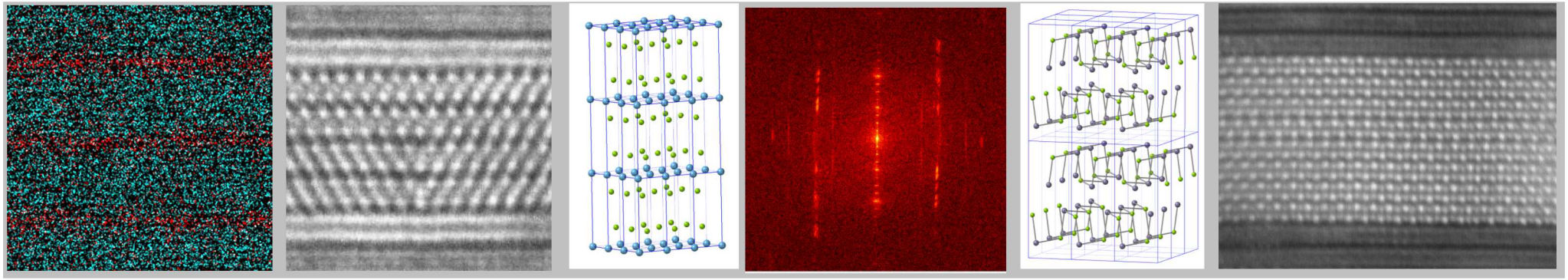
SAND2019-9365C

Exceptional service in the national interest

Sandia National Laboratories



Atomic Resolution Analysis of Defect Structures in Multilayer Chalcogenide Films

D.L. Medlin[1], R. Fischer[2], R. Gannon[2], D.M. Hamann[2], D.C. Johnson[2]

1. Sandia National Laboratories, 7011 East Avenue, MS 9161, Livermore, CA 94551 (USA).
2. Dept. of Chemistry, University of Oregon, Eugene, OR 97403 (USA).

dlmedli@sandia.gov

U.S. DEPARTMENT OF ENERGY

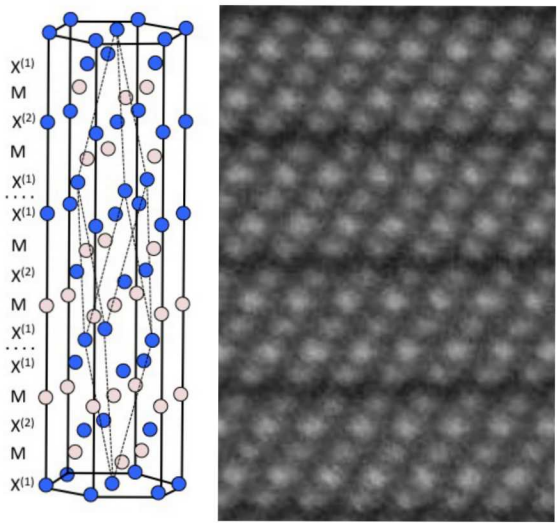
National Nuclear Security Administration

Sandia National Laboratories is a multimission laboratory managed and operated by National Technology & Engineering Solutions of Sandia, LLC, a wholly owned subsidiary of Honeywell International, Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525.

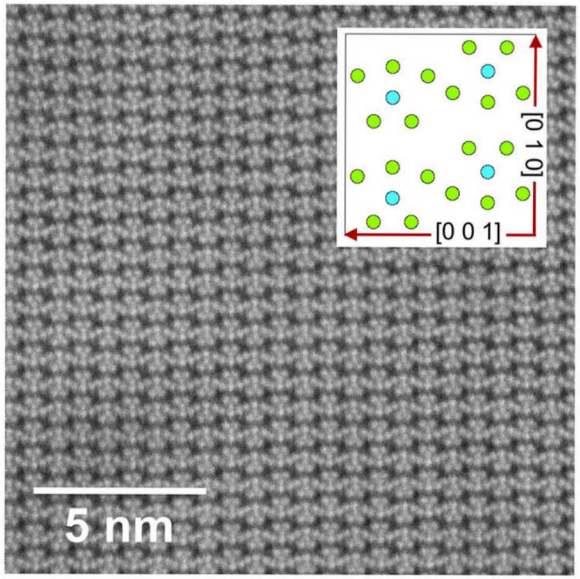
Layered Chalcogenides: Diversity of compositional and structural arrangements

Sandia National Laboratories

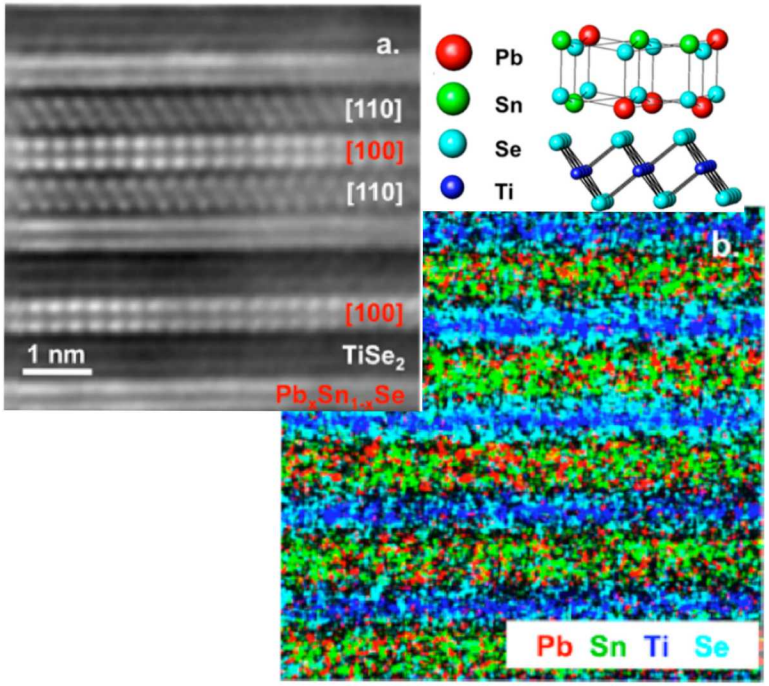
Example: Bi_2Te_3



Example: $ZrTe_5$



Example: $PbSnSe/TiSe_2$ Multi-layers



Anisotropic, layered structures contribute to useful and interesting thermal, electronic, optical properties,

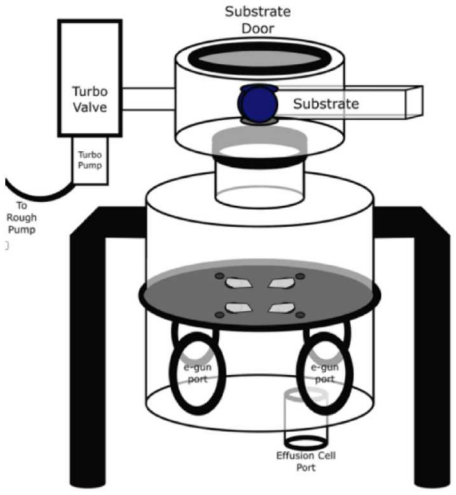
Thermoelectrics, Photothermoelectric Effect, Topological Insulators, Dirac Semimetals

The MER method: flexible approach for tailoring atomic-sequence of layered chalcogenides

Sandia National Laboratories

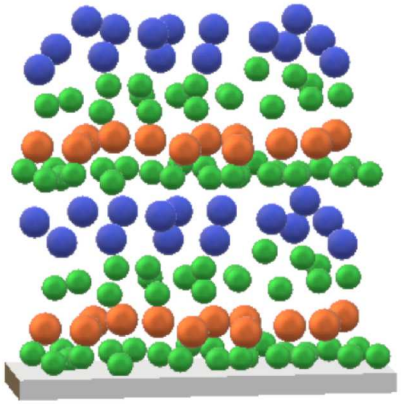
Modulated Elemental Reactants (MER) method:

- Precursor structure designed to mimic the final product
- Deposit a target number of atoms of each element per layer
- Gentle annealing to crystallize, typically 5 - 30 minutes at 250 – 450°C



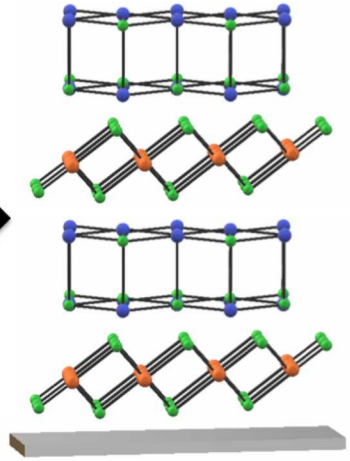
Sn
Ti
Se

Amorphous



Δ

Crystalline



In-plane rotational ("turbostratic") disorder

SiO_2/Si substrate (NOT epitaxial)

