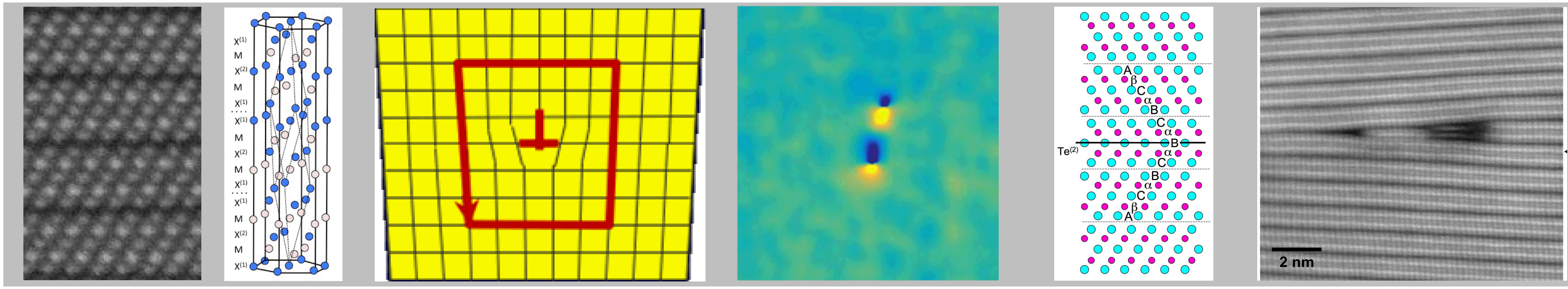
SAND2018-8011C

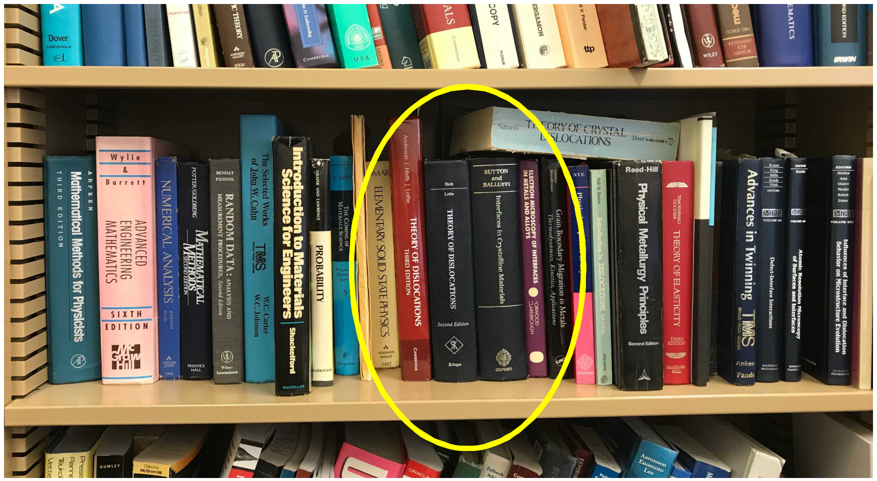


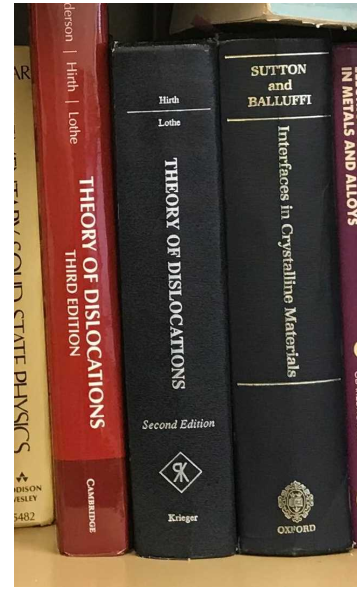
Atomic-Scale Investigation of Dislocations and Interfacial Line Defects in Layered Chalcogenide Materials

Douglas L. Medlin
Sandia National Laboratories,
Livermore, California, USA
dlmedli@sandia.gov

Some Opening Comments:

At the center of my bookshelf...





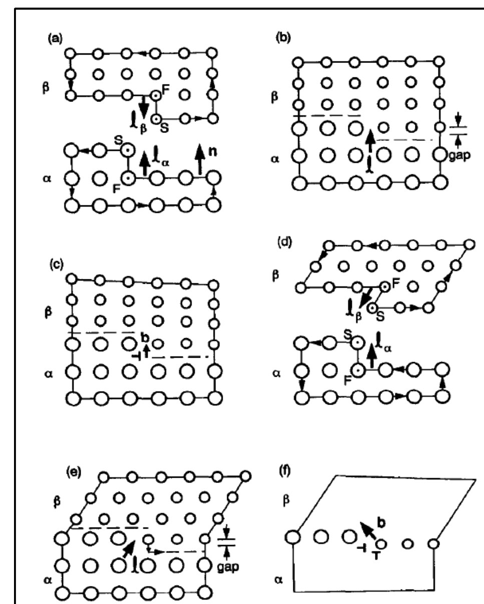
Key advances to theory of line defects at interfaces

J.P. Hirth, "Dislocations, Steps and ***Disconnections*** *at Interfaces" J. Phys. Chem. Solids 55 (10) 985-989 (1994).*

R.C. Pond, J.P. Hirth "Defects at Surfaces and Interfaces" Solid State Physics, Vol 47, 287-365 (1994)

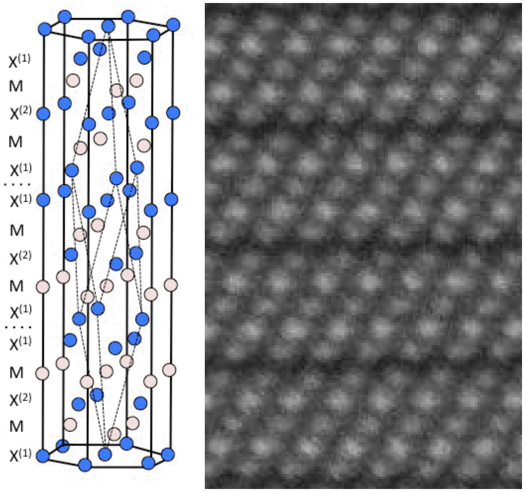
J.P. Hirth and R.C. Pond, "Steps, Dislocations and Disconnections as Interface Defects Relating to Structure and Phase Transformations: Acta Materialia 44 (12) 4749-4764 (1996)

and many more...

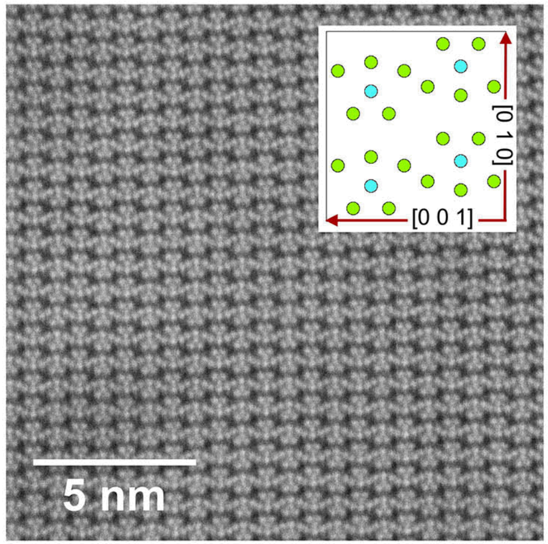


Layered Chalcogenides: Diversity of compositional and structural arrangements

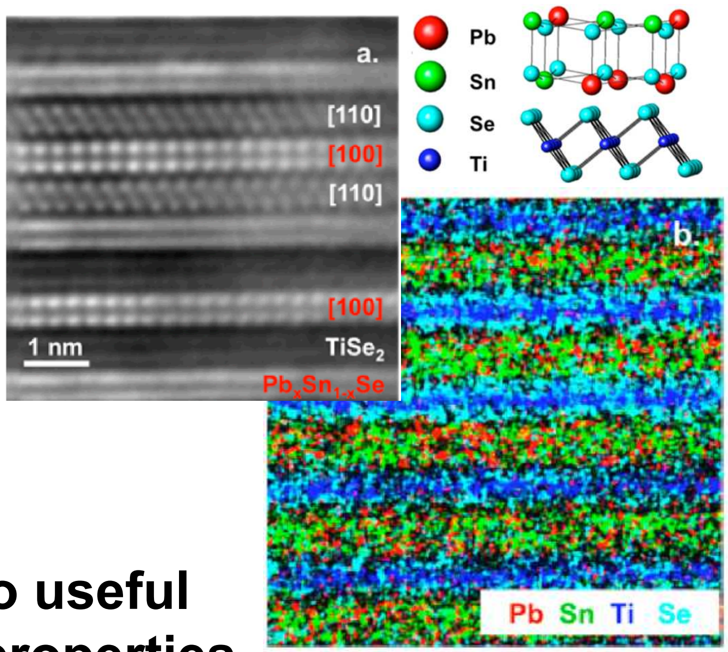
Example: Bi_2Te_3



Example: $ZrTe_5$



Example: (Pb,Sn)Se/$TiSe_2$ Multi-layers



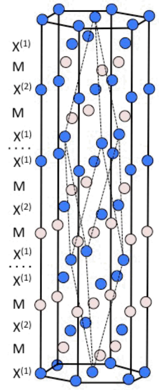
Anisotropic, layered structures contribute to useful and interesting thermal, electronic, optical properties,

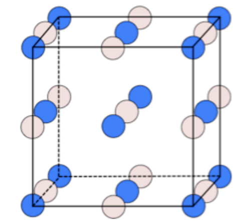
Thermoelectrics, Photothermoelectric Effect,
Topological Insulators, Dirac Semimetals

Interfaces and Dislocations play important roles in crystal growth and thermal and electronic properties of these complex materials

Outline

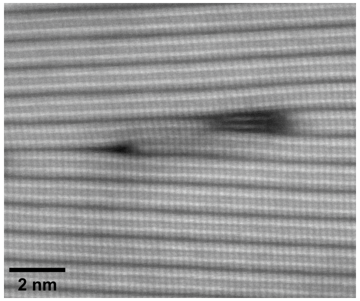
- ***Crystal structure in tetradymite-type compounds***
  - **•Layered structure gives flexibility in accommodating compositional variations**
  - **•Close structural relationship to rock-salt chalcogenides**

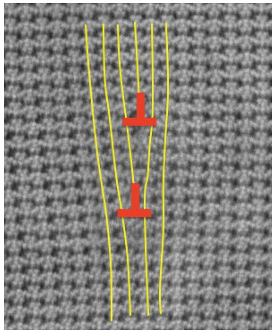




- ***Dislocation Structure:***

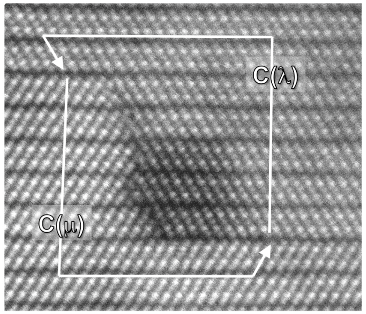
Dissociated Core Structure in:
- **Bismuth Telluride**
- **Zirconium Telluride**

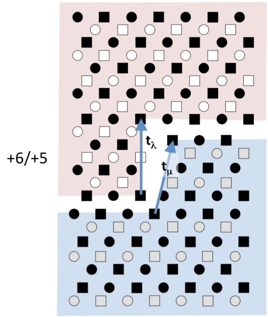




- ***Interfacial Structure***

Interfacial disconnections.
•Bi_2Te_3: Twin interface
•Rocksalt/Tetradymite interface



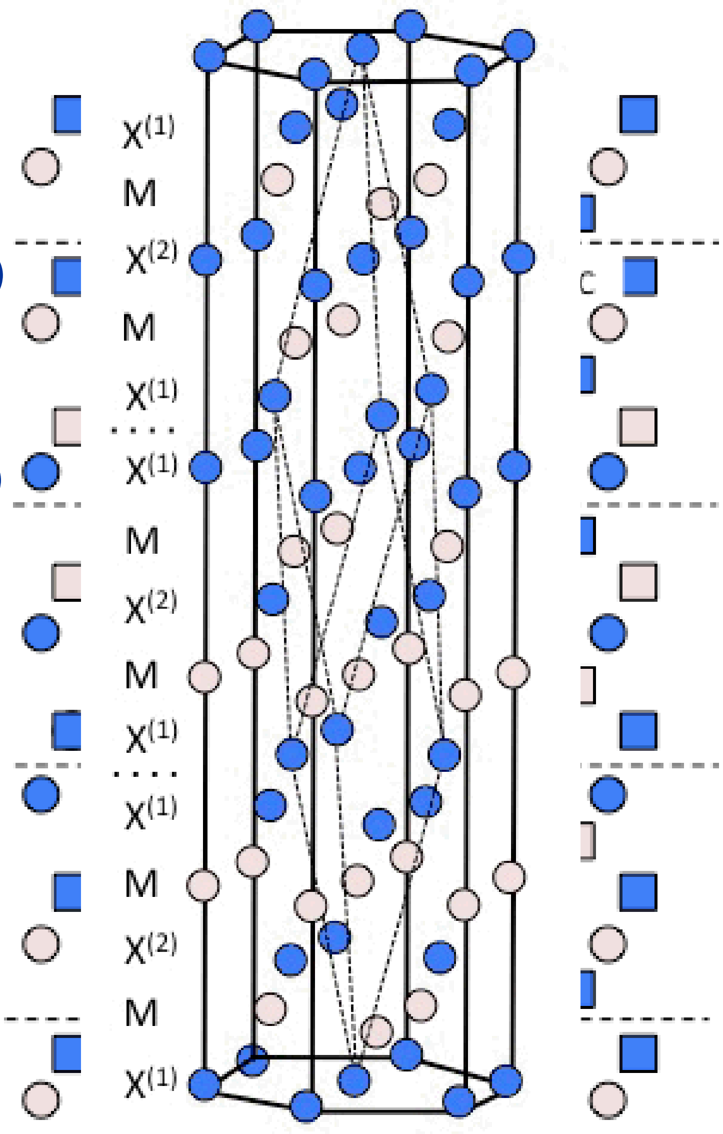


Sandia National Laboratories

Bismuth Telluride (Bi_2Te_3): Crystal Structure

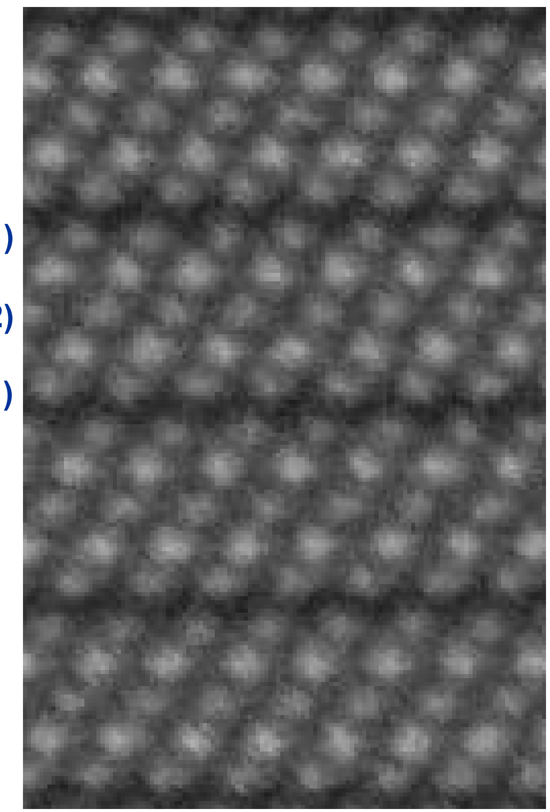
- Rhombohedral (R-3m) structure
- Based on tetradymite (Bi_2STe_2) prototype
- Isomorphous with Bi_2Se_3, Sb_2Te_3
- Three crystallographically distinct atomic sites
- $Te^{(1)}$-$Te^{(1)}$ layers: van der Waals bonding

