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

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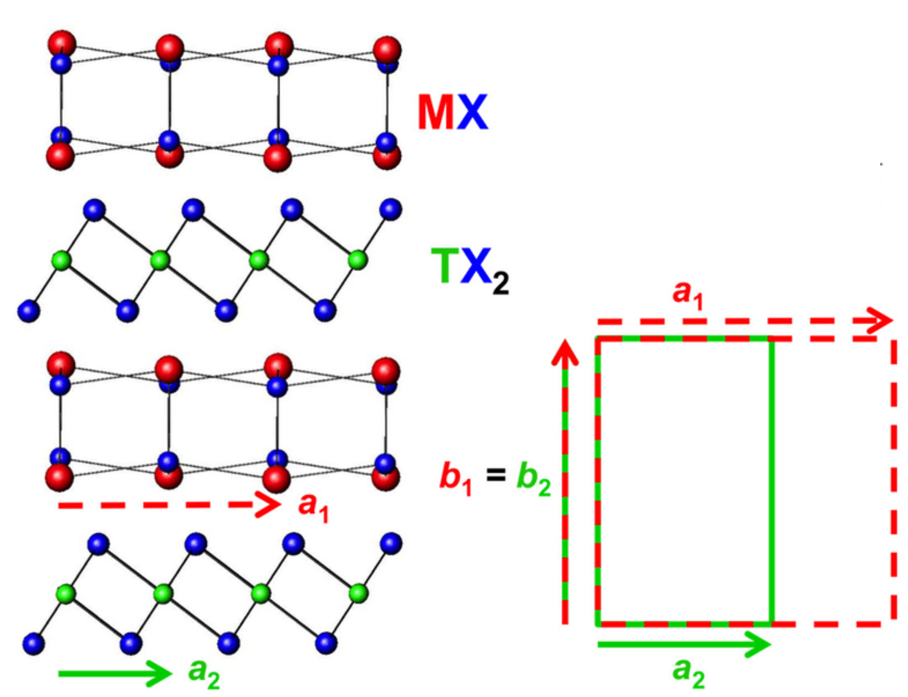
Misfit Layer Compounds

Some single-layer transition metal dichalcogenides (TMDs), such as $NbSe_2$, have been found to superconduct at critical temperatures below 10 K.[1] Vertically stacked heterostructures consisting of alternating TMD (TX_2) 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.[2]



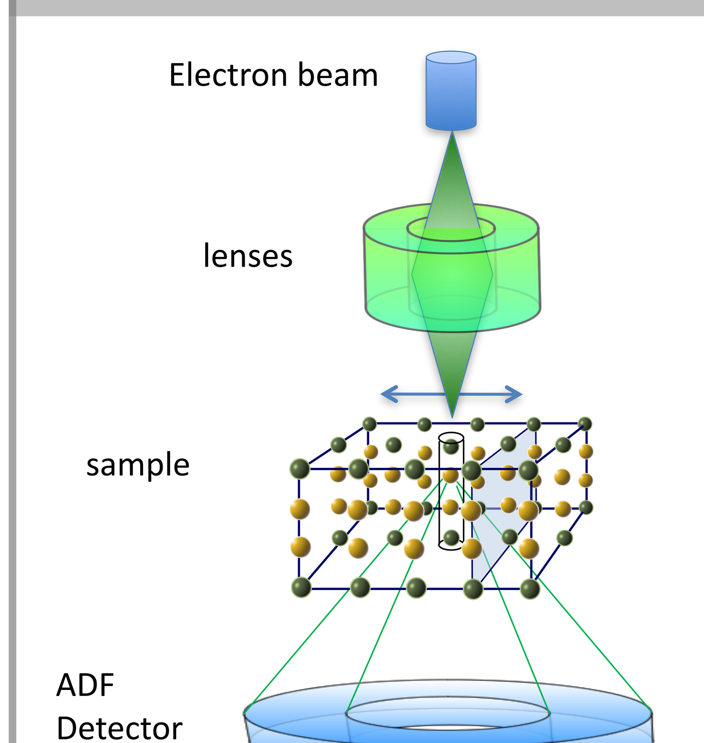
[3]

Layered misfit compounds: $(MX)_{1+\delta}(TX_2)_m$

- M = Rare Earths or Heavy Cations (Bi, Gd)
- X = Chalcogens (S, Se)
- T = Transition Metals (Nb)
- m = 1, 2
- δ = misfit parameter, a result of the differing symmetries of the layers causing the in-plane lattice vectors of the two layers to be incommensurate.[4]

The primary objective of this work was to understand and quantify the differing structural responses of three misfit compounds—$(GdS)_{1+\delta}(NbS_2)$, $(BiSe)_{1+\delta}(NbSe_2)$, and $(LaSe)_{1+\delta}(NbSe_2)_2$—and the distinct manner in which they accommodate the misfit in lattice parameters.