Focus for this talk: Crystallographic Defects in MER films

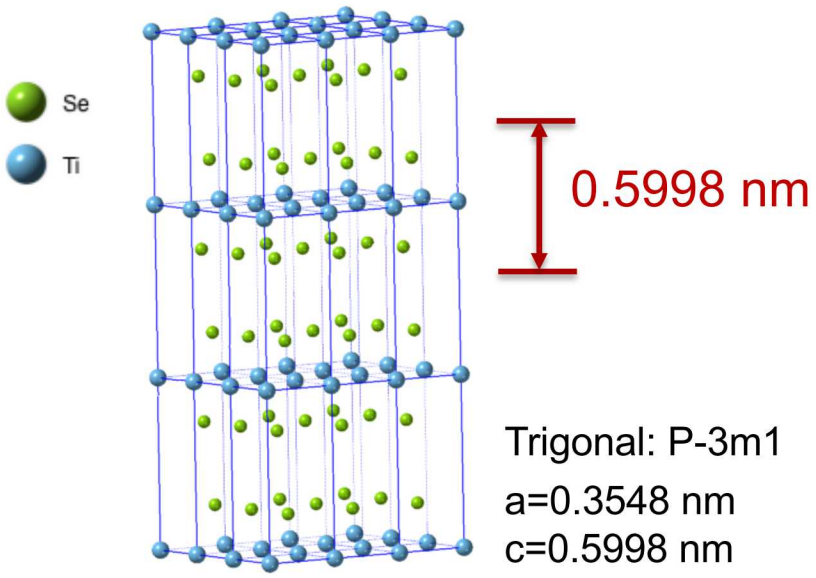
Atomic Stacking defects -- internal to layers

Layering Defects --Incomplete, missing layers

System: Multilayers of $TiSe_2$ & SnSe:

Sandia National Laboratories

$TiSe_2$



Trigonal: P-3m1

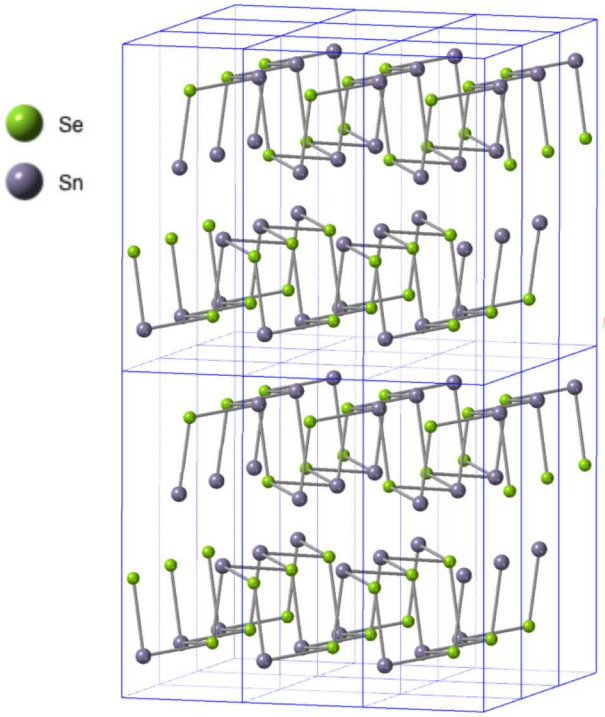
a=0.3548 nm

c=0.5998 nm

P. Erhlich, Angewandte Chemie (1948)

SnSe

Distortion from rocksalt structure



Orthorhombic: Pnma

a=1.14942 nm

b=0.4151 nm

c=0.4442 nm

M. Sist et al., Acta Cryst. B (2016)

Layer thicknesses are closely matched

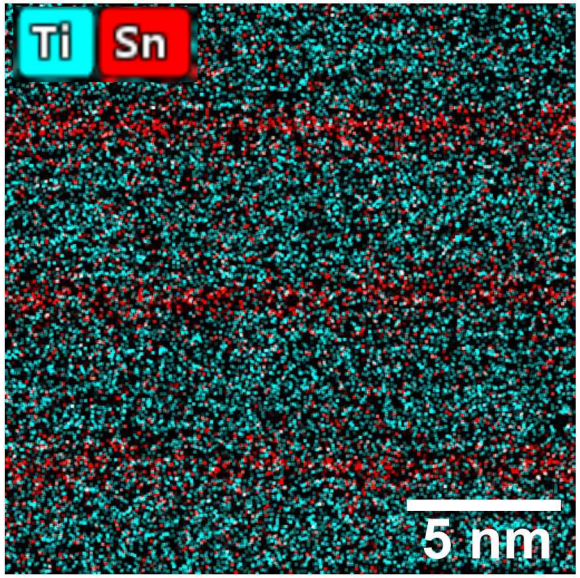
-Bulk: Phase transition to Cmcm ~810 K)

-Monolayers: rectangular unit cell,
2D space group: p2gg
(Hamann et al., Inorganic Chemistry, 2017)

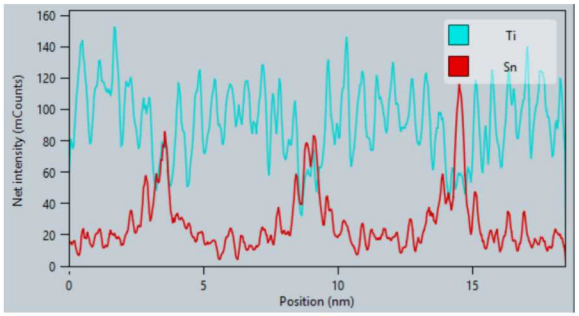
Example layered structure: 1 SnSe /8 $TiSe_2$

Sandia National Laboratories

EDS Spectrum Image

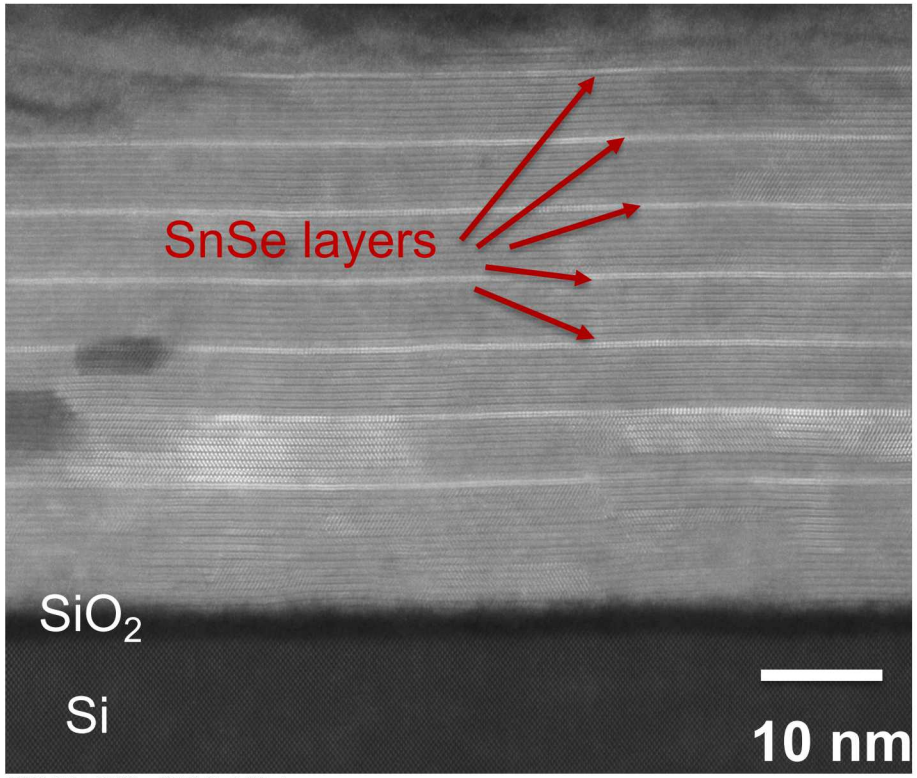


20180518_UO_Fischer/DH1-8/003)EDSmap_2p55mx/Si-EDS-HAADF 0908.emd,
net, postfilter 3 pix average

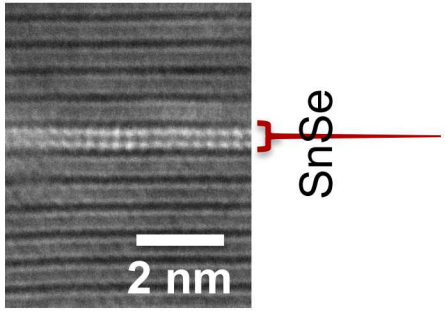


20180518_UO_Fischer/DH1-8/003)EDSmap_2p55mx/Si-EDS-HAADF 0908.emd,
net, prefiltering 3 pix average, postfilter 3 pix average