Te(1)
Bi
Te(2)
Bi
Te(1)



HAADF-STEM

Te(1)
Bi
Te(2)
Bi
Te(1)



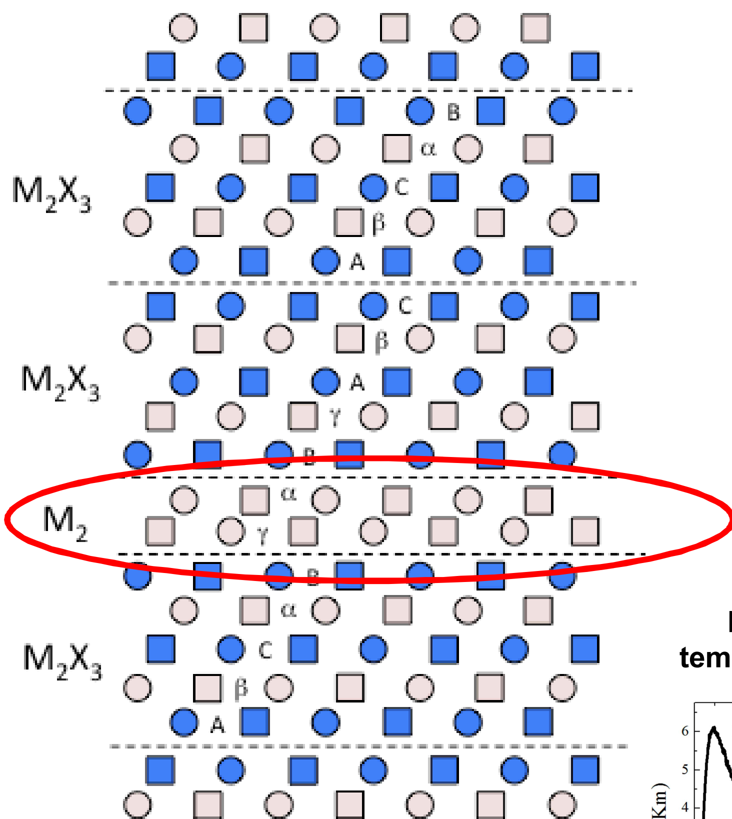
Bi: Z=83
Te: Z=52

Atomic number difference enables Bi and Te to be distinguished in HAADF-STEM

Sandia National Laboratories

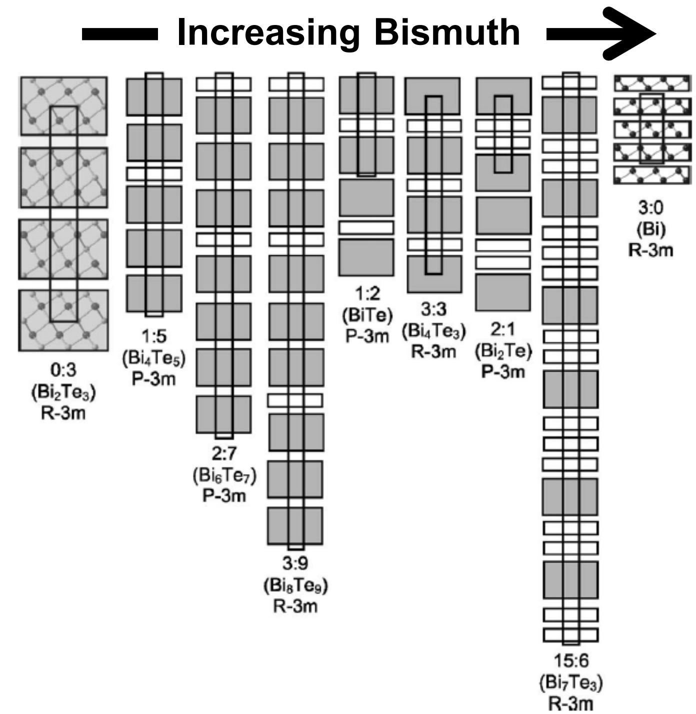
Layered structure allows flexibility in accommodating variations in composition

Insertion of metal bi-layers

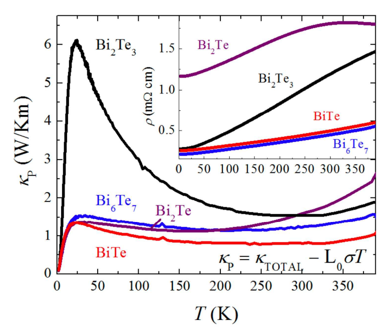


Example:
$(Bi_2)_m(Bi_2Te_3)_n$ homologous series

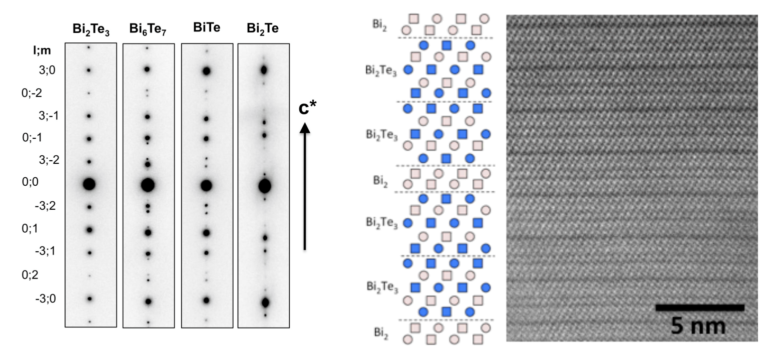
J.W.G. Bos, H.W. Zanderbergen, M.-H. Lee, N.P. Ong, R.J. Cava, Phys. Rev B 2007



Dramatic reduction in low-temperature thermal conductivity



Electron diffraction and HRSTEM show ordering in $(Bi_2)_m(Bi_2Te_3)_n$ series

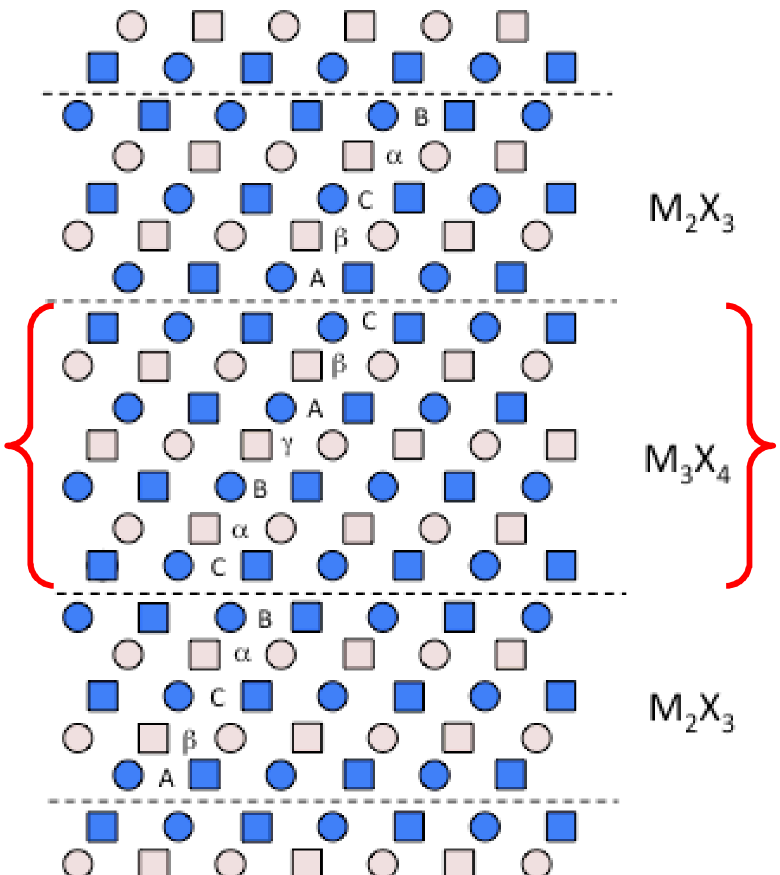


P. Sharma, D.Medlin, et al. PRB 83 (2011) 235209.

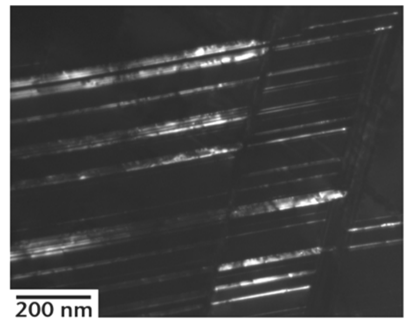
Medlin & Snyder, JOM 2013

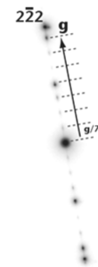
Layered structure allows flexibility in accommodating variations in composition

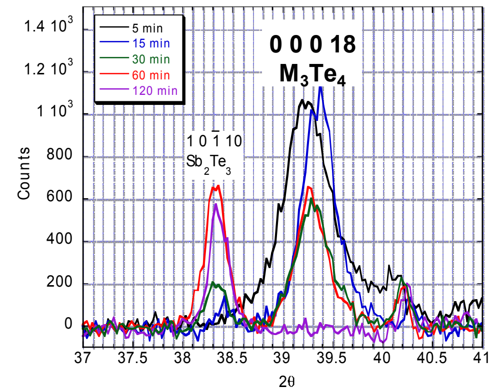
Metal rich, 7-Layer M_3X_4 fault

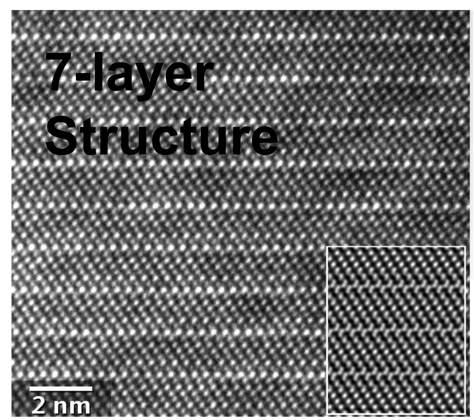


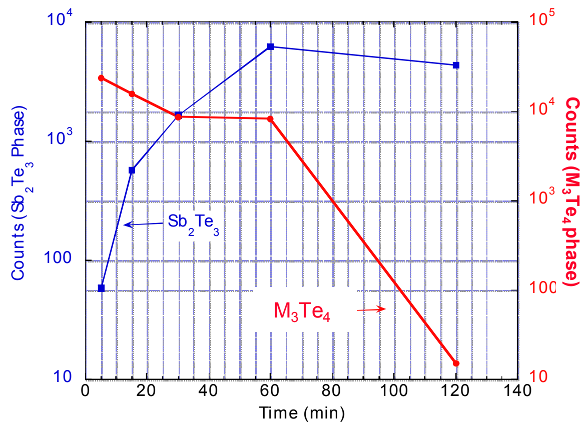
Example: $(Ag,Sb)_3Te_4$ transition phase during nucleation of Sb_2Te_3 precipitates in $AgSbTe_2$











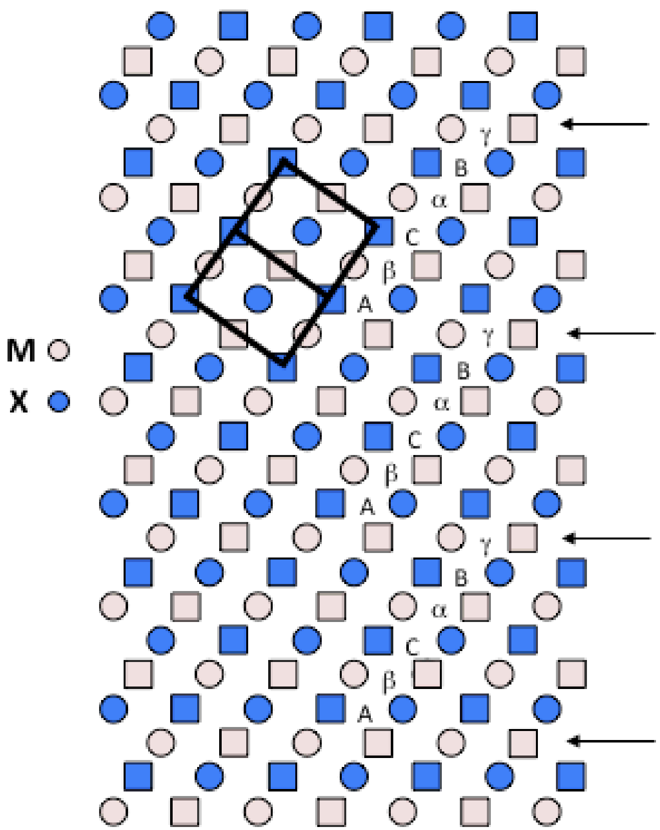
Sharma, Sugar, & Medlin, Journal of Applied Physics (2010).
Sugar and Medlin, Journal of Materials Science (2011)