Scanning Transmission Electron Microscopy (STEM)

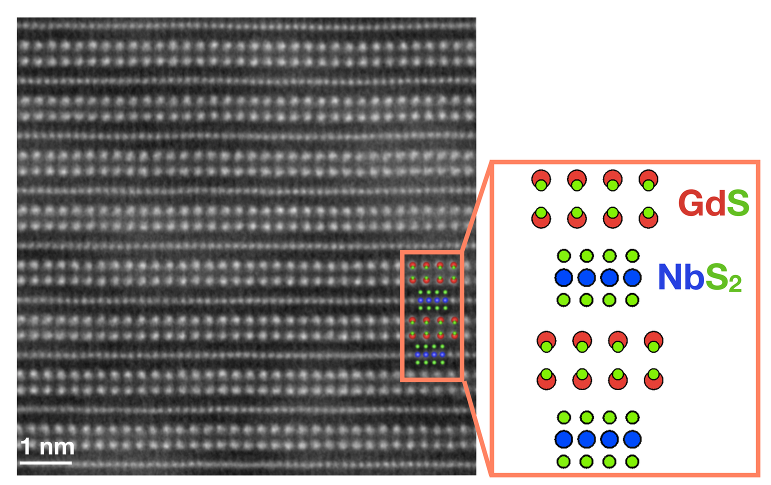


[5]

- sub-Å beam is scanned to obtain 2D images
- Direct, real-space images of materials at the atomic scale with atomic contrast

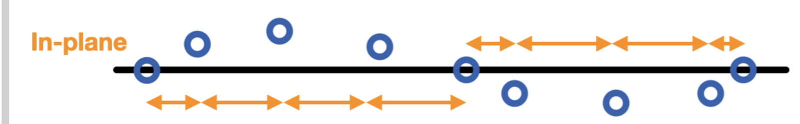
Methods

Data Acquisition

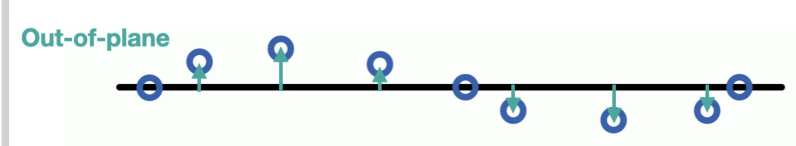


Three misfit compounds were imaged on a Thermo Fisher Scientific Spectra 300 X-CFEG STEM to probe in-plane and out-of-plane distortions.

Distortions of Interest



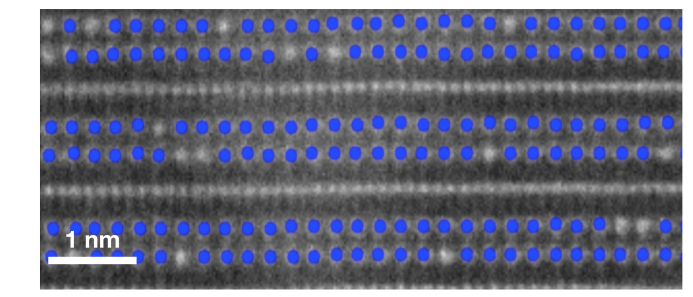
in-plane distortions are contractions and expansions of atomic spacings along atomic rows



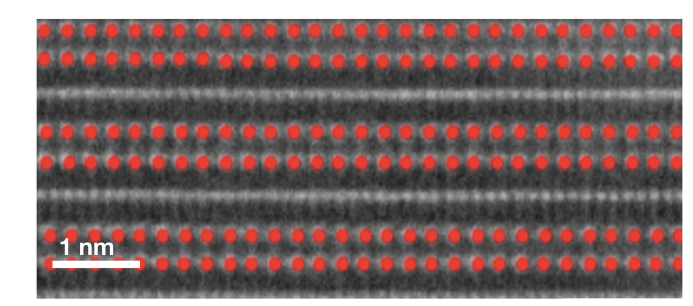
out-of-plane distortions are displacements of atoms from the atomic rows

Quantifying these picometer-scale structural distortions required the development of a careful analytical framework to define and create an appropriate reference.