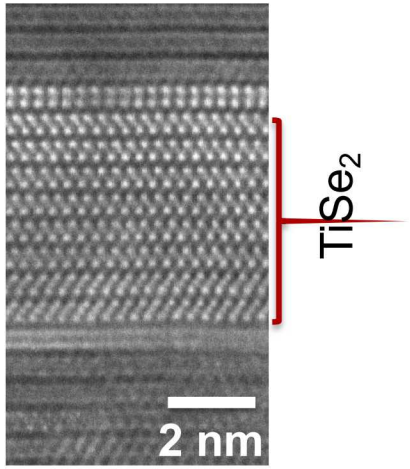
HAADF-STEM



20180518_UO_Fischer/DH1-8/002_area2/08.45.20_dfstem_fov73p81nm.jpg



08.48.48_dfstem_fov18p45nm.jpg

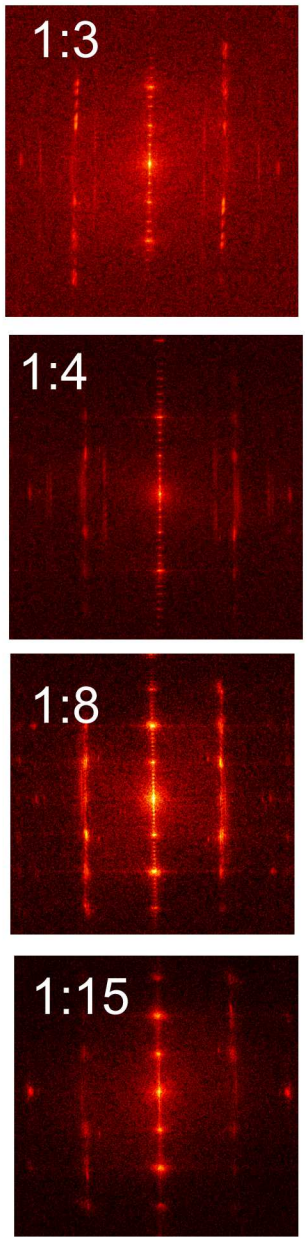


08.49.36_dfstem_fov18p45nm.jpg

Thermo Fisher Themis Z STEM, 300 keV

Layer Periodicities from FFTs of HR-STEM images

Sandia National Laboratories



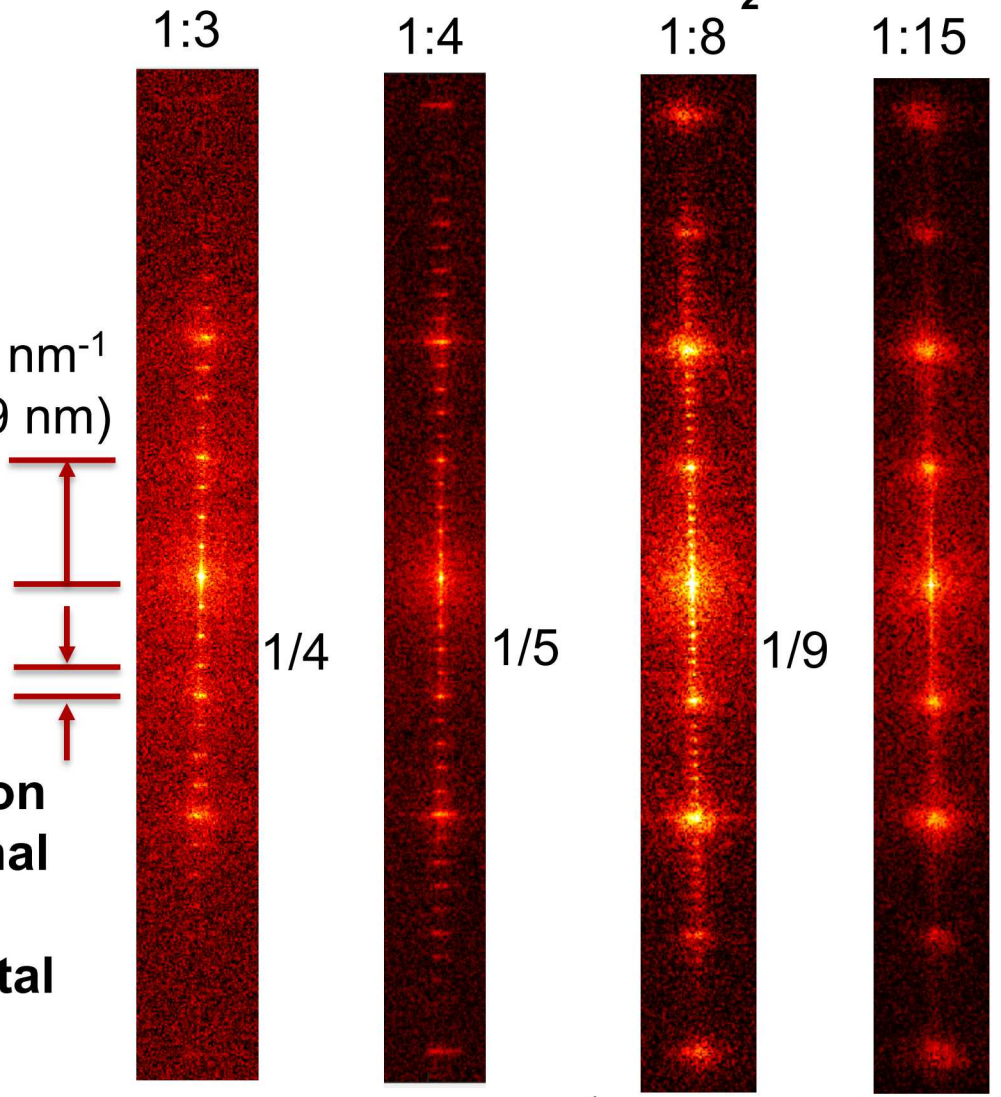
Fundamental Spatial Frequency:

Characteristic of individual $TiSe_2$ trilayers and SnSe bilayers, which have similar thickness

1.69 nm^{-1} (0.59 nm)

Low-frequency component depends on period of compositional modulation and sub-divides the fundamental spatial frequency:

n-SnSe : m-$TiSe_2$

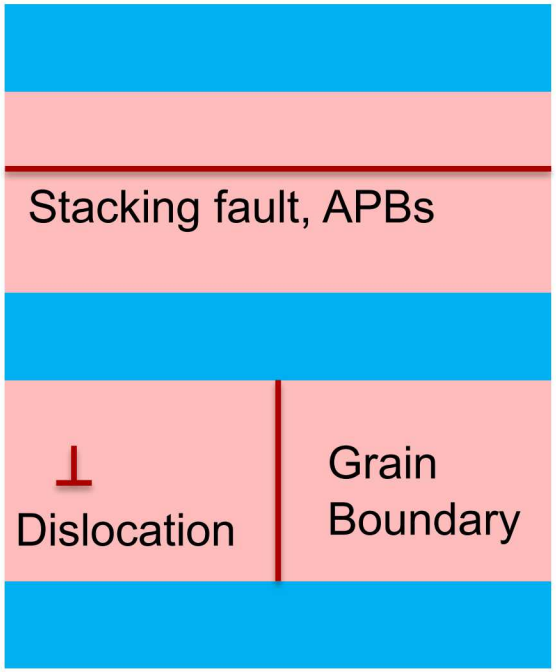


	1:3	1:4	1:8
Measured:	0.421 nm^{-1}	0.335 nm^{-1}	0.190 nm^{-1}
	2.38 nm	2.99 nm	5.26 nm
Expected:	2.37 nm	2.97 nm	5.37 nm

Defects: Broad Classifications

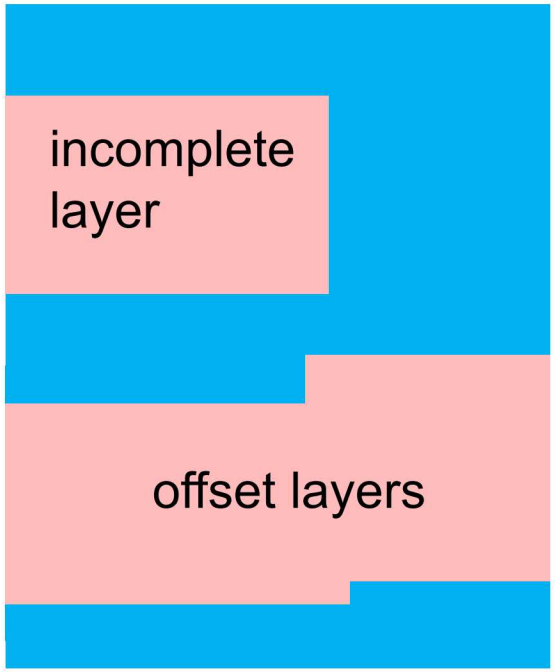
Sandia National Laboratories

Intralayer defects



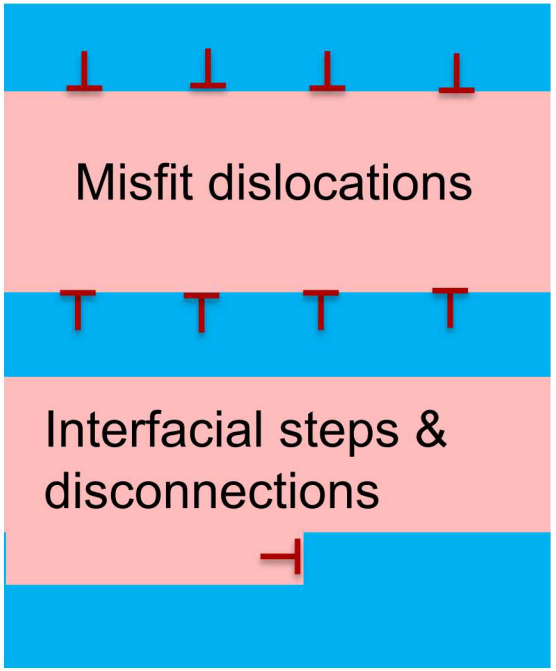
Crystalline defects within the confines of an individual layer