Sandia National Laboratories

Tetradymite and Rocksalt structures are closely related

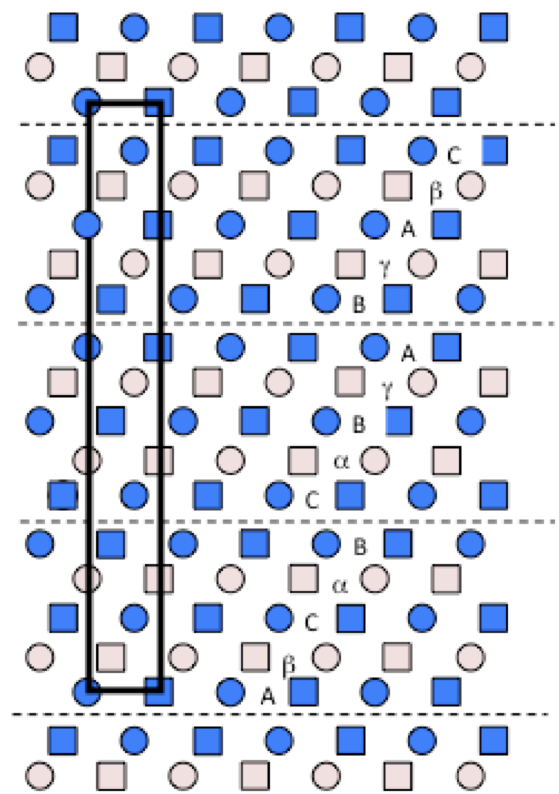
Rocksalt (MX) Structure

Fm-3m

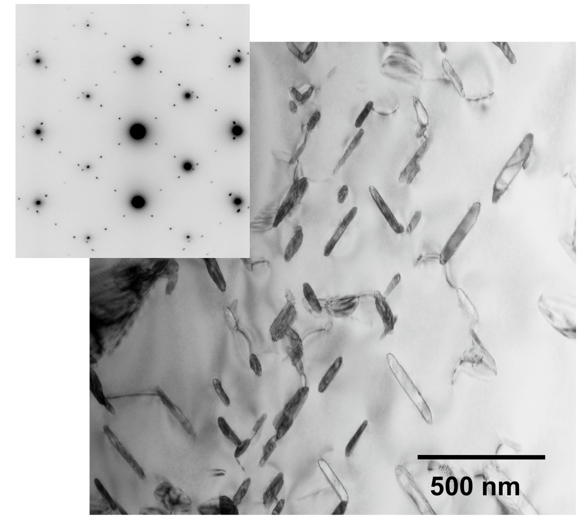


Tetradymite (M_2X_3) Structure

R-3m



Example:
Crystallographically Aligned Sb_2Te_3 precipitates in PbTe



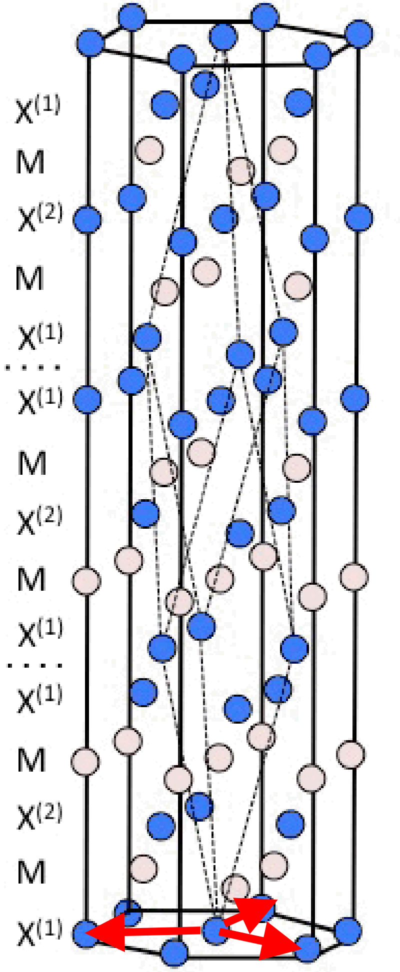
Heinz, Snyder, Ikeda, and Medlin, Acta Mat. 2011

- **Solid-state phase transformations in chalcogenides**
- **Structural interpretation of extended defects**

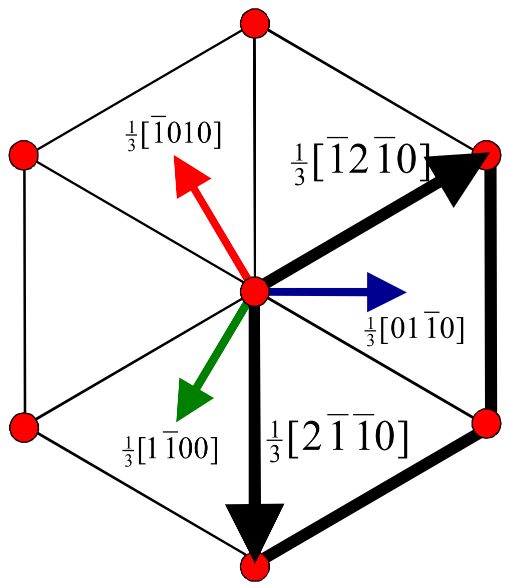
How do these structural considerations impact Dislocations and Interfaces?

Dislocations in Bismuth Telluride

Burgers vectors lying in basal plane



Looking down on basal plane



Array of 1/3<2-1-1 0> Dislocations in Bi_2Te_3

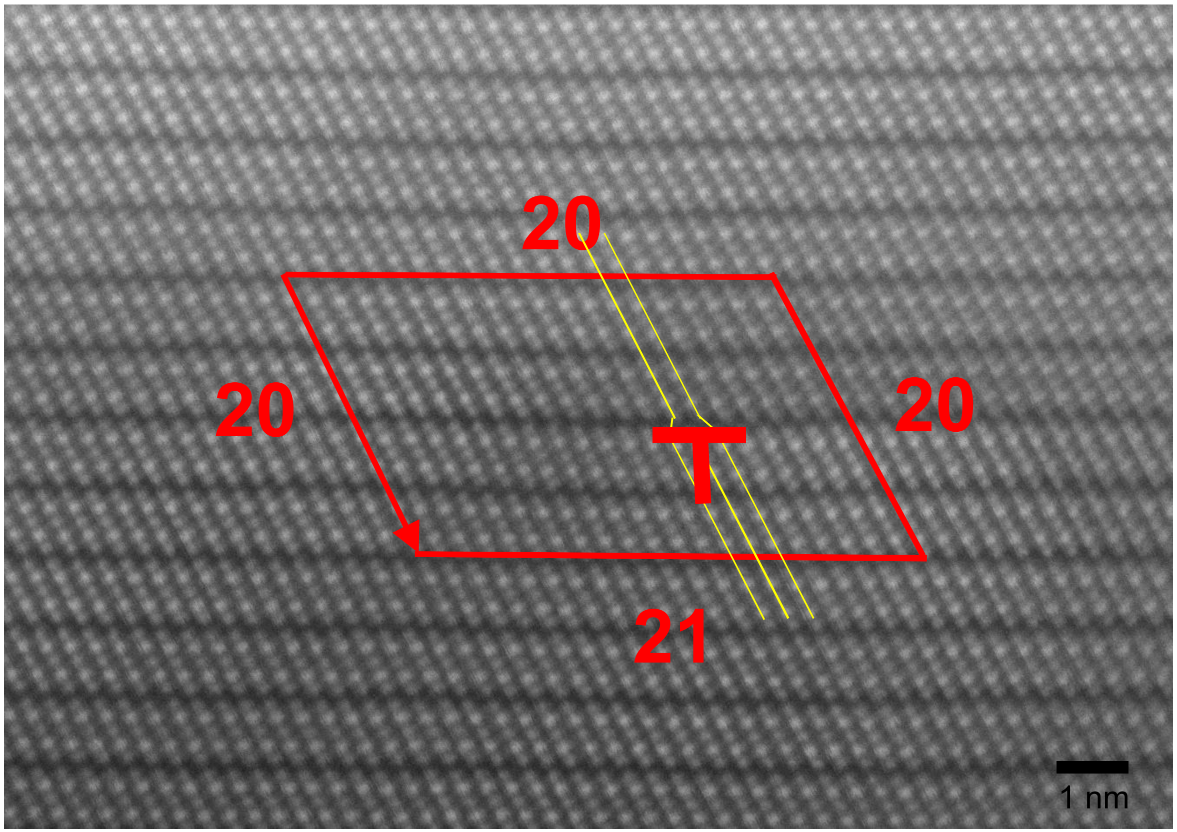
Fig. 1. Dislocation network in Bi_2Te_3. Note that certain segments of dislocations and certain node-points have left the foil

Sandia National Laboratories

Dislocation Core structure: Termination at $Te^{(1)}$-$Te^{(1)}$ layer

5-layer Bi_2Te_3 "quintet"

[0 0 0 1]



b=1/3<2 -1 -1 0>

60° mixed dislocation

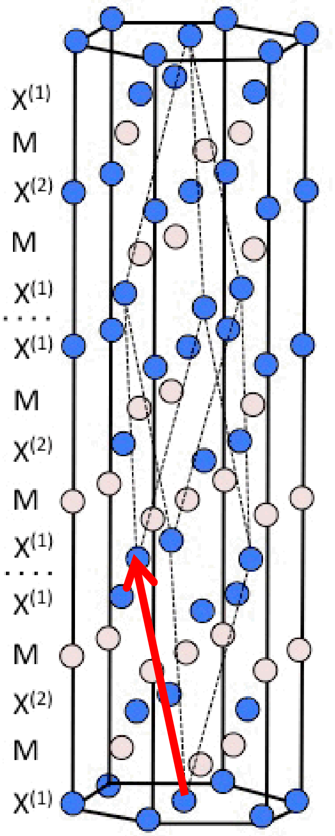
Stoichiometric Core

HAADF-STEM
300 keV

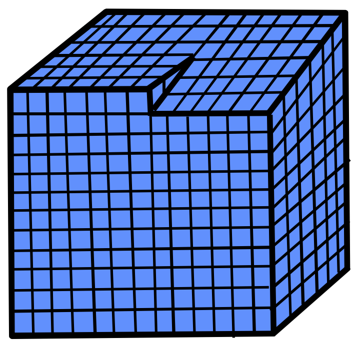
<2 -1 -1 0 > projection

Sandia National Laboratories

Non-basal dislocations:
Screw dislocations important to crystal growth

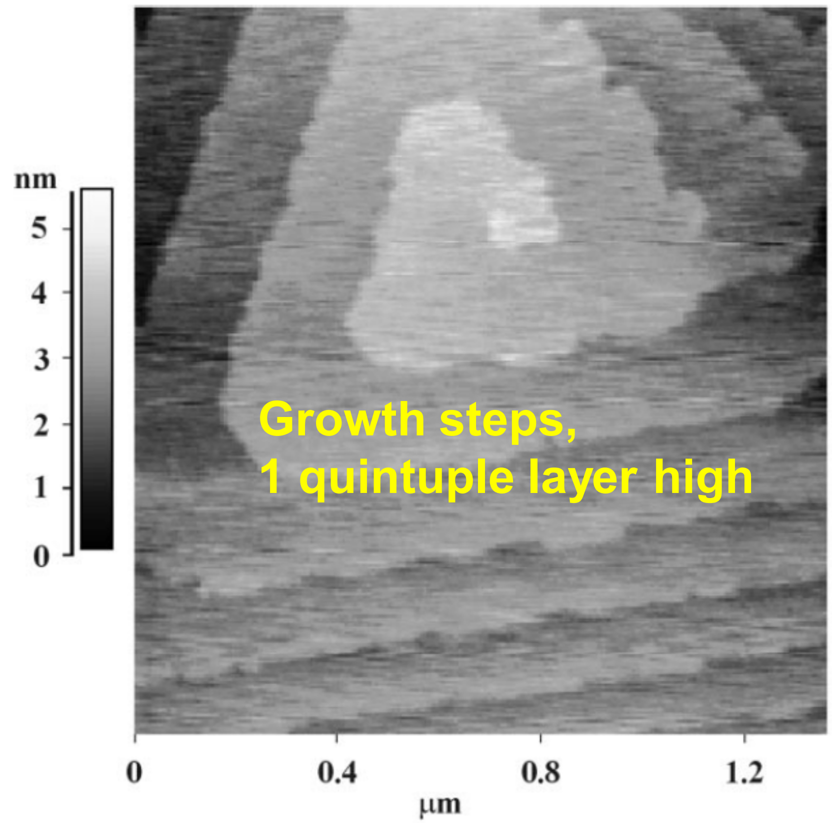


Screw Dislocation



$b = (1/3)[0\text{-}111)_H$
$= [001]_R$

Example: spiral growth steps at screw dislocation in Bi_2Te_3 thin film

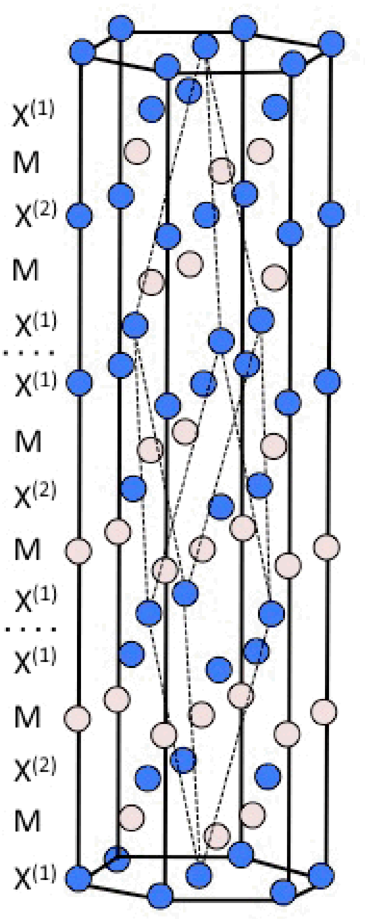


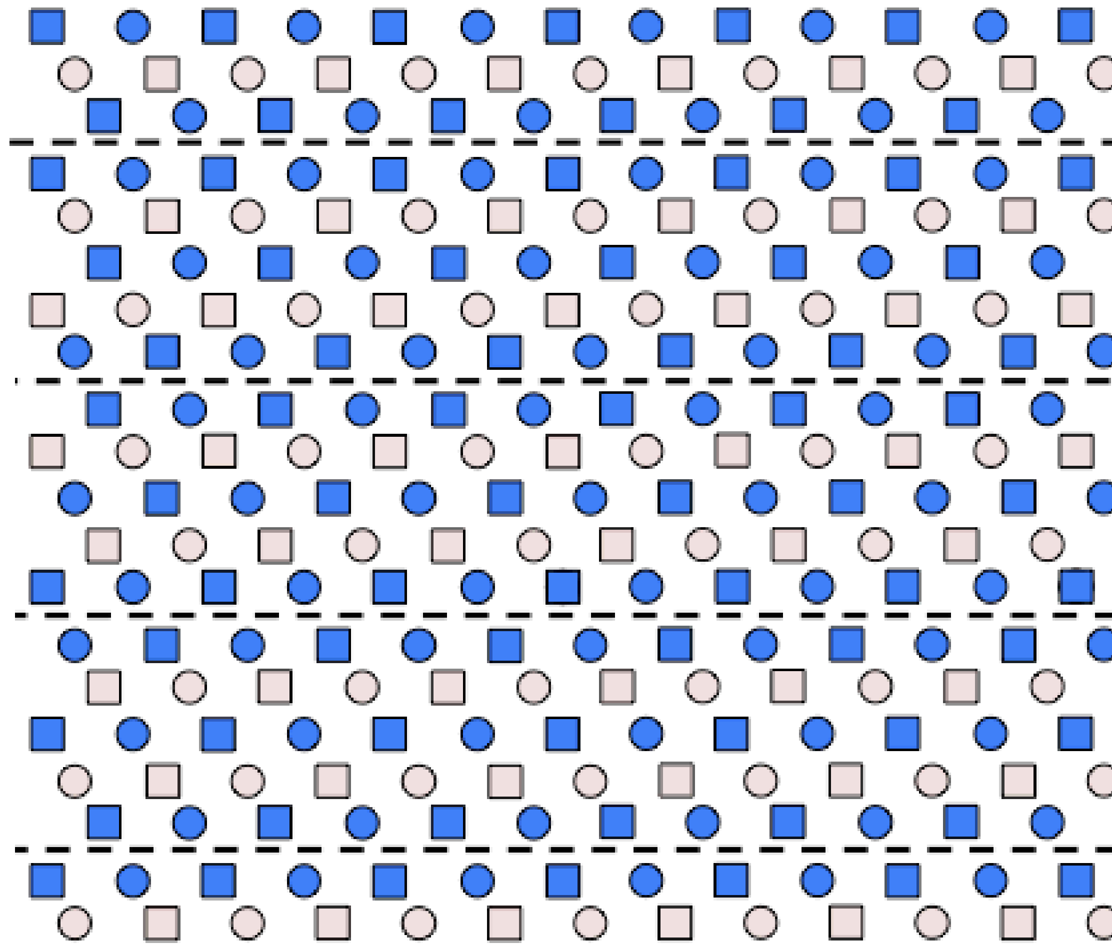
M. Ferhat, J.C. Tedenac, J. Nagao, J. Crystal Growth (2000)

What about edge dislocations with non-basal Burgers vectors?