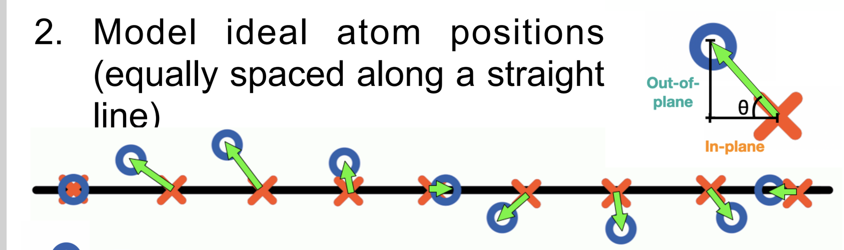
General Approach



1. Find atoms in HAADF-STEM images



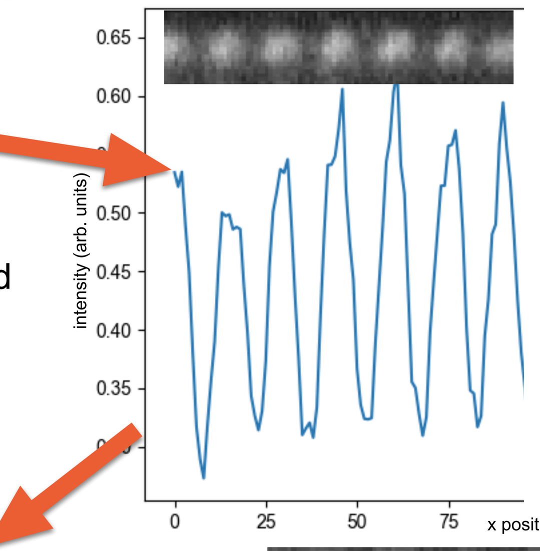
2. Model ideal atom positions (equally spaced along a straight line)



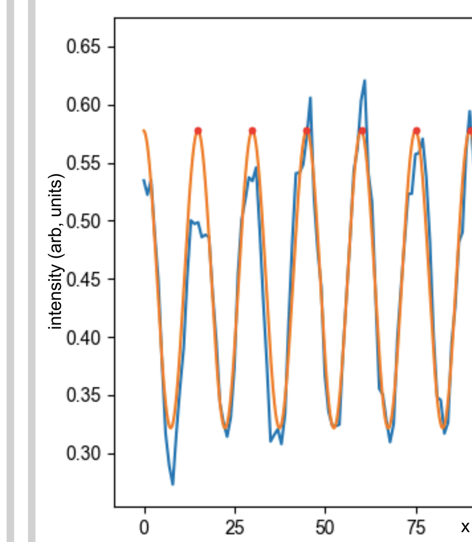
3. Compare real atom positions to ideal reference positions

Modeling Ideal Atom Positions

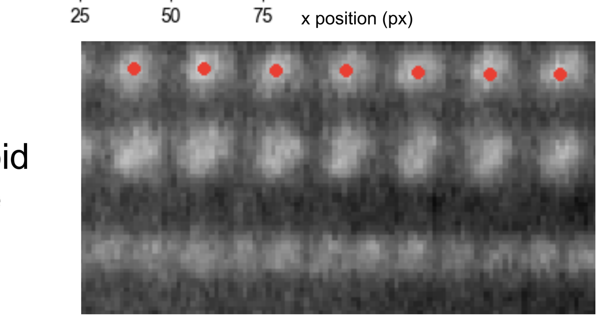
Separate atoms into rows and draw line of best fit through each row