Interlayer defects



Morphological defects in the layer arrangements

Interfacial defects

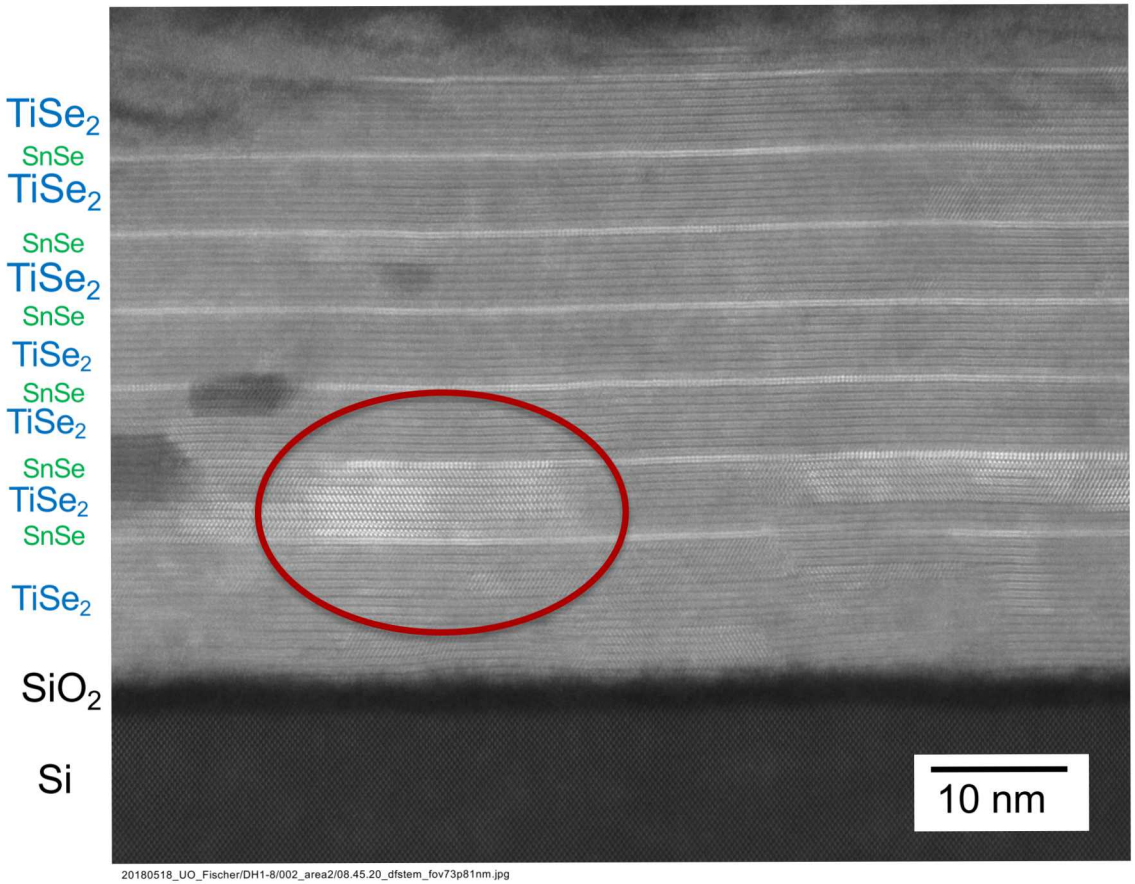


Crystalline defects at the interfaces between layers

Intralayer defects: GBs and twinning

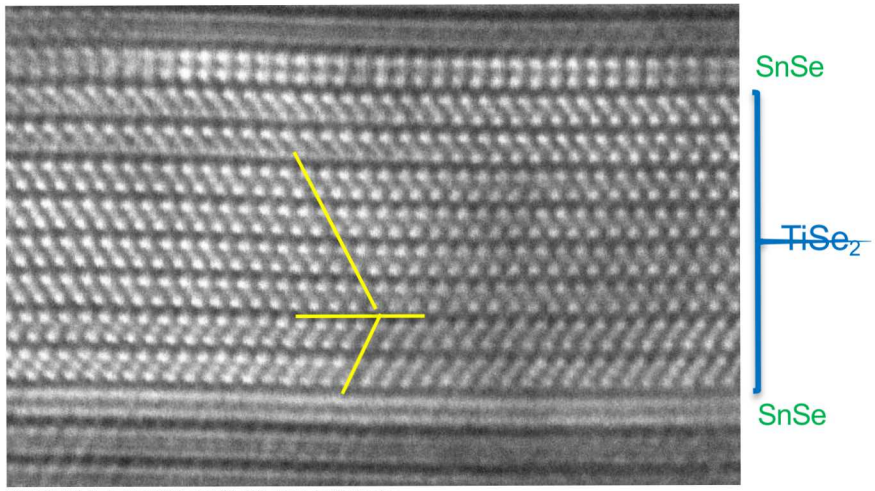
Sandia National Laboratories

1 SnSe : 8 $TiSe_2$

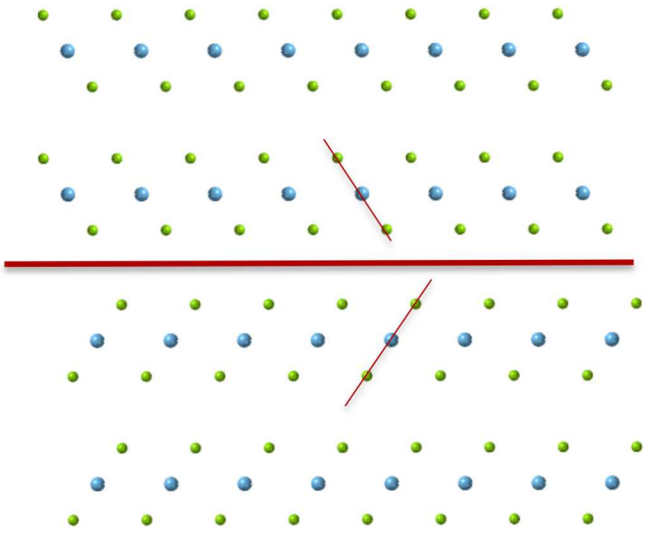


20180518_UO_Fischer/DH1-8/002_area2/08.45.20_dfstem_fov73p81nm.jpg

Twin boundary in $TiSe_2$ layer



20180518_UO_Fischer/DH1-8/002_area2/08.49.36_dfstem_fov18p45nm.jpg



[-2 1 1 0]

[2 -1 -1 0]