Sandia National Laboratories

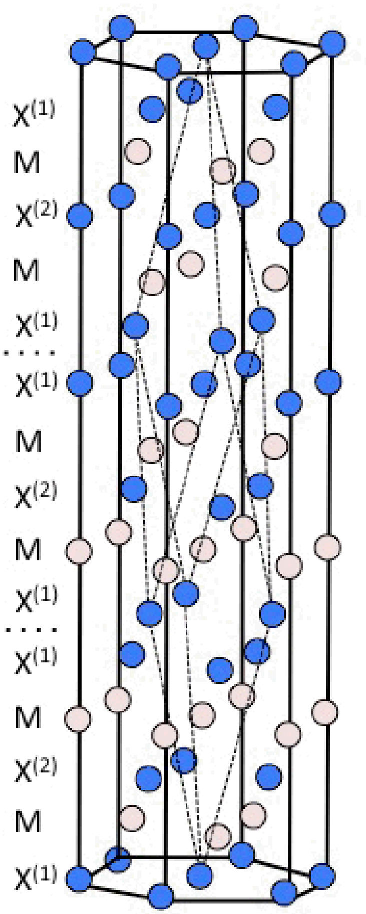
Non-basal edge dislocations: What happens if we pull out a quintuple unit?

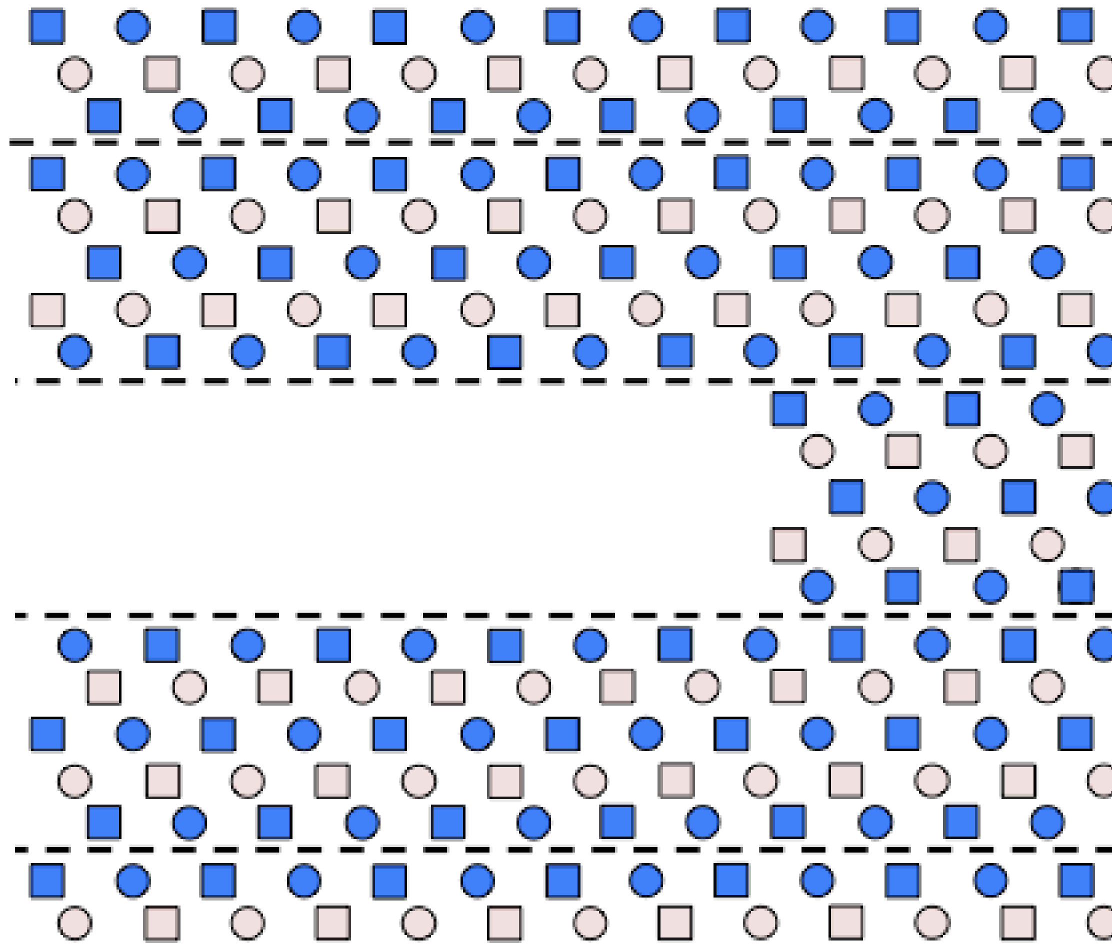




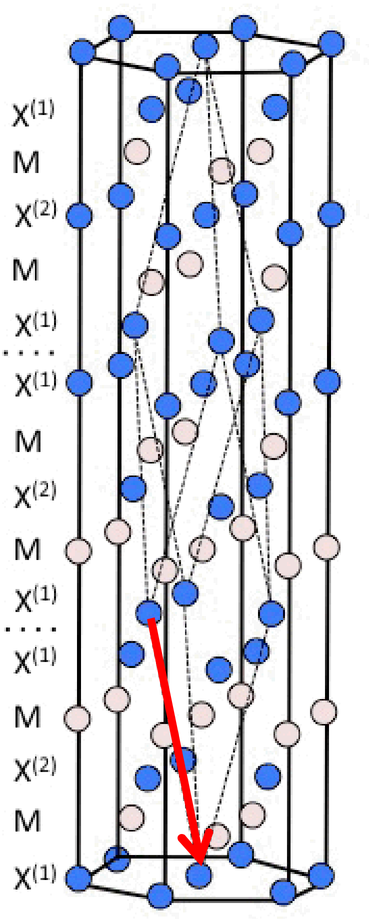
Sandia National Laboratories

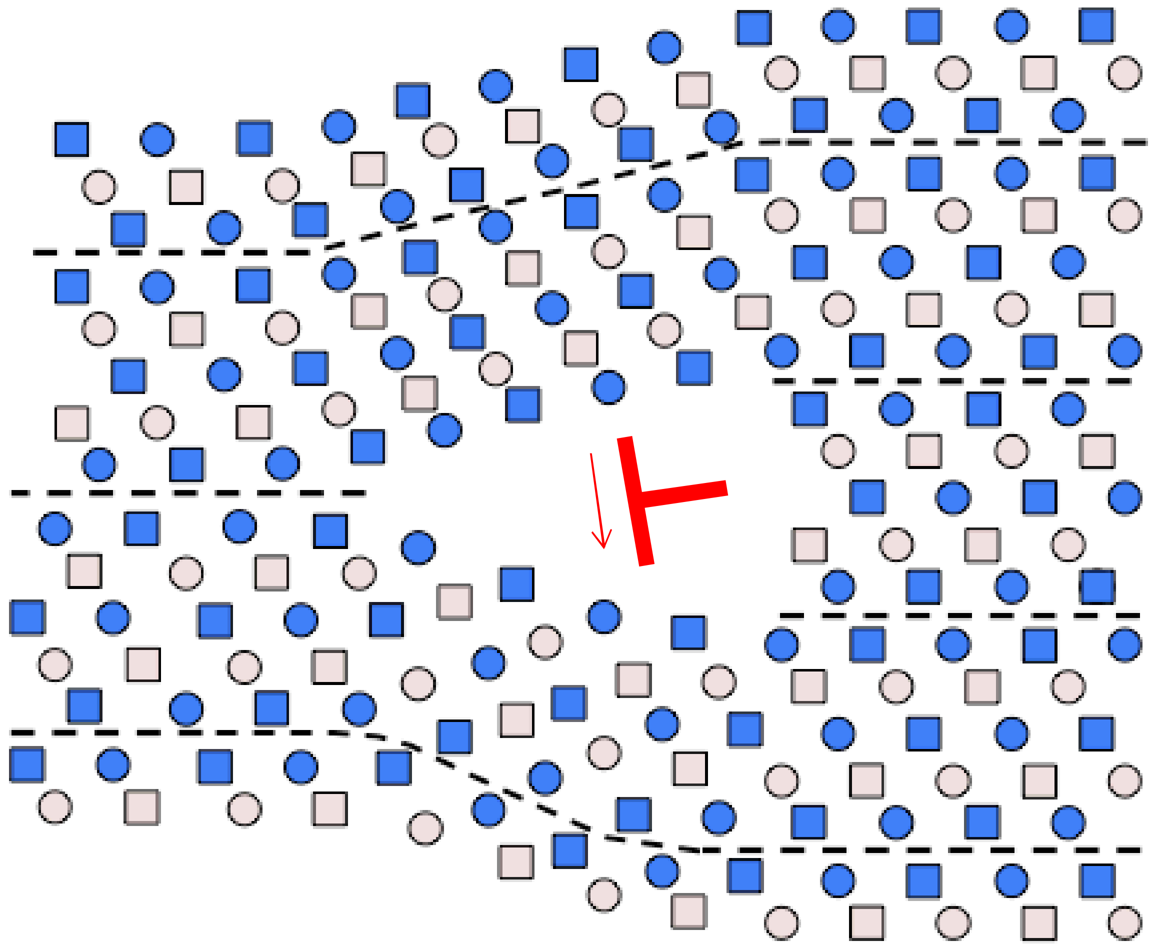
Non-basal edge dislocations:
What happens if we pull out a quintuple unit?





Non-basal edge dislocations: What happens if we pull out a quintuple unit?

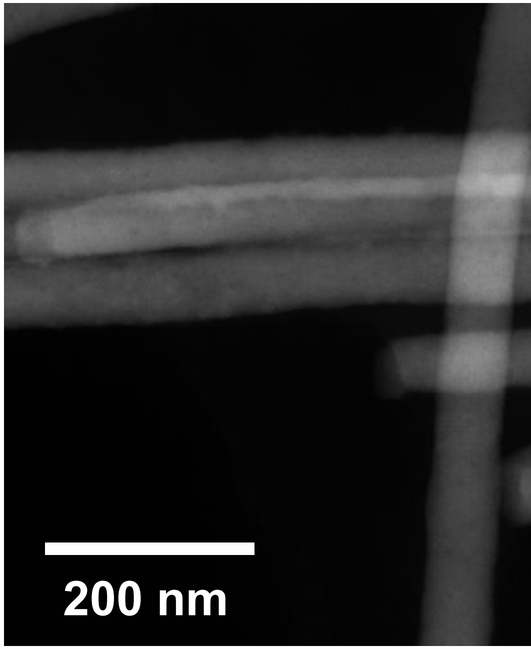


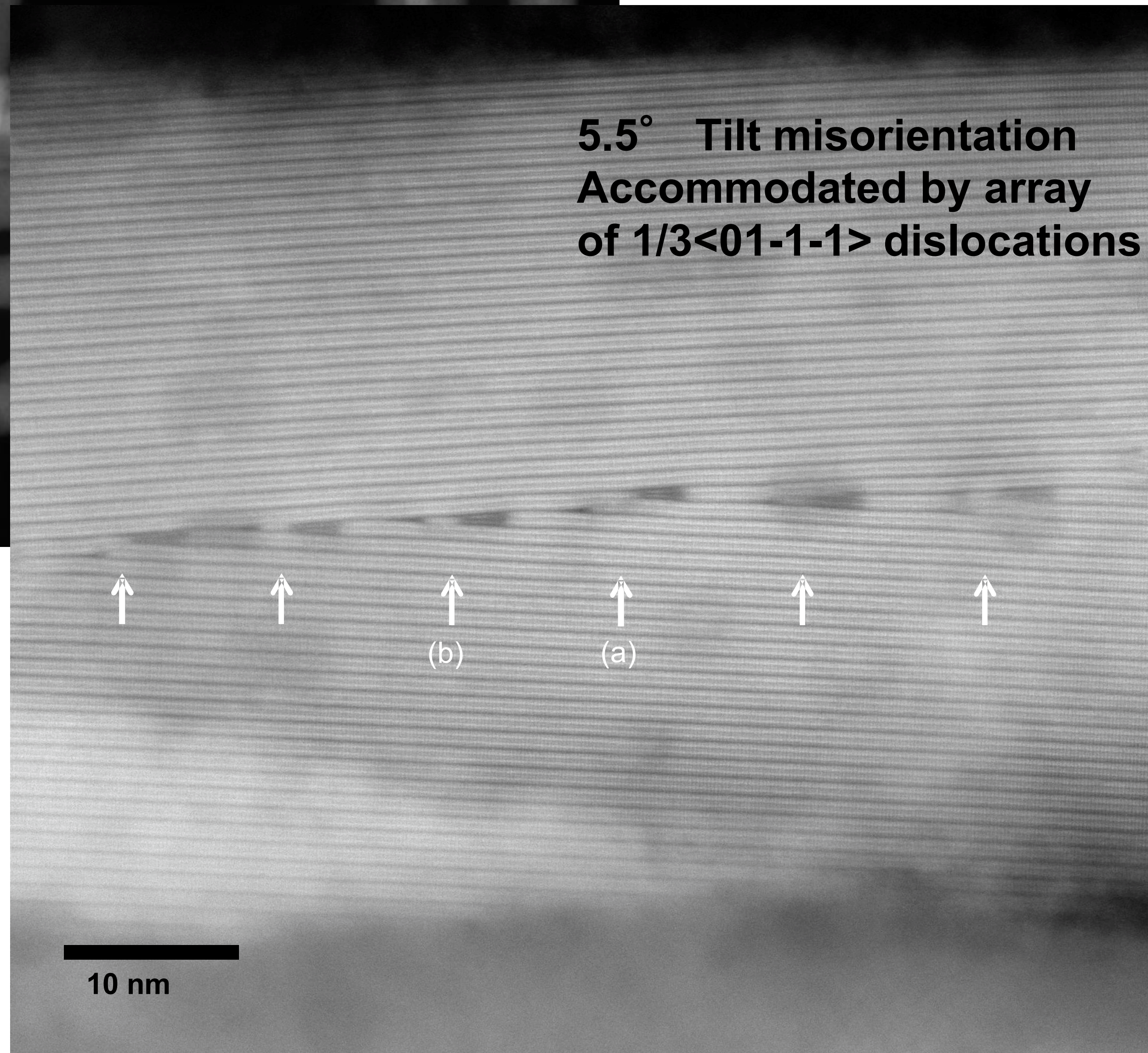


$b = (1/3)[01\text{-}1\text{-}1)_H = [00\text{-}1]_R$

Sandia National Laboratories

Dislocations in Bi_2Te_3 Nanowires





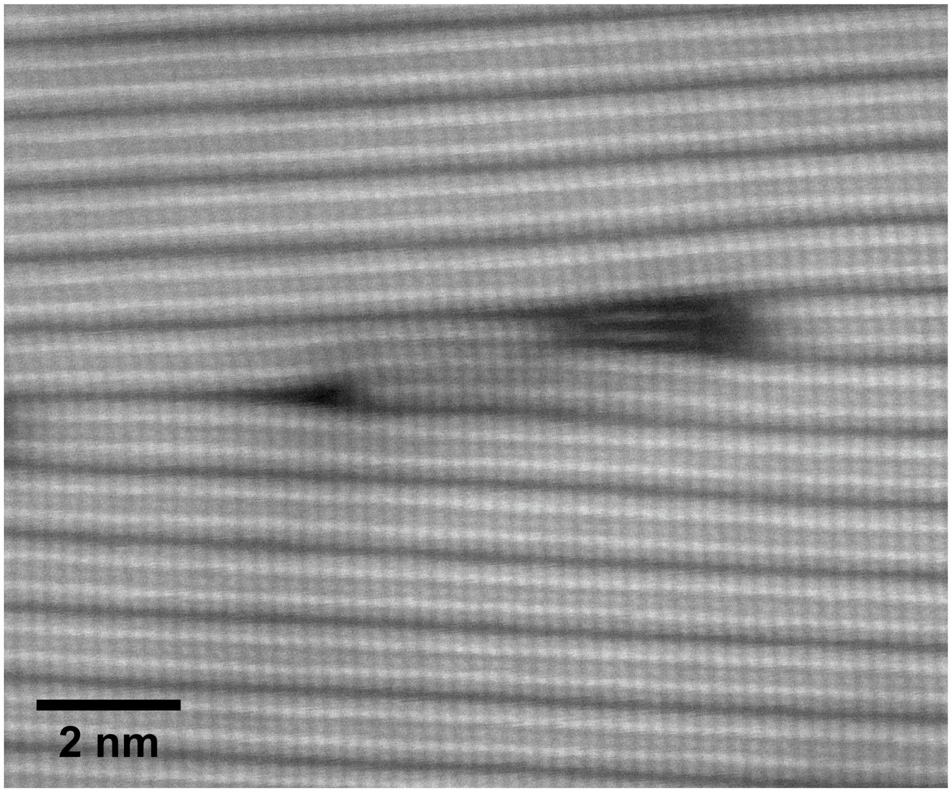
Wires formed by electrochemical deposition in nanoporous AAO templates.