Plot a line profile down each line of best fit

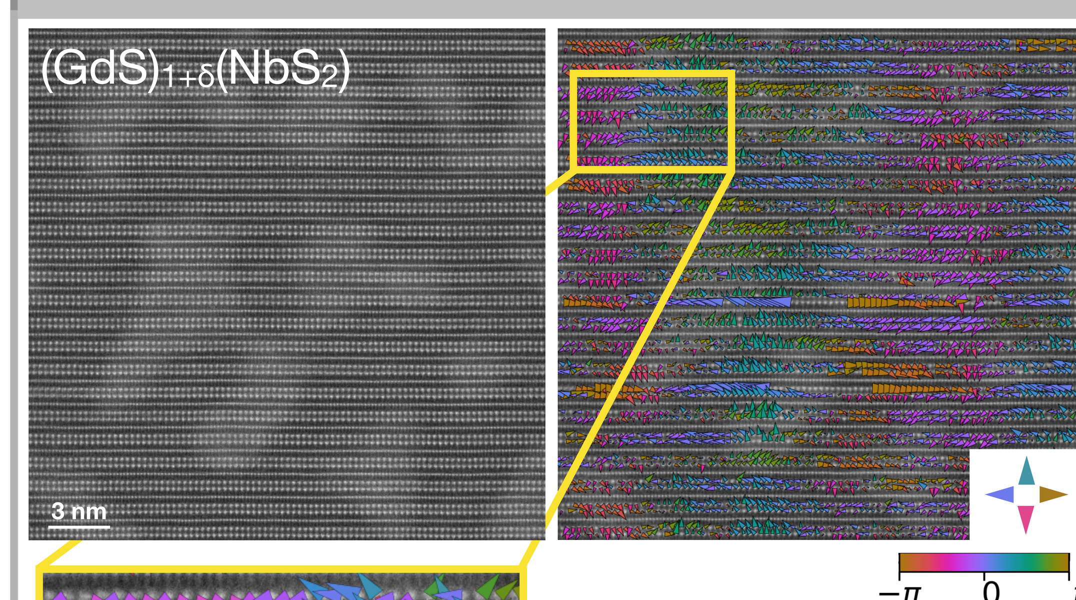


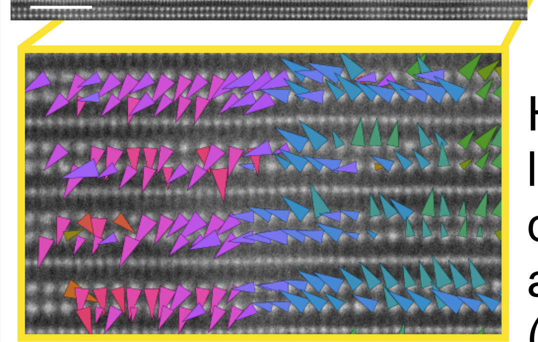
Fit a sinusoid to the line profiles



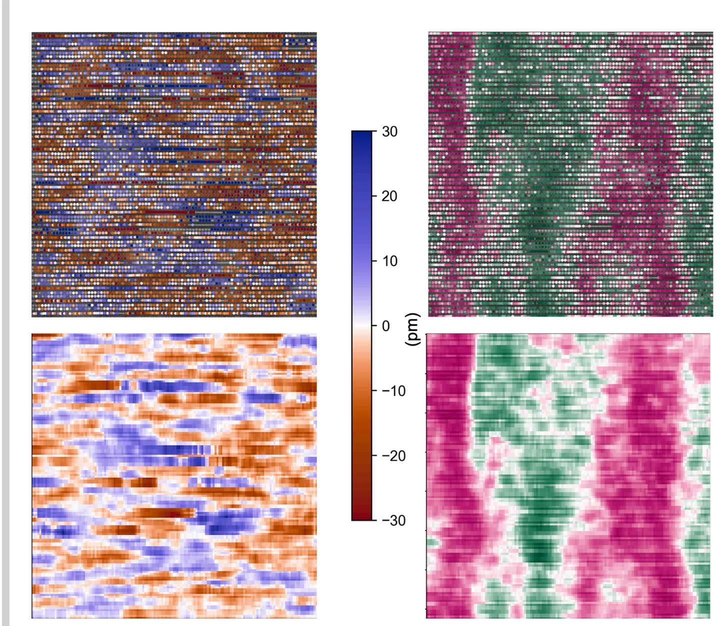
Project the x positions of the peaks of the sinusoid onto the line of best fit to get the *x*, *y* positions of the ideal atoms

