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Periodic Surface Modulation of $(LaSe)_{1.14}(NbSe_2)$ Observed by Scanning Tunneling Microscopy

O. Šofranko[a,*], R. Leriche[b], A.P. Morales[b], T. Cren[b], S. Sasaki[c], L. Cario[c], P. Szabo[a], P. Samuely[a] and T. Samuely[a]

[a]Centre of Low Temperature Physics, Institute of Experimental Physics SAS, P.J. Šafárik University, 040 01 Košice, Slovakia

[b]Sorbonne Université, CNRS, Institut des Nanosciences de Paris, UMR7588, F-75252 Paris, France

[c]Institut des Matériaux Jean Rouxel (IMN), Université de Nantes, CNRS, 2 rue de la Houssinière, BP 32229, 44322 Nantes Cedex 3, France

Fourier transformation of atomically resolved STM topography of $(LaSe)_{1.14}(NbSe_2)$ revealed a surface modulation along the hexagonal surface 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.

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1. Introduction

The layered transition metal dichalcogenides (TMD), TX_2, 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 state occurring in TMDs [10], often accompanied by other (possibly) competing phases.

It is worth noting that 2H-$NbSe_2$ superconductivity ($T_c = 7.2$ K) meets triangular (3Q) charge density wave phase ($T_{\mathrm{CDW}} = 33$ 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 at room temperature to the silica plate can be stretched when cooling down to 4 K. This is due to the mismatch between the 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 $\sim 3a_0$ period (below 33 K), where a_0 is the triangular $NbSe_2$ lattice constant, the two more CDW phases were observed, i.e., 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 ($T_c = 1.2$ K) single crystals with residual-resistance-ratio of RRR~ 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 $\sim 2a_0$, 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

*corresponding author; e-mail: sofranko@saske.sk

sharp Au STM tips were formed *ex situ* by electrochemical etching followed by Ar^+ sputtering and annealing *in situ*.

Samples were prepared by S. Sasaki and L. Cario at the Institut des Matériaux Jean Rouxel performing the procedure described in [18] but changing the stoichiometric ratio of elements La:Nb:Se to 1.14:1:3.14. This resulted in the synthesis of the $(LaSe)_{1.14}(NbSe_2)$ compound. Lattice parameters of both LaSe and $NbSe_2$ layers are identical with the ones described in [18]. $(LaSe)_{1.14}(NbSe_2)$ samples have a layered structure with weak iono-covalent bonds between the LaSe and $NbSe_2$ misfit layers, featuring a square and a hexagonal two-dimensional lattice, respectively [18]. This 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 $I_{\text{set}} = 50$ pA. Bias voltage $V_{\text{bias}} = 100$ 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 $(LaSe)_{1.14}(NbSe_2)$ single crystal after cleavage, atomically resolved STM topography (Fig. 1a) reveals a hexagonal surface lattice. LaSe layer has a square lattice [18]. Therefore, we assume that the surface is terminated by the $NbSe_2$ layer. In addition to the hexagonal lattice of individually resolved Se 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 six peaks of the FT marked by green circles in Fig. 1b correspond to the reciprocal hexagonal $NbSe_2$ lattice with period a_0. Notably, another distinct feature appears halfway along the Γ- M directions. This surface modulation with period $\sim 2a_0$, marked by white circles in Fig. 1b, is strongly reminiscent of the triangular (3Q) CDW ordering with $2a_0$ period, that was observed by Gao et al. on $NbSe_2$ under strain [17].

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

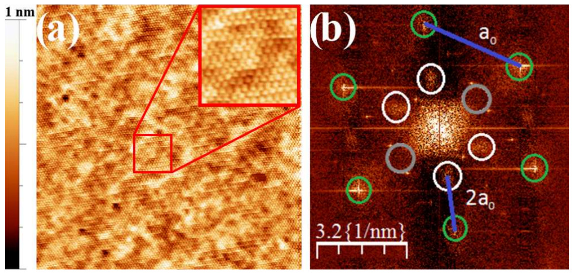

Fig. 1. (a) STM topography image (32×32 nm^2), color corresponds to the height according to the color bar on the left. A zoom outlined in red reveals individual atoms in a 4×4 nm^2 area. (b) Fourier transform of the topography. The peaks in green circles have lattice constant a_0, areas representing period $\sim 2a_0$ are marked by white and gray circles.

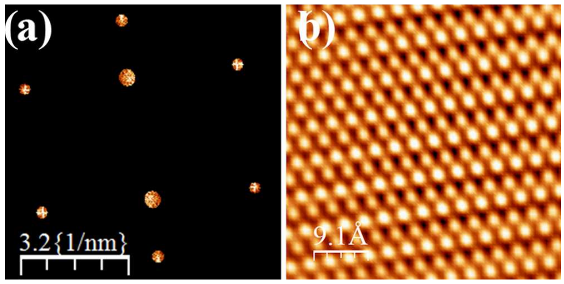

Fig. 2. (a) Relevant parts of Fourier transform, i.e., hexagonal atomic lattice peaks and one pair of peaks with $2a_0$ periodicity. (b) Zoom of topography reconstructed from the FT showing only atomic lattice and the short-range modulation with period $\sim 2a_0$.

second atomic row, i.e., $2a_0$ period, is elevated. Still, compared to the observations of Gao et al. in our case one pair of the FT peaks is missing. The expected position of these missing peaks is denoted by gray circles in Fig. 1b. Their absence in the FT image is possibly due to the reduced contrast caused by the adjacent focused sharp peaks. Several of these very sharp and pronounced peaks, as well as a long-range modulation represented by a bright spot around Γ point, are also present. They show some kind of the Moiré pattern induced by the misfit structure of the two distinct layers. The very strong signal of these modulations might in turn suppress the signal of the anticipated pair of FT peaks at $2a_0$ period in this specific direction. 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, this remains for further study.

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 $\sim 2a_0$. 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, this 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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