Quantifying Structural (Dis)order in Misfit Layer Compounds with Scanning Transmission Electron Microscopy

Hanna Z. Porter, Department of Chemistry, Harvey Mudd College

2021 Platform for the Accelerated Realization, Analysis, and Discovery of Interface Materials Research Experience for Undergraduates Program at Cornell University (PARADIM REU @ Cornell)

PARADIM REU Mentor: Berit H. Goodge, School of Applied and Engineering Physics, Cornell University

PARADIM REU Principal Investigator: Lena F. Kourkoutis, School of Applied and Engineering Physics, Cornell University

Primary Source of PARADIM REU @ Cornell Funding: Support for PARADIM is provided under NSF Grant # DMR-2039380 as part of the Materials Innovation Platform Program

Contact: hporter@hmc.edu, bhg37@cornell.edu, lena.f.kourkoutis@cornell.edu Website: www.paradim.org/reu/cornell

Abstract

Some single-layer transition metal dichalcogenides (TMDs) have been found to superconduct at critical temperatures below 10 K.¹ Vertically stacked heterostructures consisting of alternating TMD (MX₂) and rock salt (MX) layers offer a way to synthesize clean TMD layers at large length scales and tune additional parameters to enhance the superconductivity of the TMD layers. These misfit compounds can be generally described with the chemical formula (RX)_{1+ δ}(MX₂)_n where R is a heavy cation, M is a transition metal, and X is a chalcogen. δ is the misfit parameter, a result of the differing symmetries of the layers causing the in-plane lattice vectors of the two layers to be incommensurate. Here, scanning transmission electron microscopy (STEM) was used to probe the structural disorder of three misfit compounds, (GdS)_{1+ δ}(NbS₂), (BiSe)_{1+ δ}(NbSe₂), and (LaSe)_{1+ δ}(NbSe₂)₂, at the atomic scale. In particular, a computational framework for the identification and quantification of in- and out-of-plane distortions was developed. Meso-scale, coherent out-of-plane distortions were found in all three misfit compounds.

Introduction

Some single-layer transition metal dichalcogenides (TMDs), such as NbS₂, have been found to superconduct at critical temperatures below 10 K.¹ Vertically stacked heterostructures consisting of alternating TMD (MX₂) and rock salt (RX) layers offer a way to synthesize clean TMD layers at large length scales and tune additional parameters to enhance the superconductivity of the TMD layers.

These misfit compounds can be generally described by the chemical formula $(RX)_{1+\delta}(MX_2)_n$ where R is a heavy cation such as Bi, La, or Gd, M is a transition metal such as Nb, and X is a chalcogen. δ is the misfit parameter, a result of the differing symmetries of the layers causing the in-plane lattice vectors of the two layers to be incommensurate.² This incommensurability has made the study and modeling of these compounds difficult.^{3,4}

Scanning transmission electron microscopy (STEM) is a powerful tool for probing the structure of materials at the atomic scale. By investigating the structure of the misfit compounds through STEM, we can better inform computational models for these compounds and gain insight into their exotic properties, such as superconductivity. In this project, the primary research objective was to understand and quantify the differing structural responses of the misfit compounds and the distinct manner in which each compound accommodates the misfit in lattice parameters between the two layers.

Methods

Three misfit compounds, $(GdS)_{1+\delta}(NbS_2)$, $(BiSe)_{1+\delta}$

(NbSe₂), and (LaSe)_{1+ δ}(NbSe₂)₂, were imaged on a Thermo Fisher Scientific Spectra 300 X-CFEG STEM operating at 300 kV in the high-angle annular dark-field (HAADF) collection geometry. By scanning a focused beam of

electrons across the sample and collecting scattered electrons in the HAADF detector at each scan position, an atomic resolution image of the misfit compounds can be obtained. Because heavier nuclei scatter electrons to higher angles, using a HAADF collection geometry ensures that intensity in the HAADF-STEM images scales with atomic number.

To investigate the structural responses of the misfit compounds, an analytical framework was developed to characterize the out-of-plane and in-plane distortions of these compounds using the acquired images. As shown in Figure 1, in-plane distortions are contractions and expansions of atomic spacings along atomic rows, and outof-plane distortions are displacements of atoms from the atomic rows.