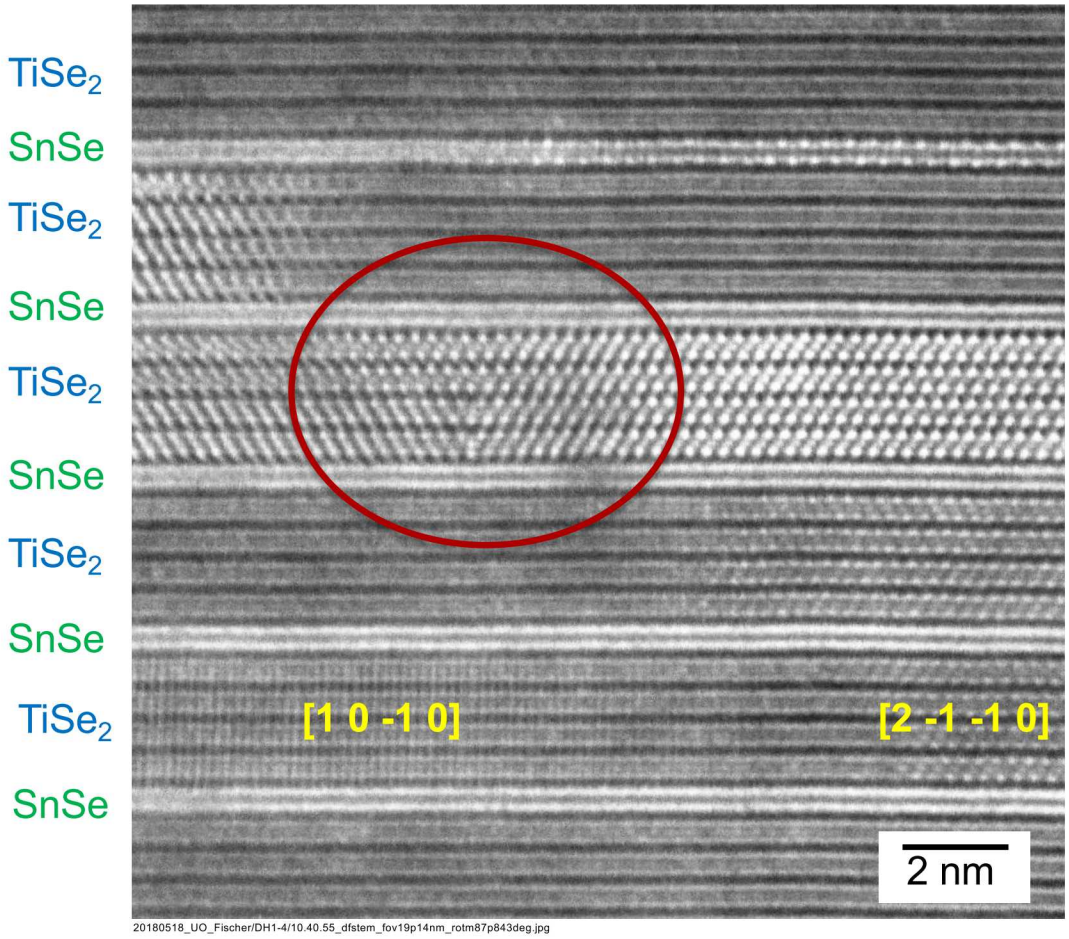
$TiSe_2$ has rhombohedral symmetry

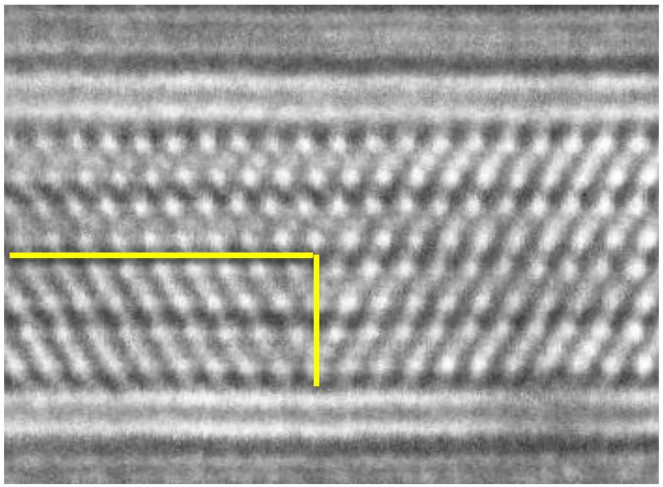
180° rotation about [0001] axis gives twin

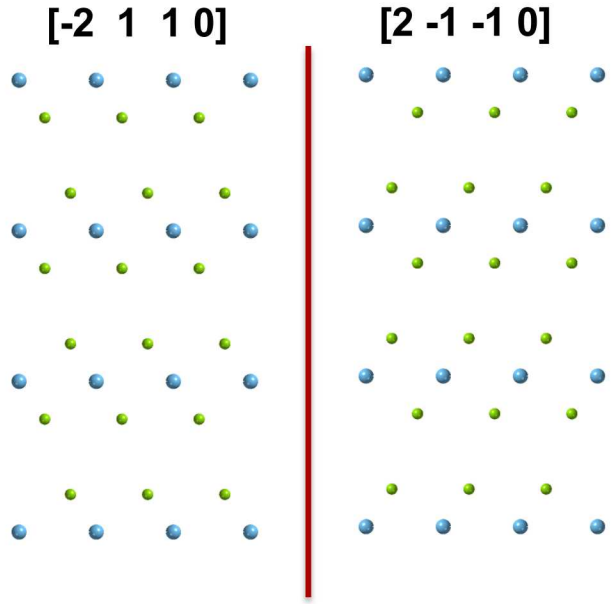
Termination of a twin within a $TiSe_2$ layer

Sandia National Laboratories

1 SnSe: 4 $TiSe_2$







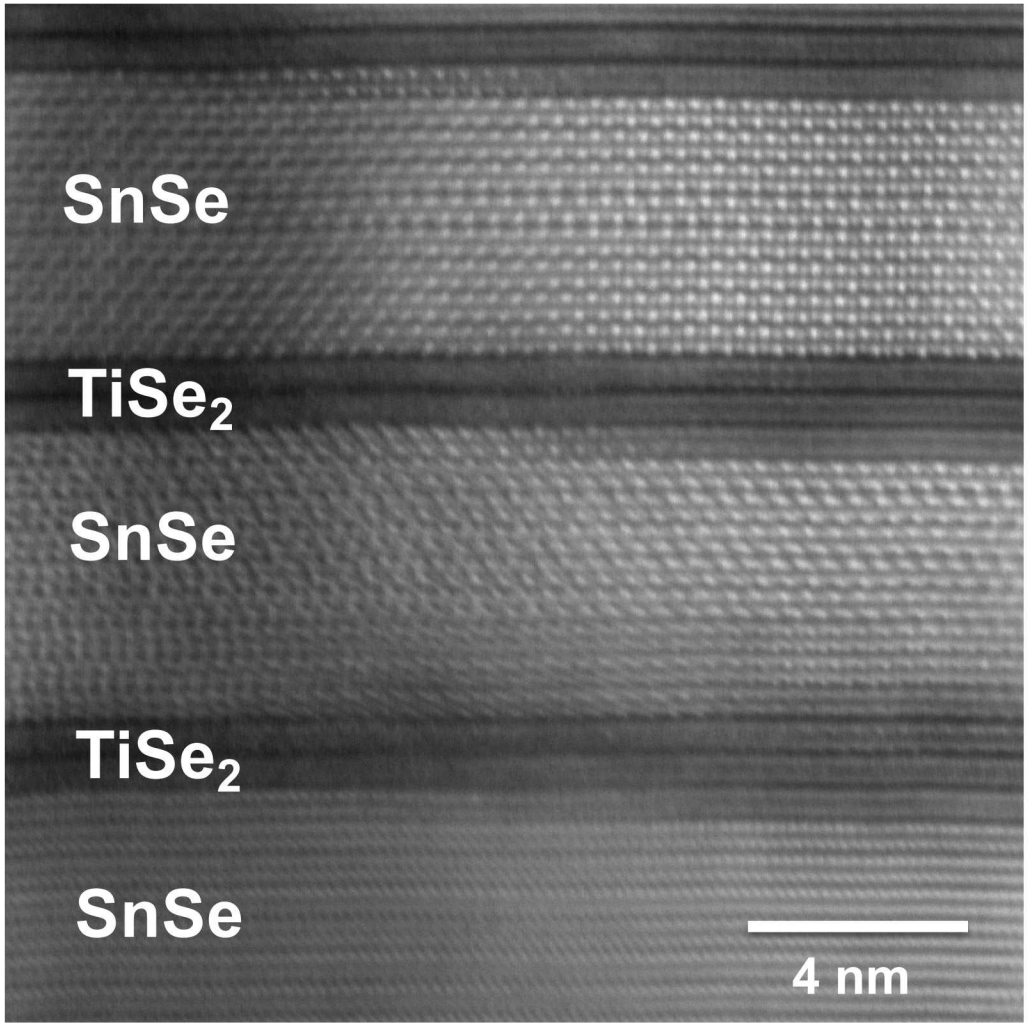
Analogous to "incoherent twin" in FCC materials

"Double-positioning" boundary

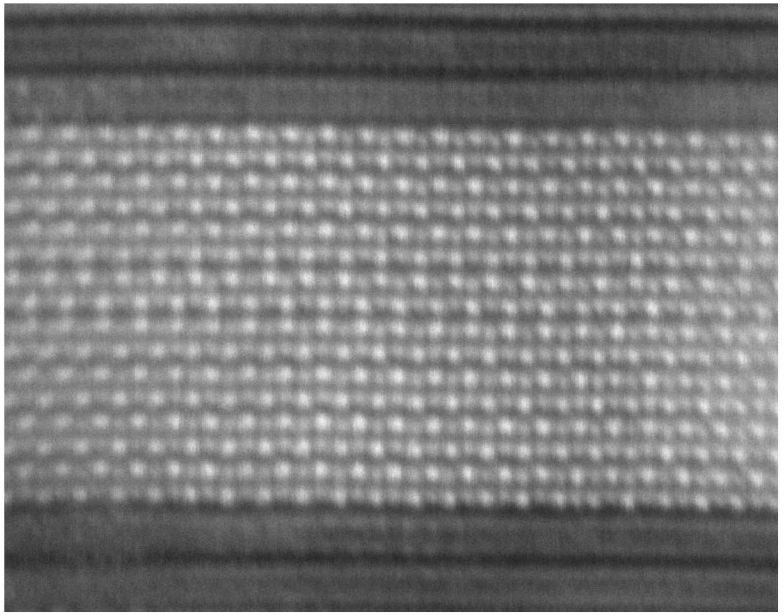
Intralayer defect: Anti-Phase Boundaries in SnSe