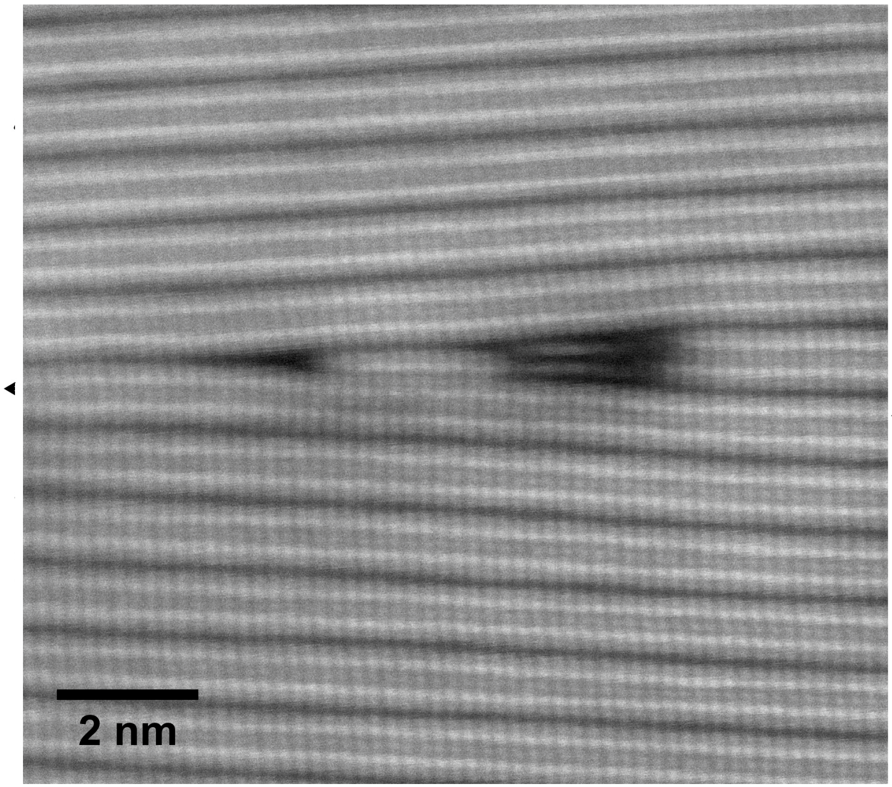
Free standing wires annealed 30 minutes at 300° C in Ar-3%H_2.

➔ Some loss of Te due to high vapor pressure

Medlin, Erickson, Limmer, Yelton, Siegal, J. Mat. Sci. 2014

Dislocations have dissociated core: two configurations



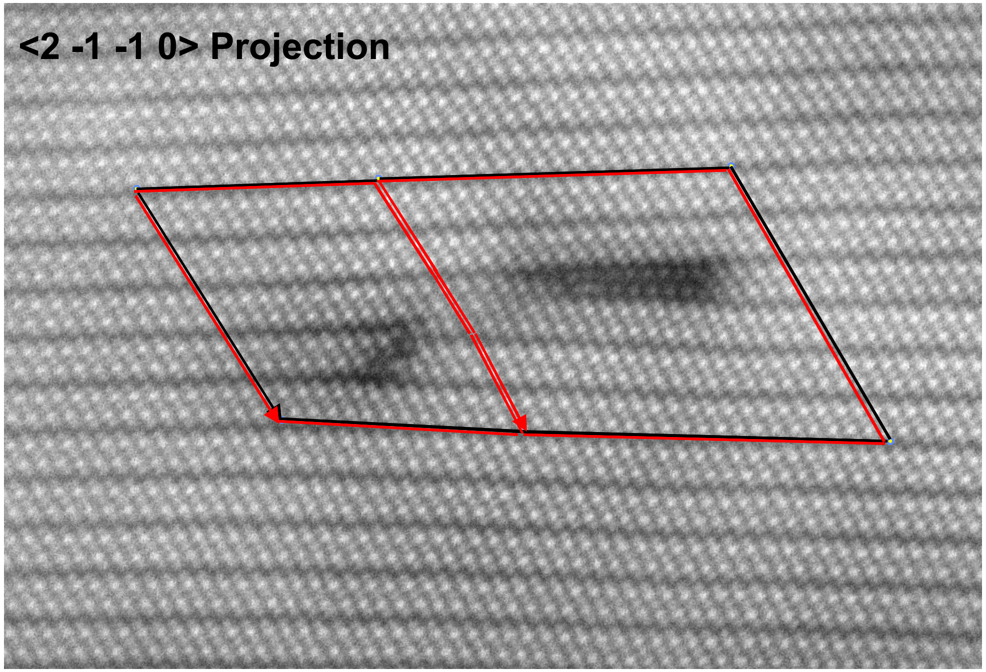


<1 0 -1 0> Projection

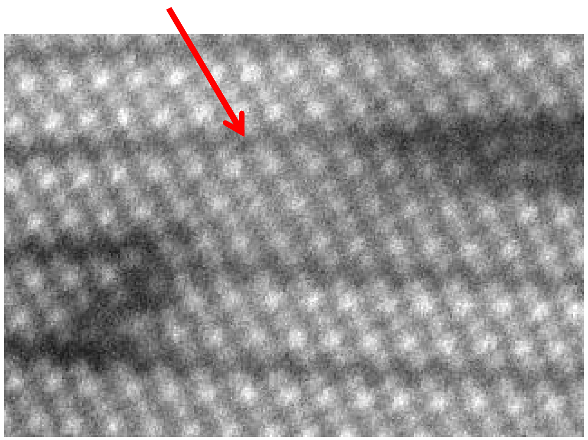
Medlin, Erickson, Limmer, Yelton, Siegal, J. Mat. Sci. 2014

Sandia National Laboratories

(1/3)[0 1 -1 -1] Dislocation in Bi_2Te_3:



Core structure:
Bi_3Te_4 7-layer fault



b = (1/3) [0 1 -1 -1] → **(1/15) [0 5 -5 -2]** **+** **(3/15) [0 0 0 -1]**

$b^2 > b_1^2 + b_2^2$

109.8 Å^2 > 22.9 Å^2 + 37.2 Å^2 =60.2 Å^2

Reduced strain energy with dissociation

Medlin, Erickson, Limmer, Yelton, Siegal, J. Mat. Sci. 2014

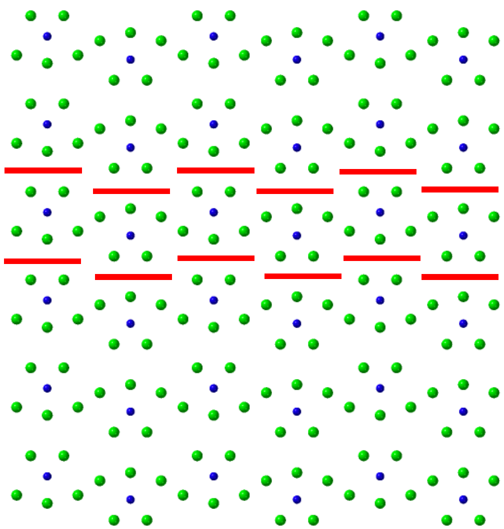
Sandia National Laboratories

$ZrTe_5$: A complex, layered chalcogenide

Material of interest as a Dirac Semimetal

Corrugated layering structure

Orthorhombic, *Cmcm*

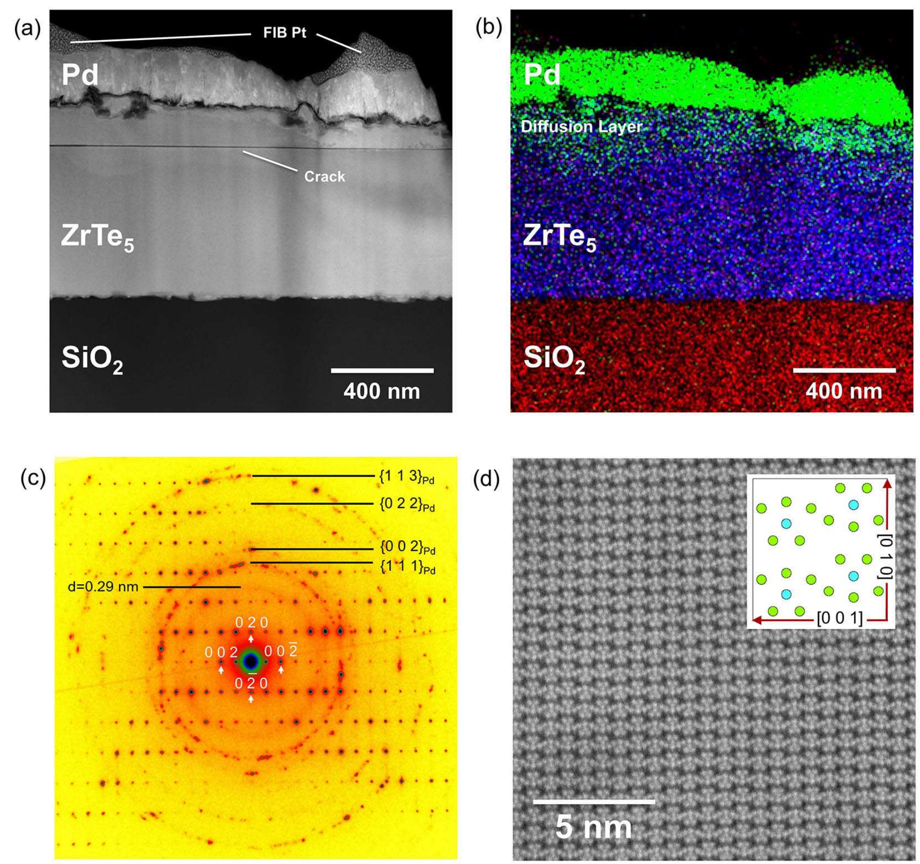


[1 0 0] projection

a=3.9875Å, b=14.530Å, c=13.724Å

H. Fjellvåg, A. Kjekshus, Solid State Communications, 60 (2) (1986) 91-93

Interdiffusion of contact metallization causes large strains

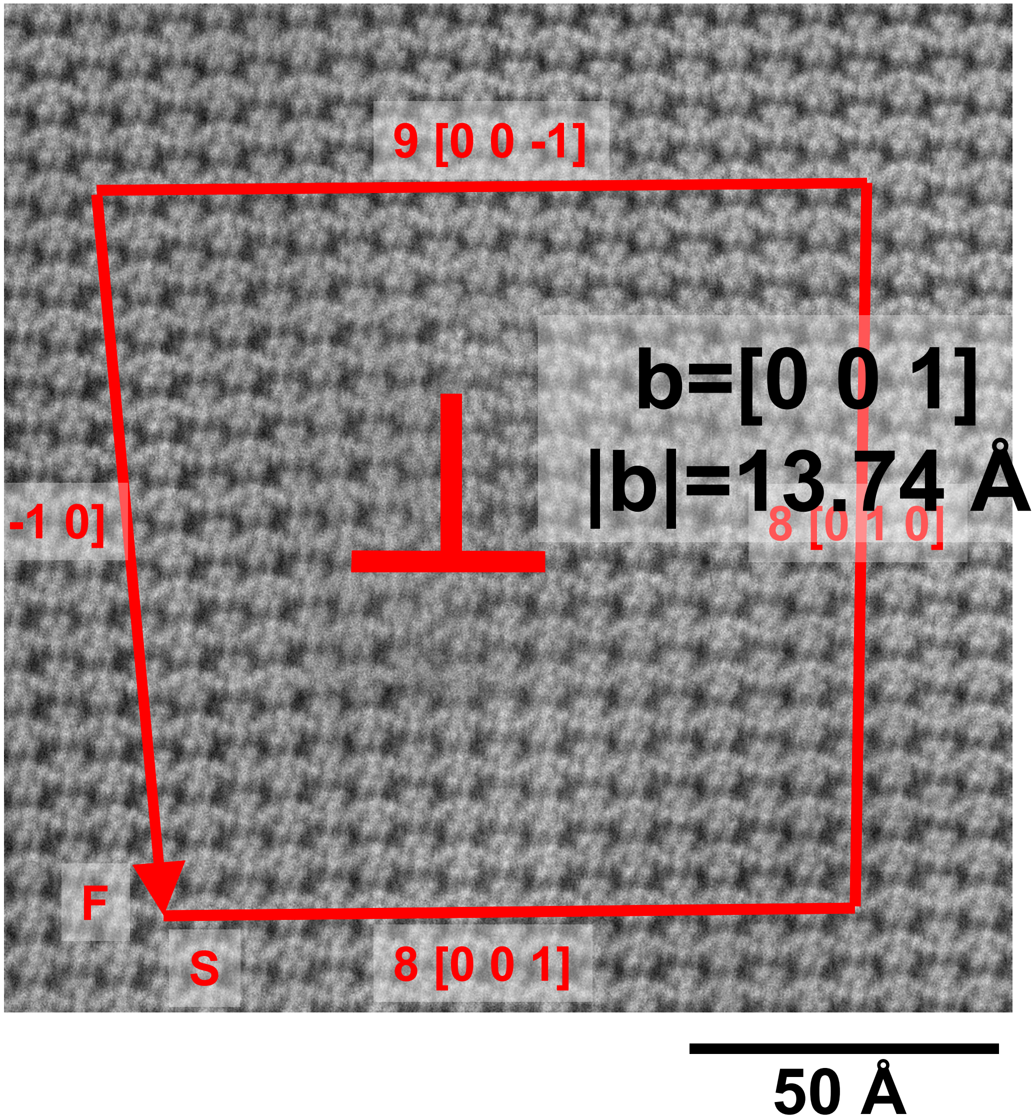


F. Léonard, W.L. Yu, K.C. Collins, D.L. Medlin, J.D. Sugar, A.A. Talin, W. Pan
ACS Applied Materials and Interfaces 9 (42) (2017) 37041-37047