Results

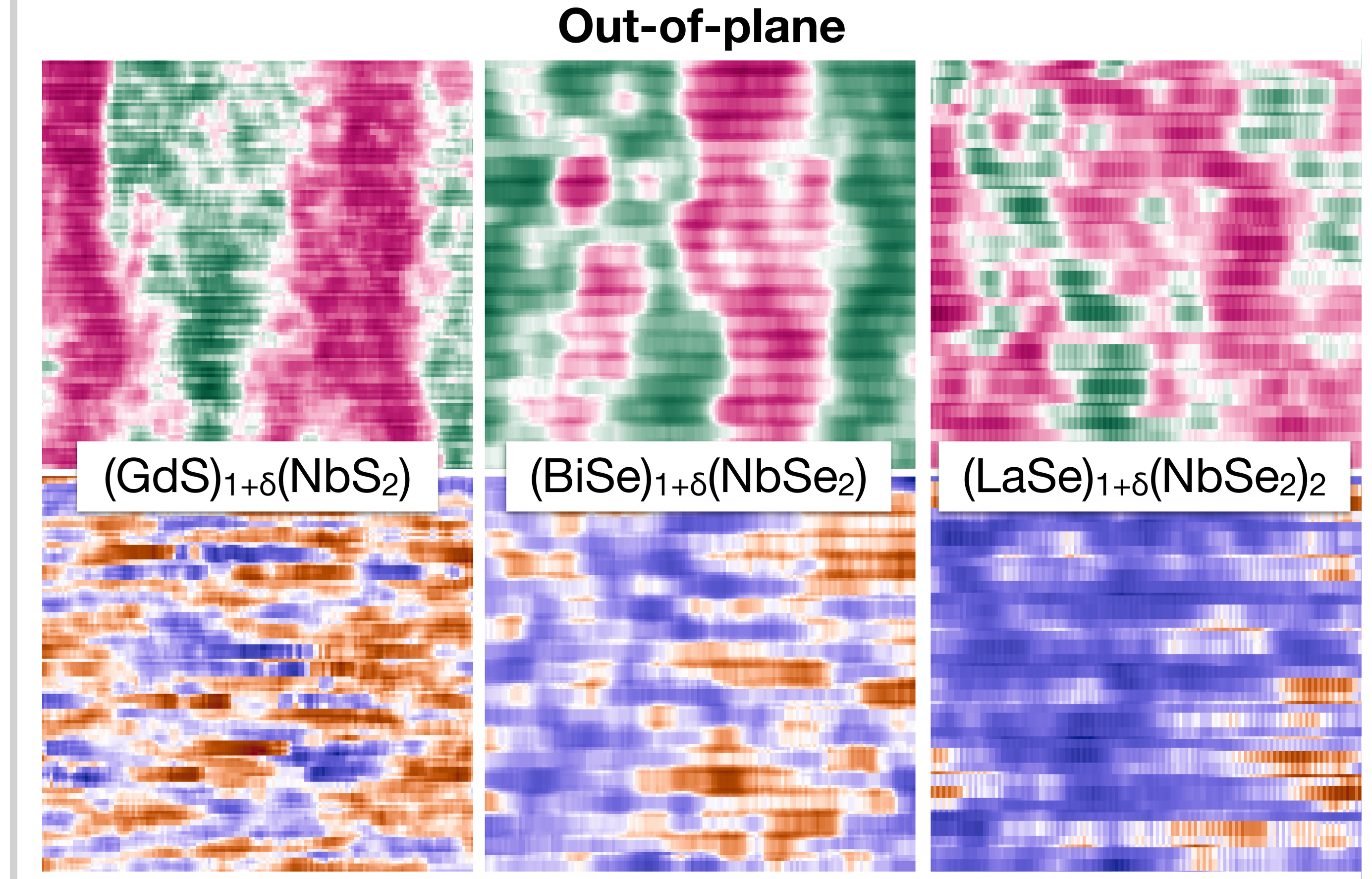




HAADF-STEM image (top left) and vector map of displacement between real and ideal atom positions (top right). A magnified section (bottom left) shows a transition region between two directions of out-of-plane distortions.



Meso-scale, out-of-plane distortions are observed in the GdS compound. Although the constituent layers of the misfit compounds are held together by relatively weak van der Waals forces, they distort coherently 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 Bi and La compounds. In contrast, the scale and frequency of coherent in-plane distortions differs between the compounds.

Conclusions

- Developed framework for analyzing in-plane and out-of-plane distortions in misfit layer compounds
- Meso-scale, coherent out-of-plane distortions in three misfit compounds
- Smaller scale, coherent in-plane distortions that are more differentiated among the compounds

Future Work

- Refine and validate approach to quantifying in-plane distortions
- Analyze additional data with the developed framework to probe length scales of in phase out-of-plane distortions and to discover patterns and differences between the different compounds
- Examine additional structural characteristics of misfit compounds

Acknowledgments

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References

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