Sandia National Laboratories

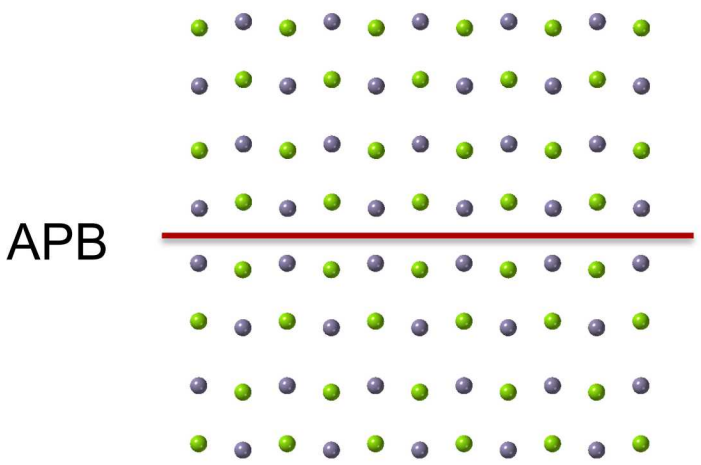
9 SnSe : 2 $TiSe_2$



20190322_UO_SnSe_TiSe2/9_2/001_area1/14.55.58_dfstem_fov18p45nm.jpg



APB



Z_{Se}=34

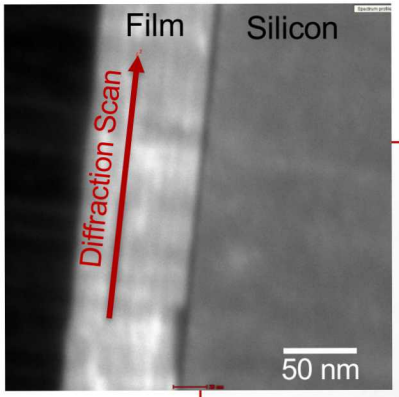
Z_{Sn}=50

[001] direction

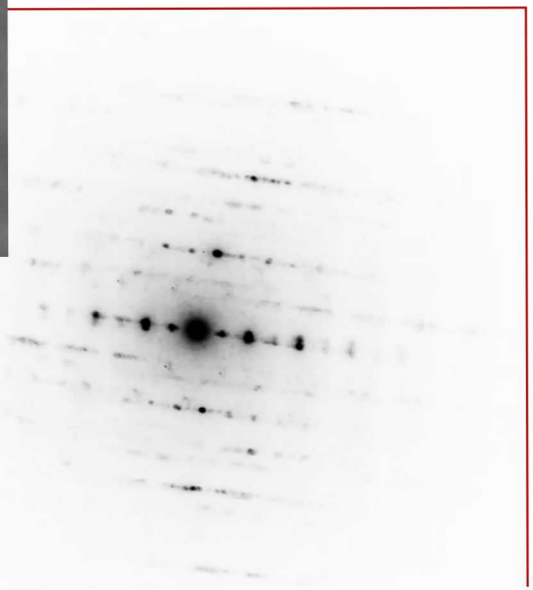
Orthorhombic Pnma structure

Spread in out-of-plane orientation

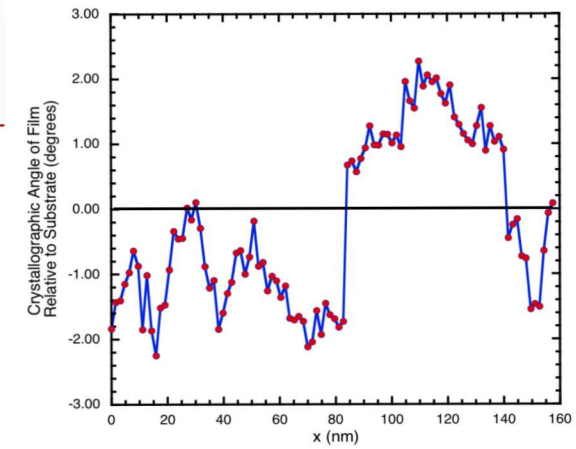
Sandia National Laboratories



Scanning Microbeam Diffraction

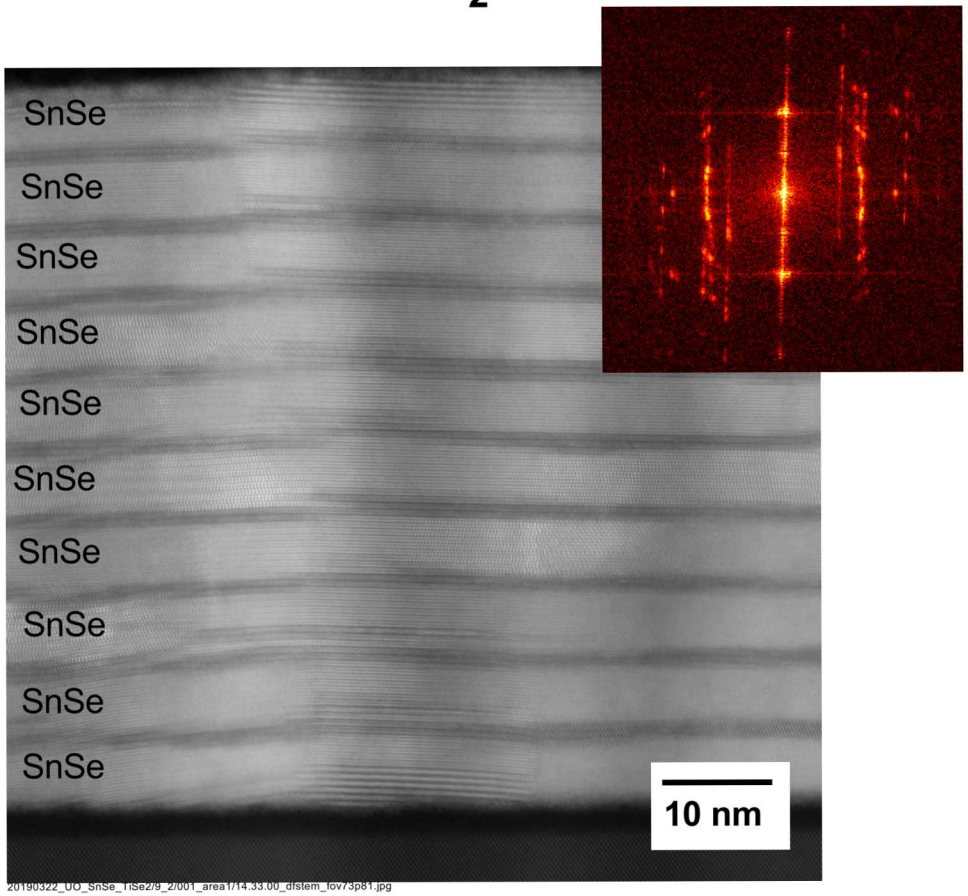


Substrate Normal