Sandia National Laboratories

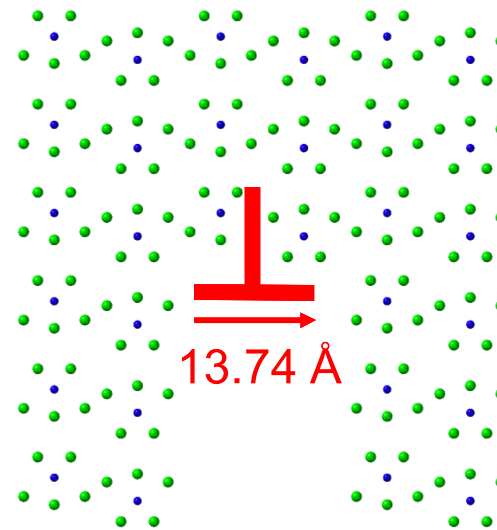
Dislocation Structure in Zirconium Telluride

HAADF-STEM



$ZrTe_5$ Crystal structure

Orthorhombic, *Cmcm*



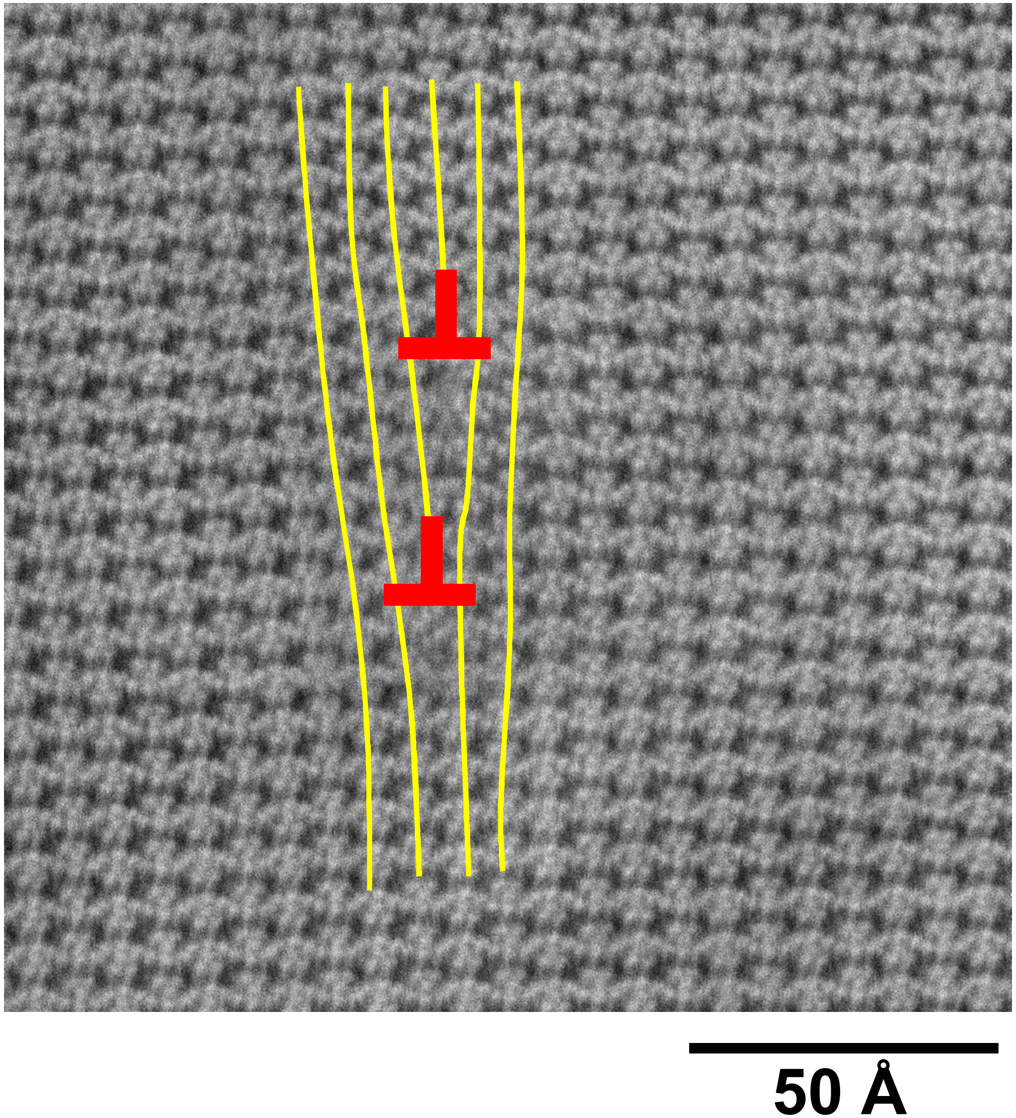
[1 0 0] projection

a=3.9875Å, b=14.530Å, c=13.724Å

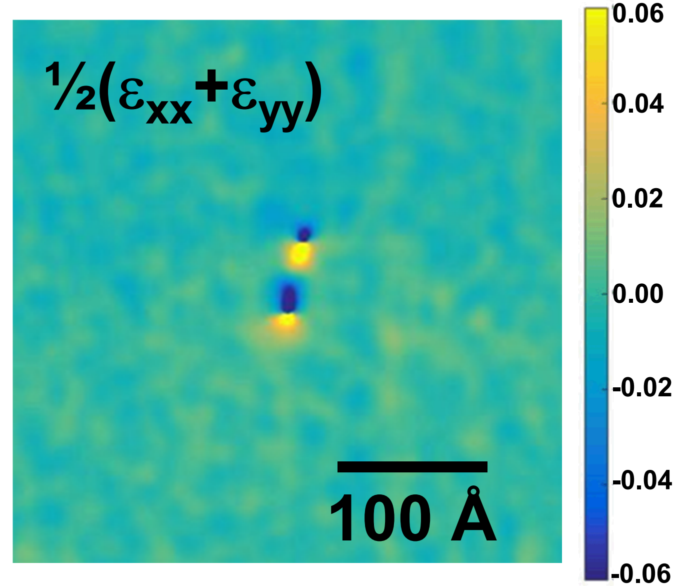
H. Fjellvåg, A. Kjekshus, Solid State Communications, 60 (2) (1986) 91-93

Dislocation Structure in Zirconium Telluride

HAADF-STEM



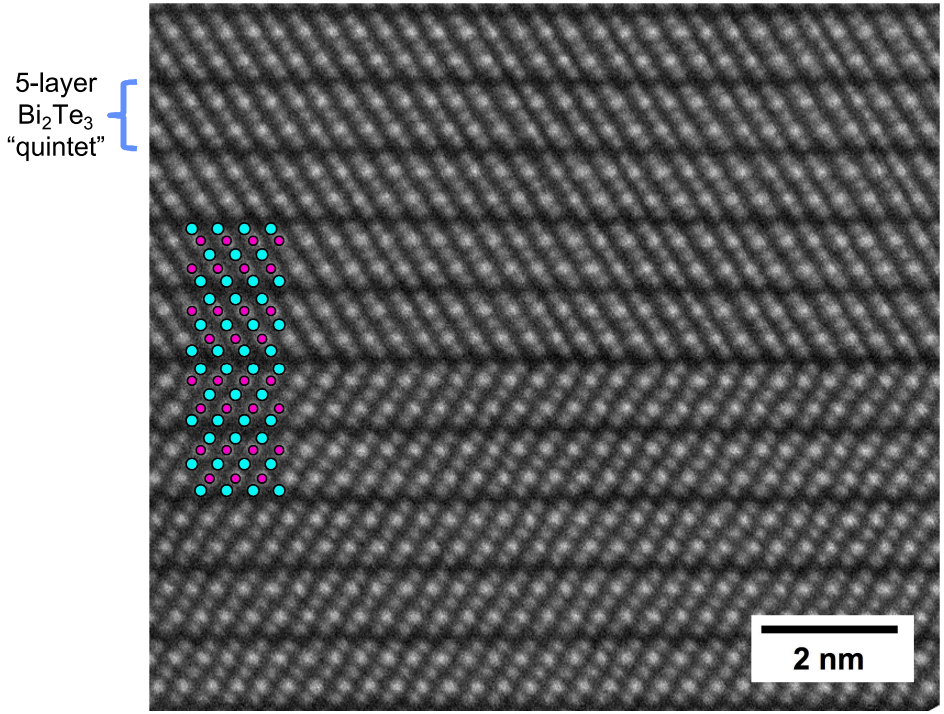
GPA Strain Map



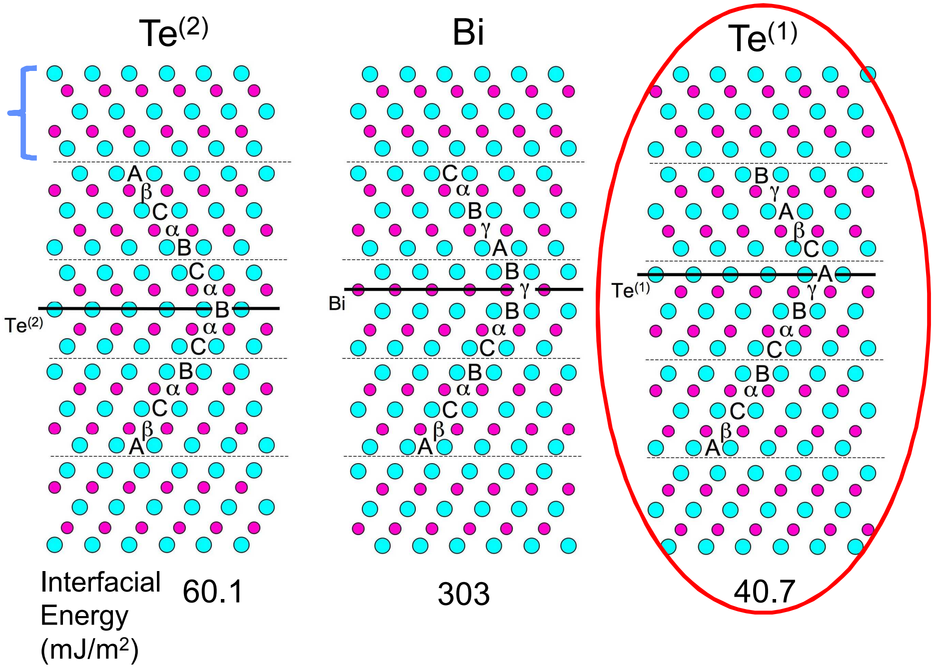
Climb dissociation into two ½[0 0 1] partial dislocations

Atomic Structure of the Bi_2Te_3 Basal Twin: Energetic preference for termination at $Te^{(1)}$ sites

HAADF-STEM Imaging:
Twin Boundary Terminated at $Te^{(1)}$ layer



DFT Calculations:
Three Possible Compositional Terminations



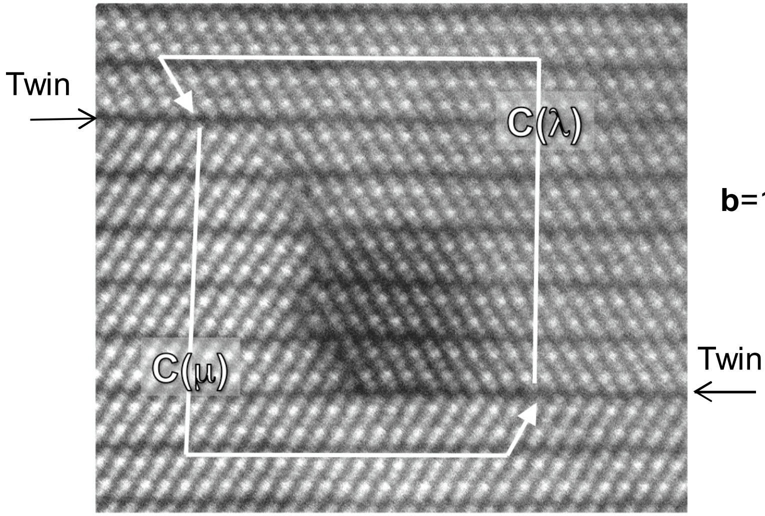
Collaboration with LBNL *National Center for Electron Microscopy*
TEAM 0.5 Microscope

D.L. Medlin, Q.M. Ramasse, C. D. Spataru, N.C. Yang, J. Appl. Phys. (2010)

Sandia National Laboratories

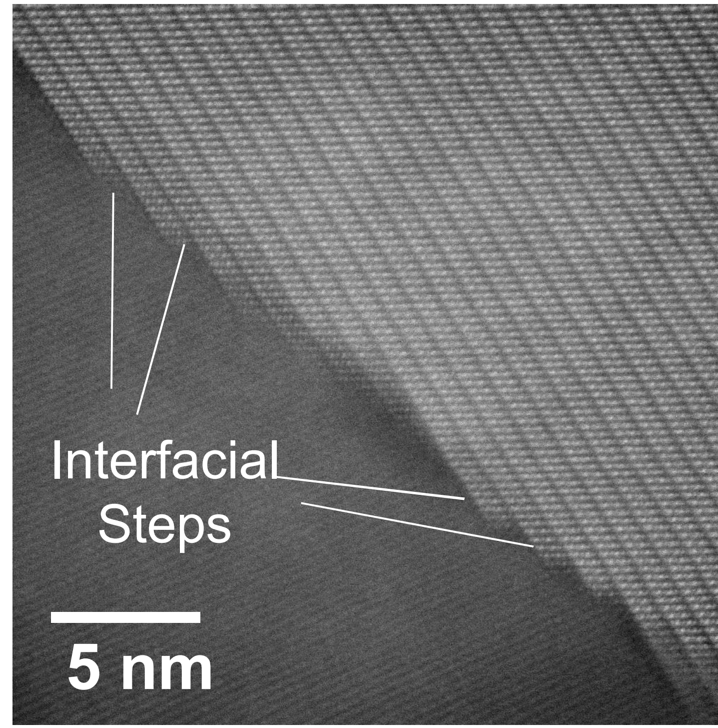
Preferential termination at $Te^{(1)}$ layers: Impact on boundary morphology

Example: step in Bi_2Te_3 Basal Twin:
25 planes high (5 quintuple layers)