Figure 1: Visualization of out-of-plane and in-plane distortions.

In order to quantify these distortions, first, the positions of real atomic columns were identified in the HAADF-STEM images. Using these positions, horizontal atomic planes were identified, and a line of best fit through each plane was calculated. This line defined the reference plane from which out-of-plane atomic distortions can be mapped (see Fig. 1a). Next, line profiles were taken along each line of best fit, and a sinusoid was fitted to these line profiles. The x positions of the peaks in the sinusoid were projected onto the line of best fit corresponding to the line profile to which the sinusoid was fitted. The x and y positions generated by this fitting of a sinusoid to line profiles along atomic rows comprise an ideal lattice of atoms where the atoms are equally spaced along straight lines.

Vectors can be drawn between the real and idealized atoms, in which the x-component corresponds to the in-plane distortions and the y-component corresponds to the out-ofplane distortions. Thus, these vectors, as well as their x and y components, can be plotted to visualize the out-of-plane and in-plane distortions of the misfit compounds.

Results and Discussion

Shown below is a HAADF-STEM image of the $(GdS)_{1+\delta}(NbS_2)$ compound as well as a map of vectors between the real and ideal atom positions.



Because it is difficult to discern patterns in the distortions from the vector map, the two components are plotted separately in Figure 3, along with coarse-grained and blurred versions of the plots to better visualize large scale patterns in the distortions.



Figure 3: Plot of in-plane distortions (left) and out-of-plane distortions (right).

The above figure shows the meso-scale, coherent out-ofplane distortions observed in the GdS compound. Although the constituent layers of the misfit compounds are held together by relatively weak van der Waals forces, they are observed to distort coherently and over long length scales (tens of nm) in the out-of-plane direction.

Similar large-scale, coherent out-of-plane distortions were found in the $(BiSe)_{1+\delta}(NbSe_2)$, and $(LaSe)_{1+\delta}(NbSe_2)_2$ compounds. The patterns of in-plane distortions appear to

be less consistent when comparing the compounds, and seem to occur at smaller length scales.



Figure 3: Out-of-plane distortions in $(GdS)_{1+\delta}(NbS_2)$ (left), (BiSe)_{1+\delta}(NbSe_2) (middle), (LaSe)_{1+\delta}(NbSe_2)_2 (right).

Conclusions and Future Work

During this project, a framework was developed to analyze in-plane and out-of-plane distortions in misfit layered compounds. Preliminary analysis of the misfit compounds using this framework revealed meso-scale, coherent, outof-plane distortions in the three misfit compounds investigated. Continued analysis of the structural disorder of the misfit compounds may inform computational models of the compounds and shed light on their superconductivity.

Further work on this project will include refinement and validation to the approach for quantifying in-plane distortions. Analysis of additional data using the developed framework is also required to identify patterns and differences in the out-of-plane and in-plane distortions in the compounds, as well as to probe the length scales of in-phase out-of-plane distortions. Finally, the framework could be further developed to examine additional structural characteristics of the misfit compounds beyond in-plane and out-of-plane distortions.

Acknowledgments

I would like to thank my mentor, Berit Goodge, Dr. Lena Kourkoutis, and the entire Kourkoutis Group for their encouragement and guidance throughout this project. This work was supported by the National Science Foundation (Platform for the Accelerated Realization, Analysis, and Discovery of Interface Materials (PARADIM)) under Cooperative Agreement No. DMR-2039380.

References

[1] E. Revolinsky, E. P. Lautenschlager, C. H. Armitage. Layer structure superconductor. *Solid State Commun.* **1**, 59–61 (1963)

[2] A. Devarakonda, H. Inoue, S. Fang, C. Ozsoy-Keskinbora, T. Suzuki, M. Kriener, L. Fu, E. Kaxiras, D.C. Bell, J.G. Checkelsky. Clean 2D superconductivity in a bulk van der Waals superlattice. *Science* **370**, 231 (2020)

[3] G.A. Wiegers. Misfit Layer Compounds: Structures and Physical Properties. *Progress in Solid State Chemistry* 24, (1996).

[4] Just the Right (Mis)fit: Tuning Superconductivity in 2D Transition Metal Dichalcogenides through Interface Coupling in Bulk Heterostructures. Proposal to PARADIM.