9 SnSe : 2 $TiSe_2$

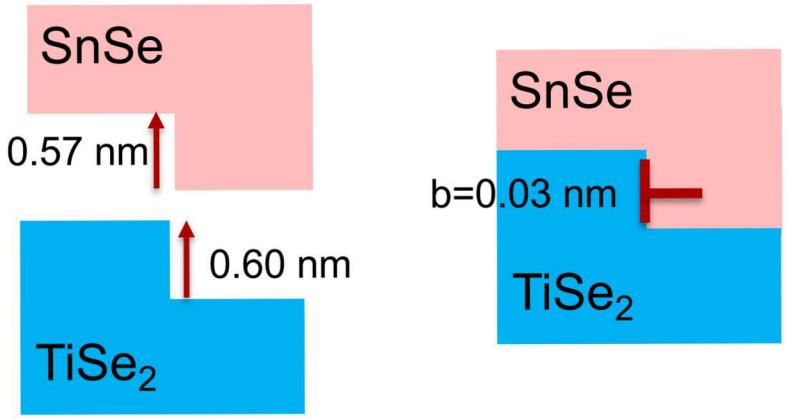
9 SnSe : 2 $TiSe_2$

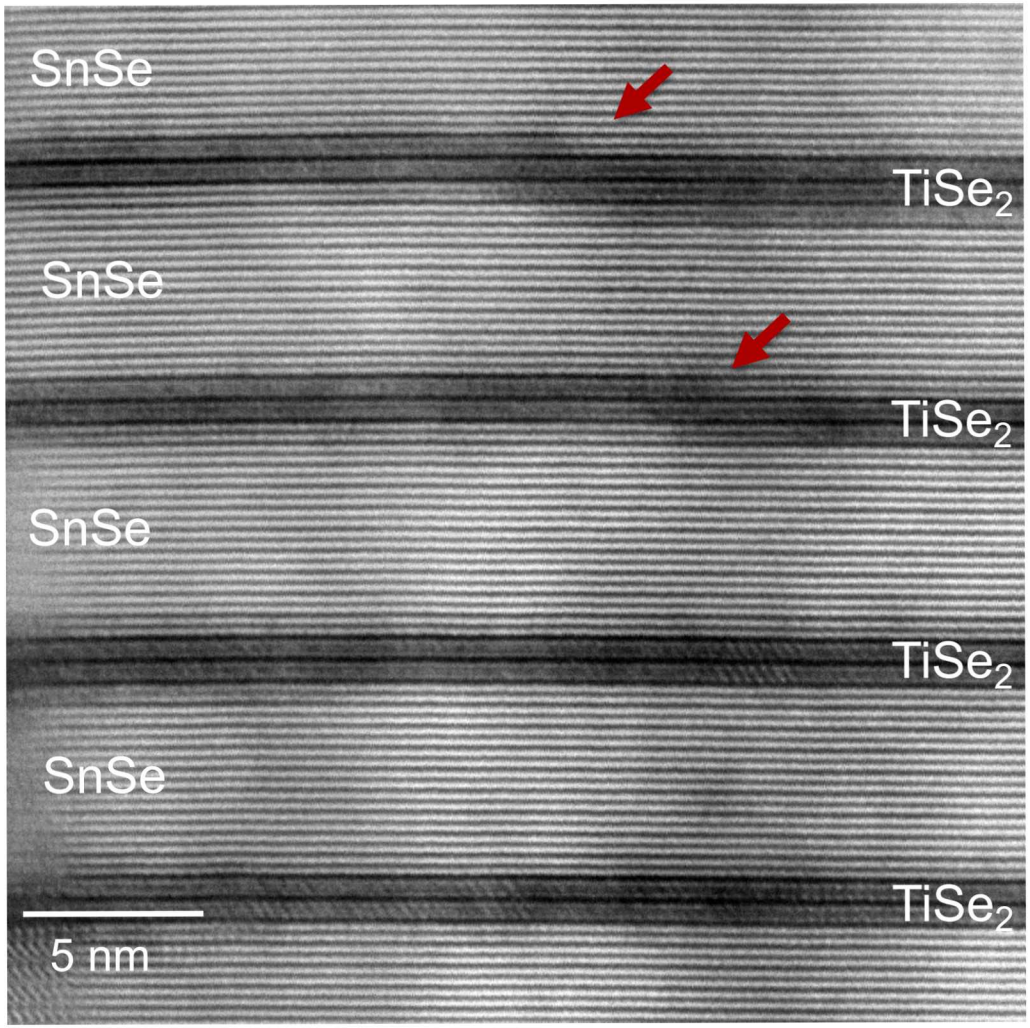


Key signature of interlayer defects

Interlayer Defects: Joining of two incomplete layers

Sandia National Laboratories

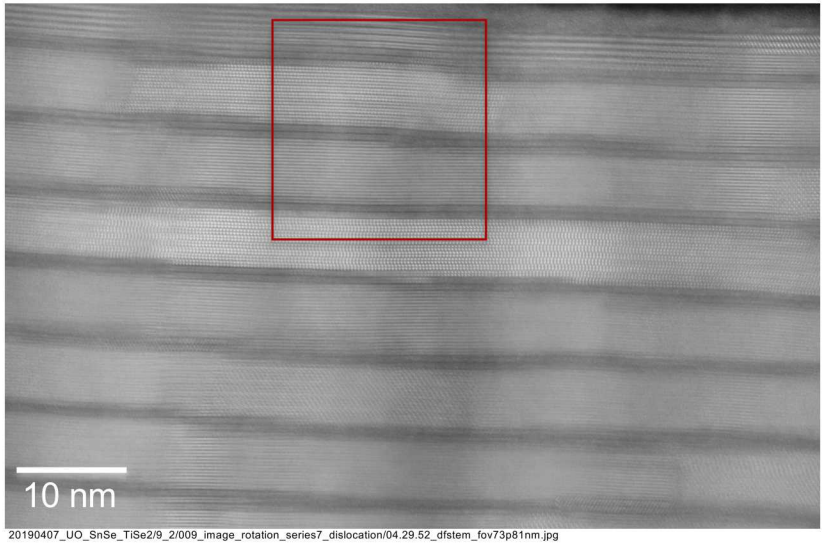


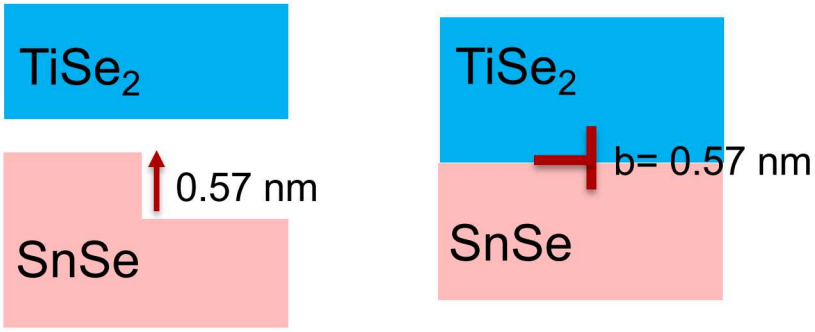


"Disconnection" == defect with both step and dislocation content

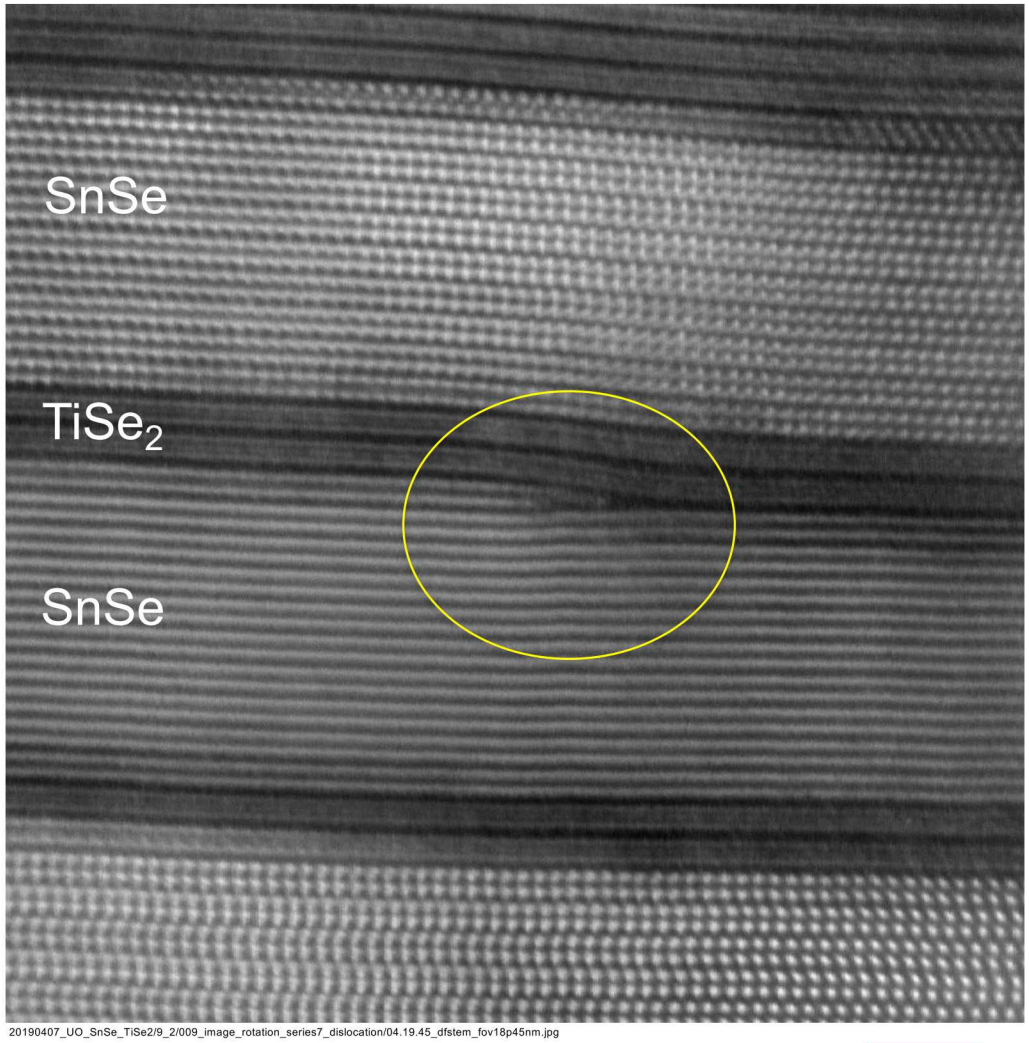
Because the step-heights are similar, the dislocation content is small

