $2a_0$, marked by white circles in Fig. 1b, is strongly reminiscent of the triangular (3Q) CDW ordering with $2a_0$ period observed by Gao et al. on $NbSe_2$ under strain [17].

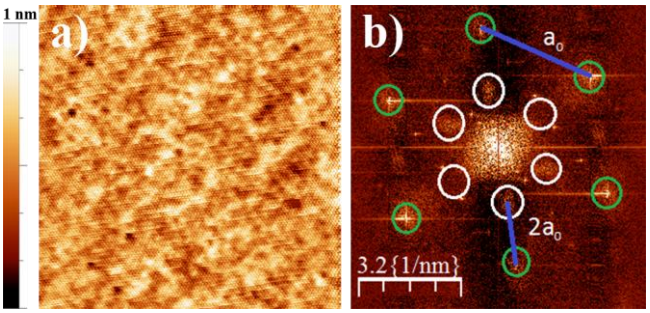

Fig. 1: a) STM topography image (32 x 32 nm^2), color corresponds to the height according to the colorbar on the left. b) Fourier transform of the topography. Bragg peaks in green circles have lattice constant a_0, areas representing period ~ $2a_0$ are marked by white circles.

To better illustrate this surface modulation, we extracted the relevant FT peaks, namely the Bragg peaks and the peaks corresponding to the $2a_0$ modulation in one direction (Fig. 2a). Fig. 2b, a zoom of the inverse FT of Fig. 2a, reveals this one particular surface modulation in real space, where every second

atomic row, *i.e.* $2a_0$ period, is elevated. Still, while Gao et al. observed this modulation along all thee Bragg vectors, in our case one pair of the FT peaks is missing. Possibly, the peaks in this direction are suppressed by the adjacent focused sharp peaks. Several of these sharp peaks, as well as a long-range modulation represented by a bright spot around Γ point, are also present. These probably represent the Moiré pattern induced by the misfit structure of the two distinct layers. However, this tentative explanation requires further analysis, which will be discussed elsewhere. Also, even though it is certain, that the misfit structure of the studied compound induces strain on the $NbSe_2$ layer, whether this strain is sufficient to alter the conventional CDW with $3a_0$ period, or if other effects are in play, remains for further study.

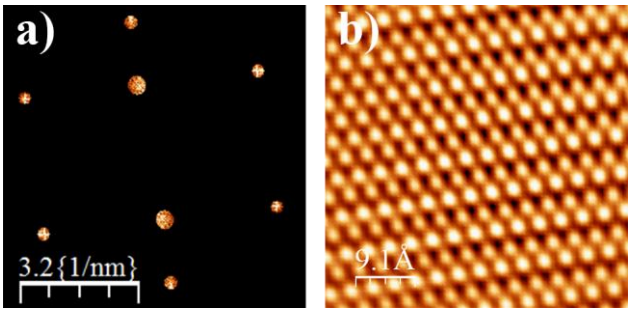

Fig. 2: a) Relevant parts of Fourier transform, *i.e.* main Braggs peaks and one pair of peaks with $2a_0$ period. b) Zoom of topography reconstructed from the FT showing only atomic lattice and the short range modulation with period ~ $2a_0$.

4. Conclusions

In conclusion, by analyzing the FT of the STM topography of $(LaSe)_{1.14}(NbSe_2)$, we have observed a short-range modulation with a period ~ $2a_0$. This is reminiscent of the CDW in $NbSe_2$ under strain. [17] Indeed, the LaSe layer in our studied compound induces strain on the $NbSe_2$ layer due to incommensurability of their respective 2D crystal lattices. However, whether this strain is big enough to induce such change in the periodicity of the CDW, or a different unheeded effect is in play, remains for further investigations. A theoretical model of the $(LaSe)_{1.14}(NbSe_2)$ system that could shed more light on the unresolved issues is currently being developed.

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