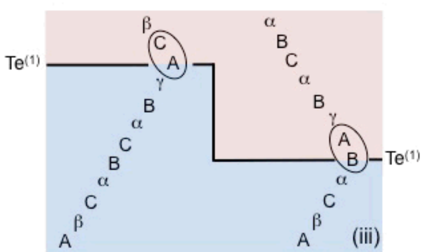


b=1/3<10-10>

Grain boundary vicinal to (0001):
Steps of integral 5-plane Bi_2Te_3 Quintets

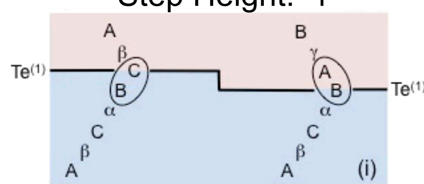


Step Height: 5

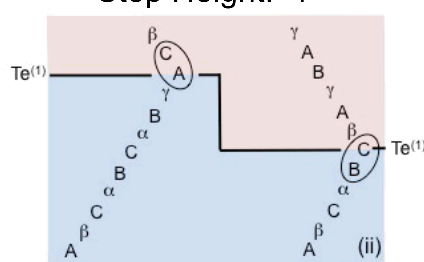


b=1/3<10-10>

Step Height: 1



Step Height: 4

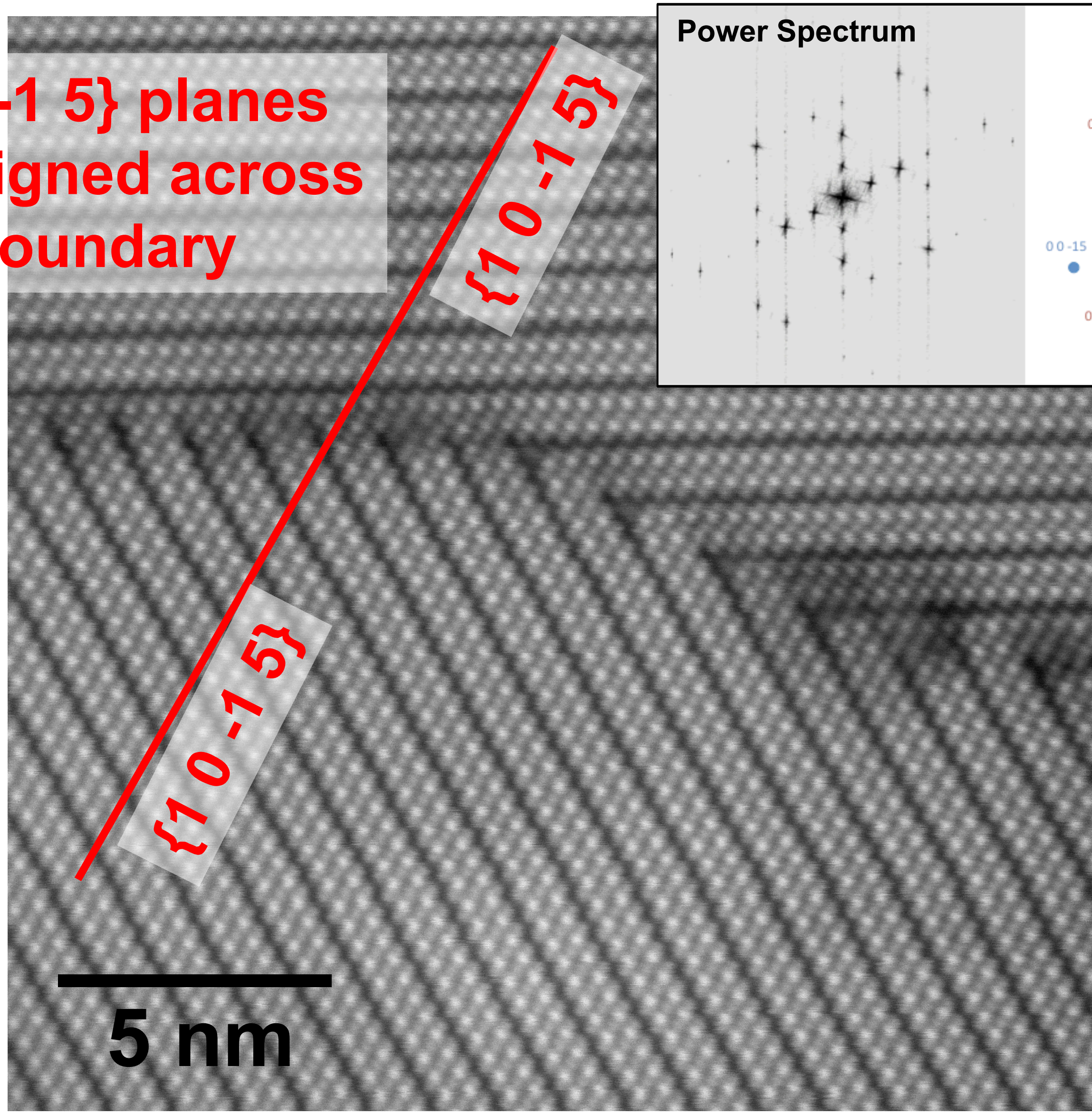


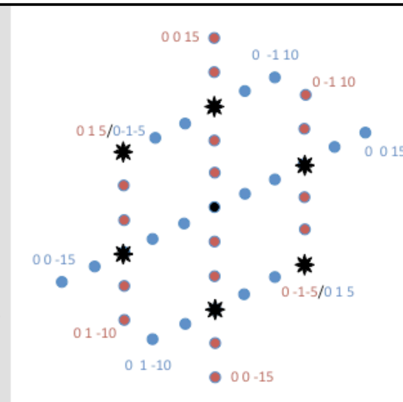
Medlin and Yang, Journal of Electronic Materials, (2012)

Medlin and Snyder, JOM (2013)

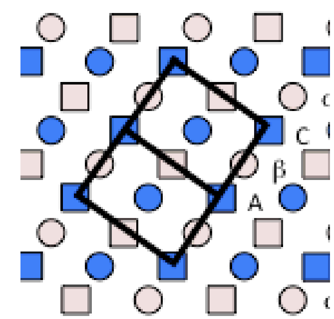
Sandia National Laboratories

Atomic-resolution observations:
Boundary with {1 0 -1 5} twin orientation relationship





HAADF-STEM
300 keV

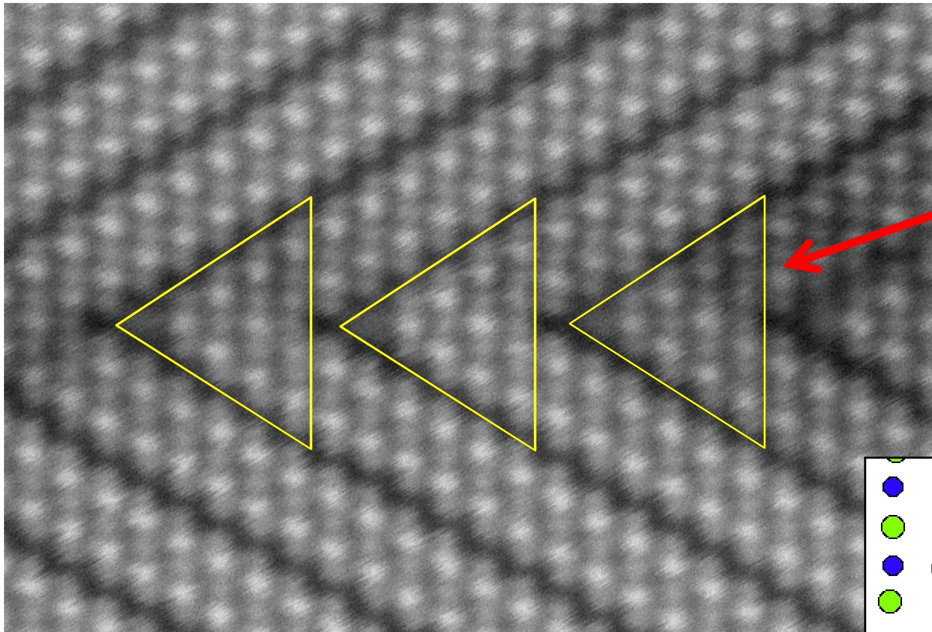


{1 0 -1 5} planes in Bi_2Te_3 analogous to {100} planes in rocksalt

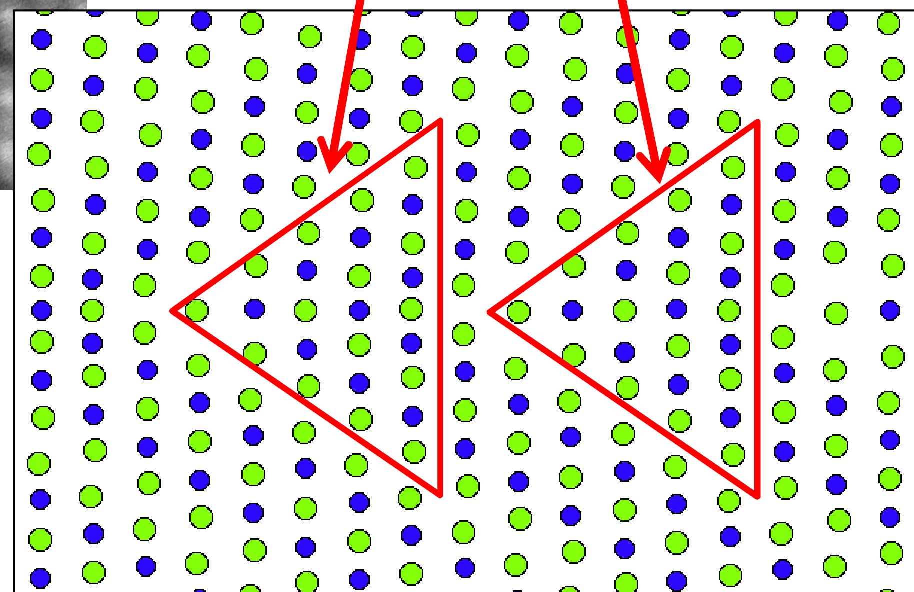
Sandia National Laboratories

Symmetrical Interface Configuration

(0,-1,1,13) interface inclination (rational approximant)



Rocksalt coordinated grain boundary units



Each triangular unit:
10 Bi 15 Te

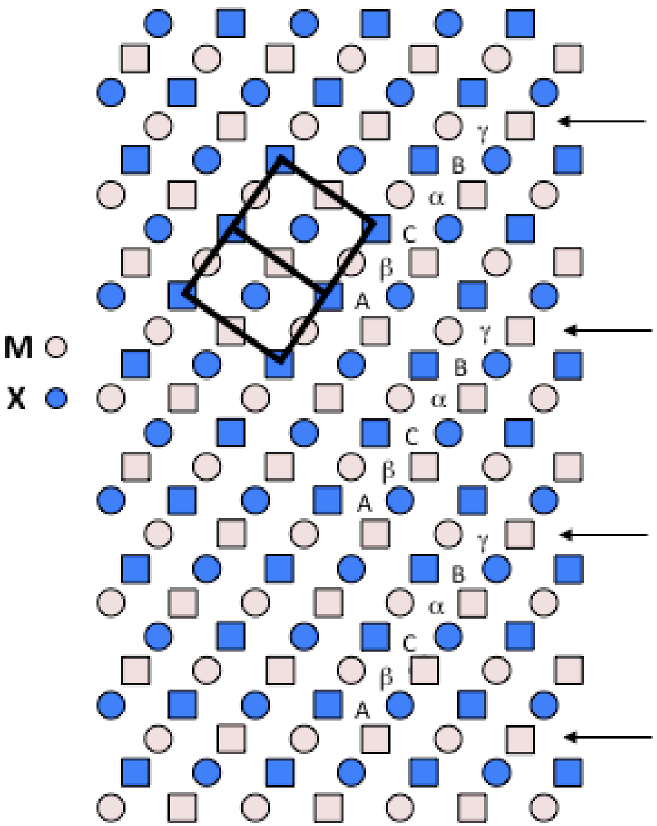
2:3 ratio of Bi and Te maintained at interface

Sandia National Laboratories

Heterophase Rocksalt/Tetradymite interfaces

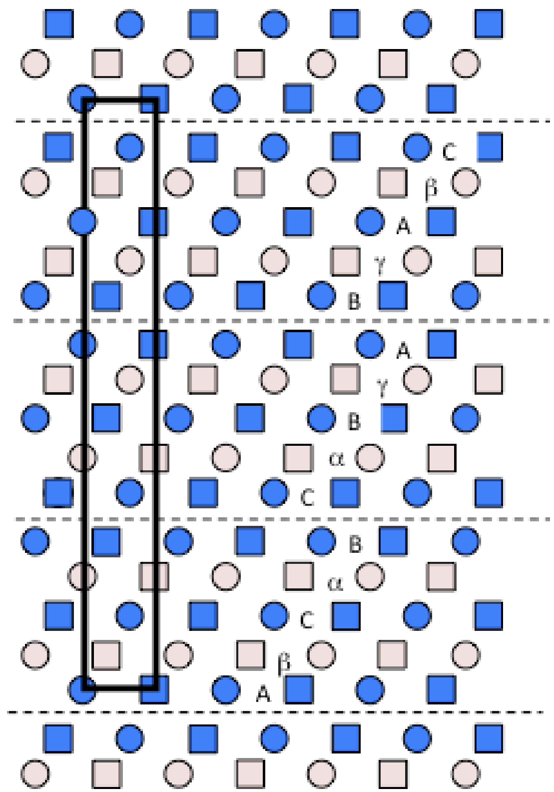
Rocksalt (MX) Structure

Fm-3m

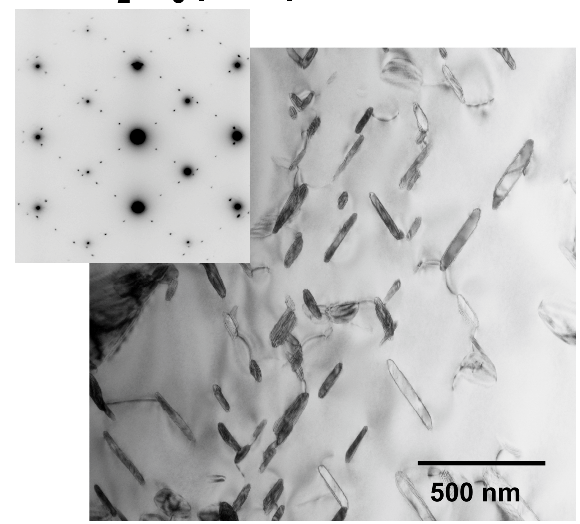


Tetradymite (M_2X_3) Structure

R-3m



Example:
Crystallographically Aligned Sb_2Te_3 precipitates in PbTe



Heinz, Snyder, Ikeda, and Medlin, Acta Mat. 2011

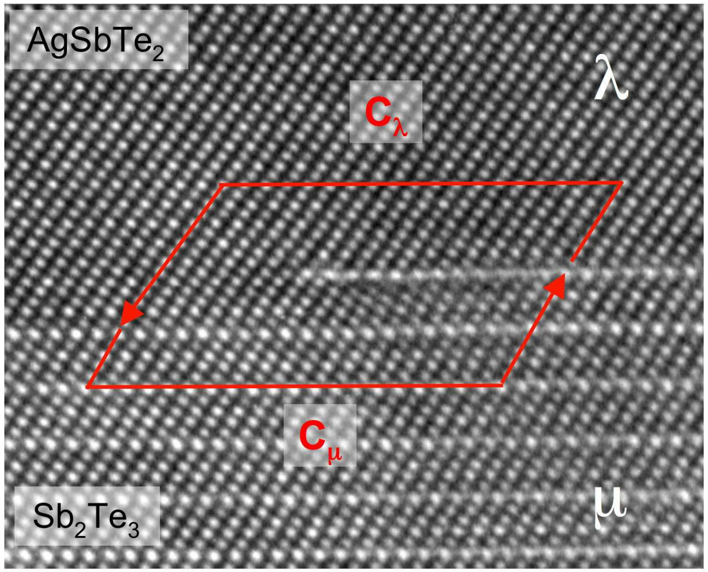
Disconnections help us understand atomic mechanisms for precipitate growth and strain accommodation

Sandia National Laboratories

Disconnections in Phase Transformations

Example: Sb_2Te_3 precipitate in $AgSbTe_2$ thermoelectric

Burgers vector:



Upper crystal circuit

Lower crystal circuit

$$\mathbf{b} = -(\mathbf{C}_\lambda + \mathbf{P}\mathbf{C}_\mu)$$

-Coordinate Transformation from Tetradymite to Rock-salt.