Interlayer Defects: Incomplete Layer between Full Layers





Much larger Burgers vector

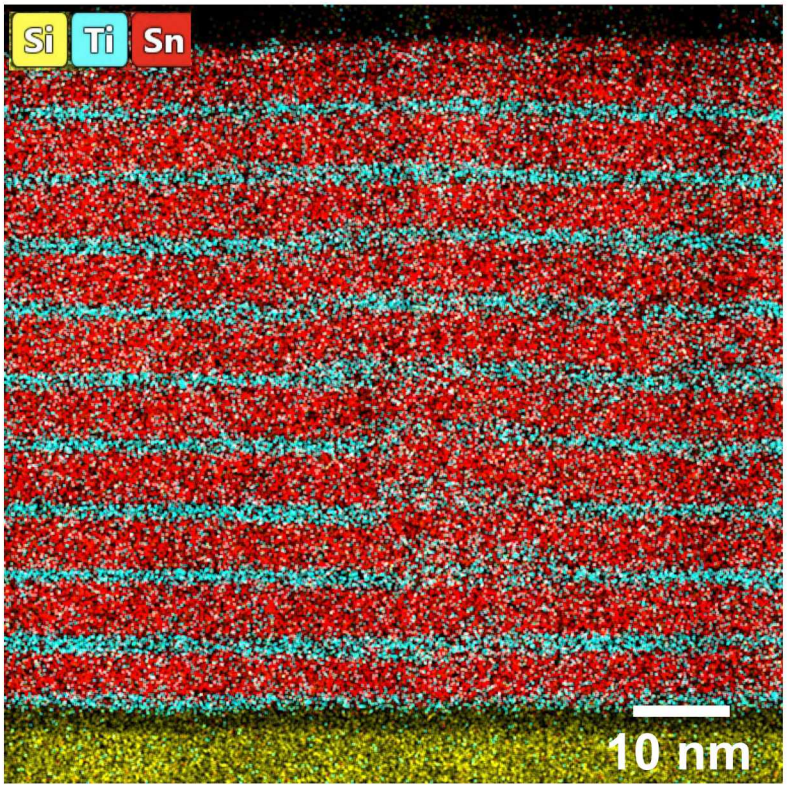


Bending associated with the dislocation strain at incomplete layers is the likely origin of spread in out-of-plane orientation.

Interlayer Defects: Offset layers

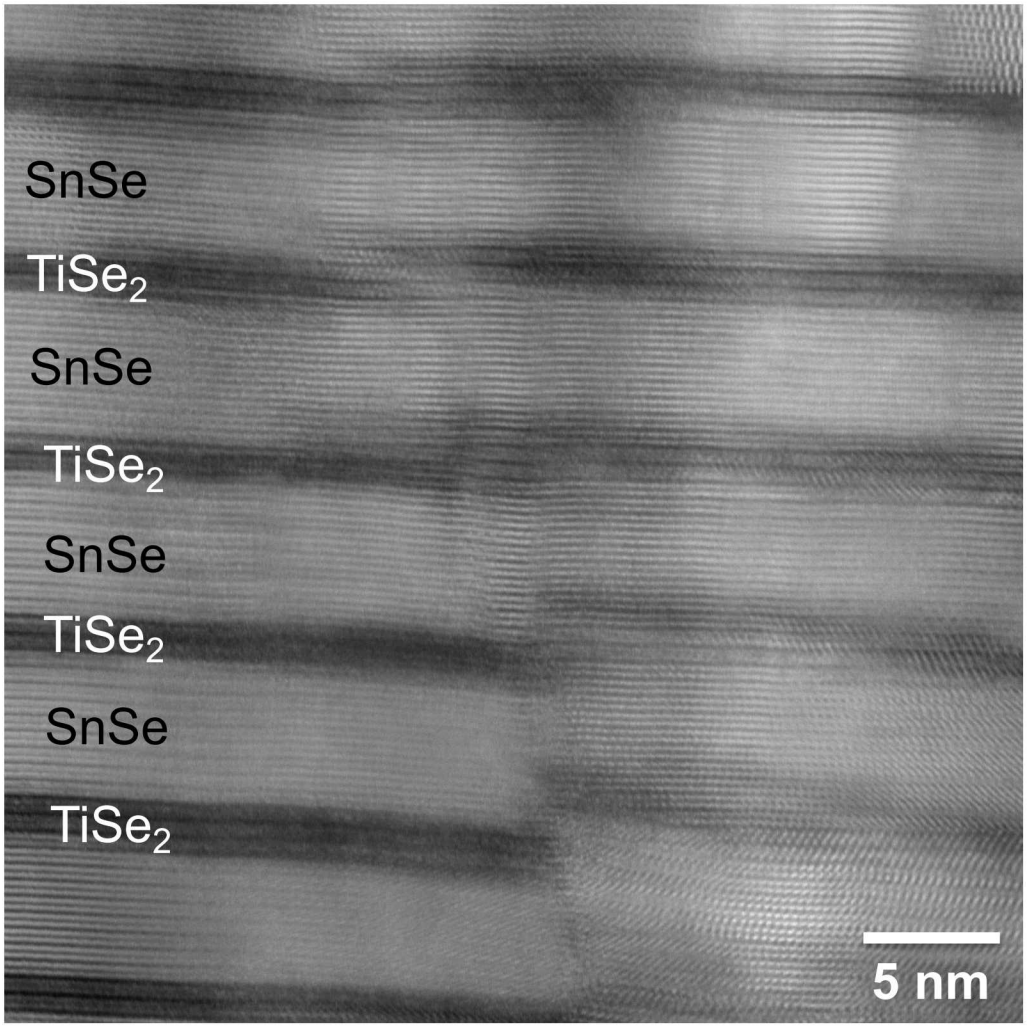
Sandia National Laboratories

EDS Spectrum Image



20190407_UO_SnSe_TiSe2/9_2/006_EDSSI_910kx/SI EDS-HAADF 0305.emd

HAADF-STEM



20190407_UO_SnSe_TiSe2/9_2/005_image_rotation_series5/02.48.38_dfstem_fov36p91nm.jpg

Summary: Wide variety of defects possible in multilayer chalcogenide films

Sandia National Laboratories

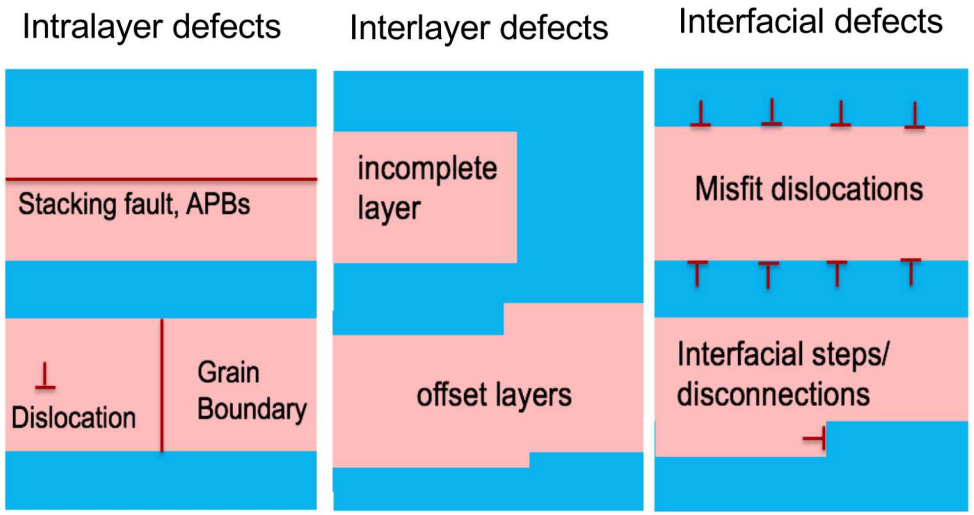
Examples from SnSe / $TiSe_2$ system

Intralayer defects

Crystalline defects within the confines of an individual layer

Interlayer defects

Defects in the morphology of the defect layers



Close connection between morphological aspects of interlayer defects and manifestation of interfacial crystalline line-defects

Impact:

-Identification of defects is first step to understanding formation mechanisms.

-Potential to tailor defects to control thermal and electronic transport properties.

Acknowledgements

University of Oregon:

Renae Gannon
Robert Fischer
Danielle Hamann
David Johnson

The University of Oregon acknowledges support from the National Science Foundation under grant DMR-1710214 and NSF GRFP-1309047

We also acknowledge the Center for Advanced Materials Characterization in Oregon (CAMCOR) at the University of Oregon.

Sandia National Laboratories:

Sandia National Laboratories is a multimission laboratory managed and operated by National Technology and Engineering Solutions of Sandia, LLC, a wholly owned subsidiary of Honeywell International Inc. for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA-0003525.

Douglas Medlin acknowledges support in part from the Sandia LDRD office.