-Coherently strained reference Frame (0.79% misfit)

Medlin and Sugar, Scripta Materialia, 2010.

Resolve b into components normal and parallel to interface

$$\mathbf{b}_n = (a_{cub} - c_{hex}/3\sqrt{3})[111]$$

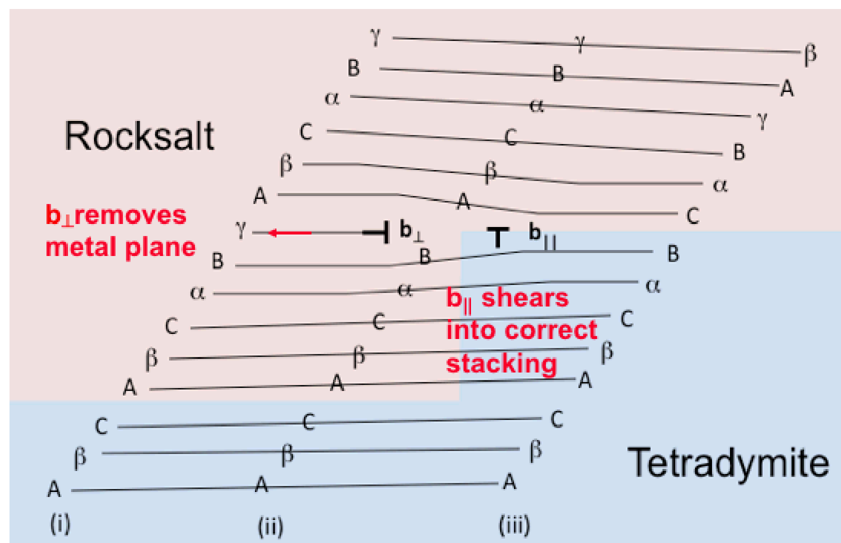
•mismatch of step heights.

•$|b_n|$=0.3747Å

$$\mathbf{b}_{||} = \frac{a_{cub}}{6}[\bar{1}2\bar{1}]$$

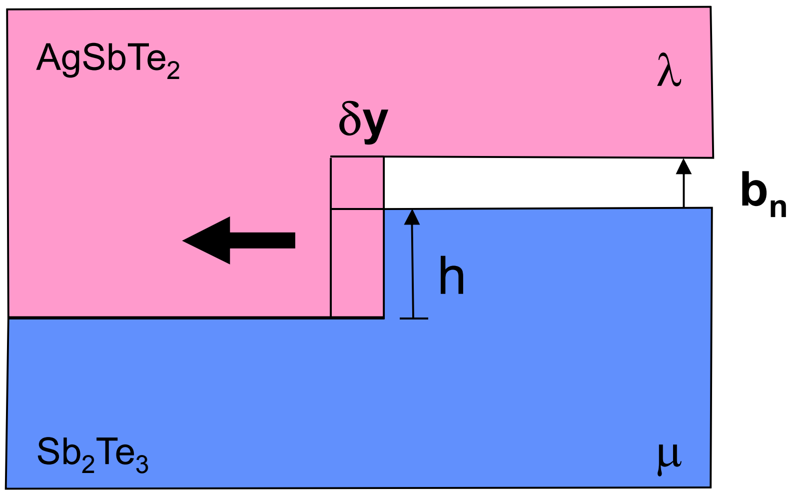
•Analogous to Shockley partial Dislocation

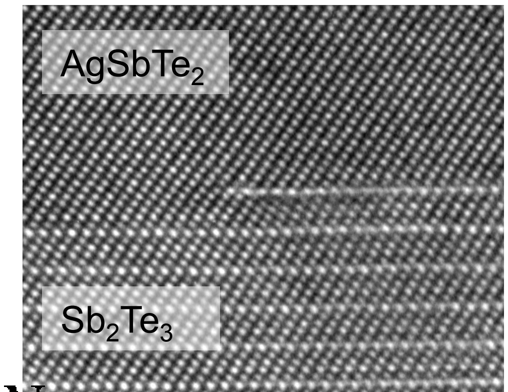
•$|b_{||}|$=2.48Å



Defect properties give local mass flux required for transformation

Partition flux for defect motion into step and dislocation components





$$\frac{\Delta N_i}{L\delta y} = \underbrace{(\chi_i^{\lambda} - \chi_i^{\mu})h}_{\text{step}} + \underbrace{\chi_i^{\lambda} b_n}_{\text{dislocation}}$$

Hirth & Pond, Acta Mat 1996

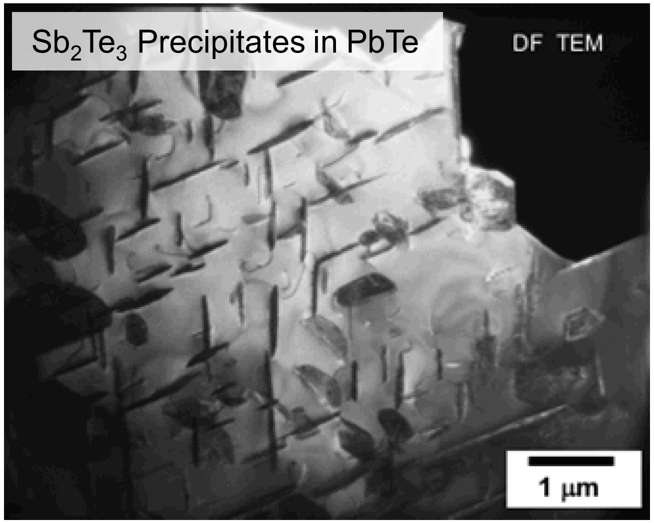
Species	Step flux (atoms/Å²)	Dislocation flux (atom/Å²)	Total flux (atom/Å²)
Ag	$\frac{2}{3}\frac{c_{hex}}{a_{cub}^3}$ +0.09043	$\frac{2}{a_{cub}^3}\left(\sqrt{3}a_{cub} - c_{hex}/3\right)$ +0.00334	$\frac{2\sqrt{3}}{a_{cub}^2}$ +0.09377
Sb	$\frac{2}{3}\frac{c_{hex}}{a_{cub}^3} - \frac{8\sqrt{3}}{3a_{cub}^2}$ -0.03459	$\frac{2}{a_{cub}^3}\left(\sqrt{3}a_{cub} - c_{hex}/3\right)$ +0.00334	$-\frac{2\sqrt{3}}{3a_{cub}^2}$ -0.03126
Te	$-\frac{4}{a_{cub}^3}\left(\sqrt{3}a_{cub} - c_{hex}/3\right)$ -0.00668	$+\frac{4}{a_{cub}^3}\left(\sqrt{3}a_{cub} - c_{hex}/3\right)$ +0.00668	0

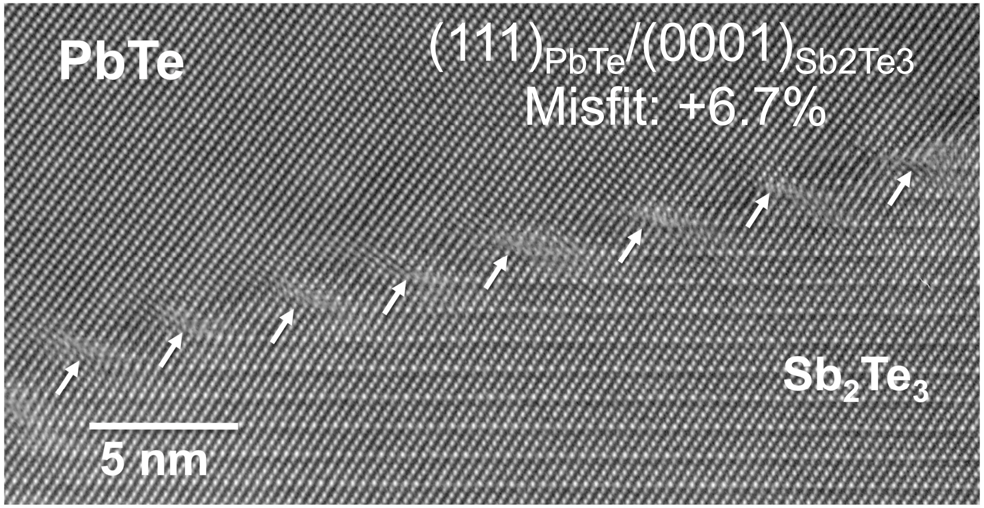
Reject Ag and Incorporate Sb in ratio of 3:1

Tellurium:
Step and Dislocation fluxes cancel.
No long-range Te transport required.

Sandia National Laboratories

A Rocksalt/Tetradymite Interface with Large Misfit





Sandia National Laboratories

Relationship between disconnection spacing and misfit strain

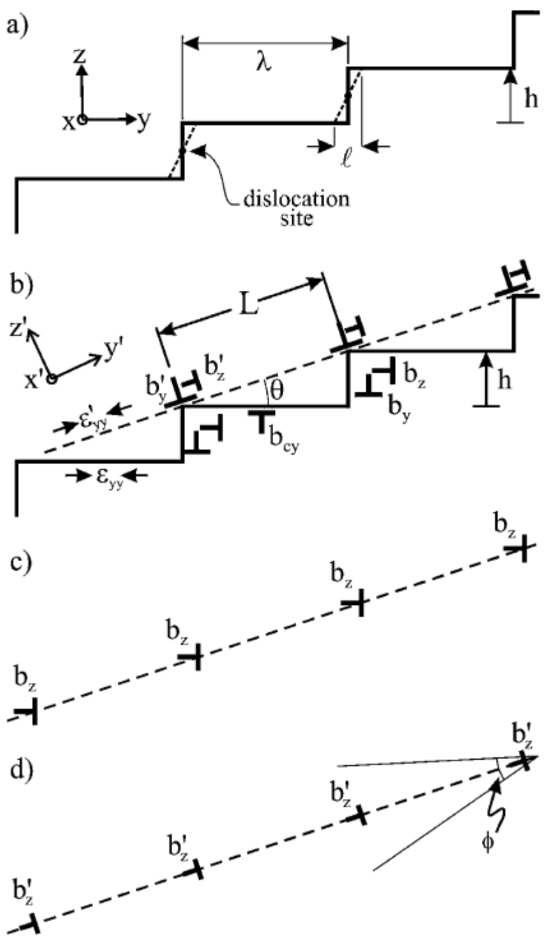


Fig. 6. Schematic illustration of the defect configuration of the HP (a) steps, (b) disconnections and coherency defects, (c) offset dislocation components b_z, and (d) dislocation components b'_z.

Pergamon

Available online at www.sciencedirect.com

SCIENCE DIRECT

Acta Materialia 51 (2003) 5385–5398

Acta MATERIALIA

www.actamat-journals.com

A comparison of the phenomenological theory of martensitic transformations with a model based on interfacial defects

R.C. Pond [a,*], S. Celotto [a], J.P. Hirth [b]

[a] *Department of Engineering, University of Liverpool, Brownlow Hill, Liverpool L69 3BX, UK*
[b] *114 E. Ramsey Canyon Road, Hereford, AZ 85615, USA*

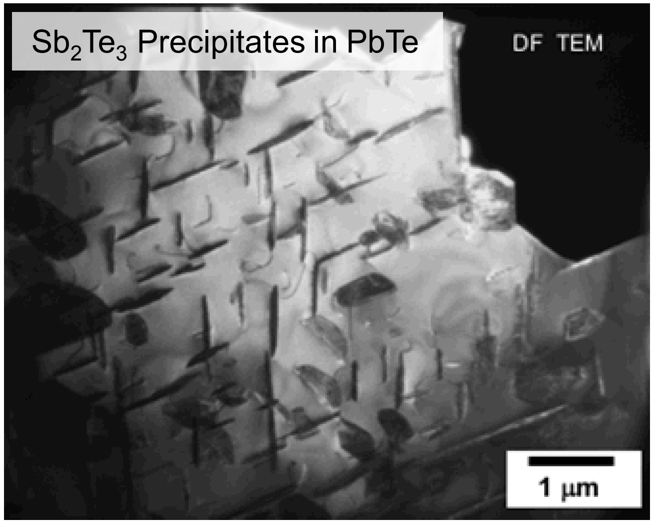
Received 25 June 2003; received in revised form 25 June 2003; accepted 11 July 2003

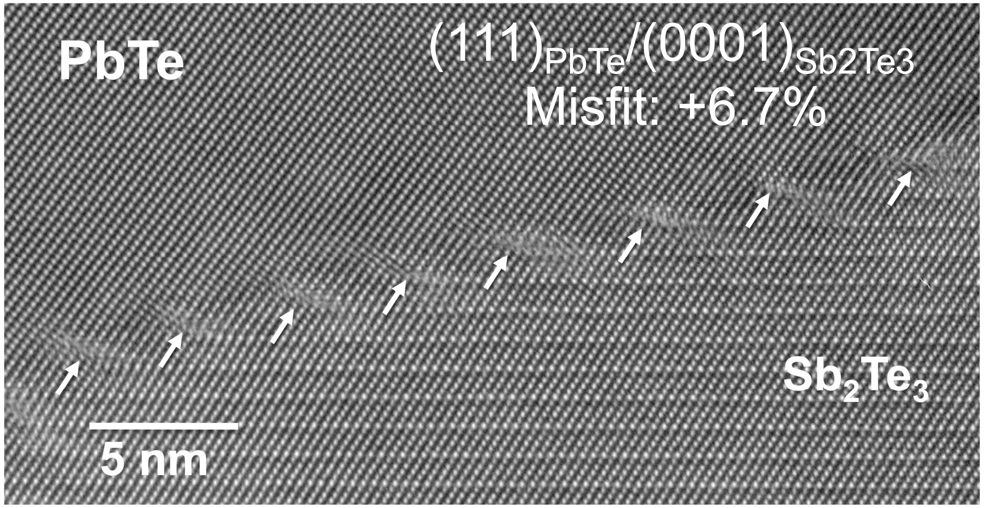
•Adjust spacing so that dislocation content of the disconnections balances the coherency strain on the terraces.

•Dislocation components resolved onto habit plane

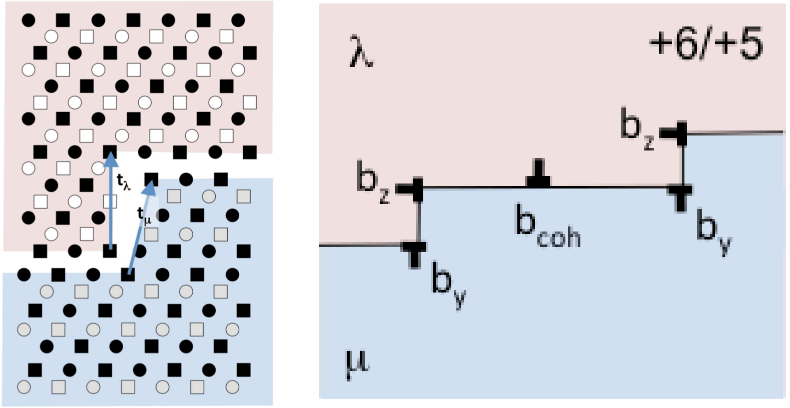
Sandia National Laboratories

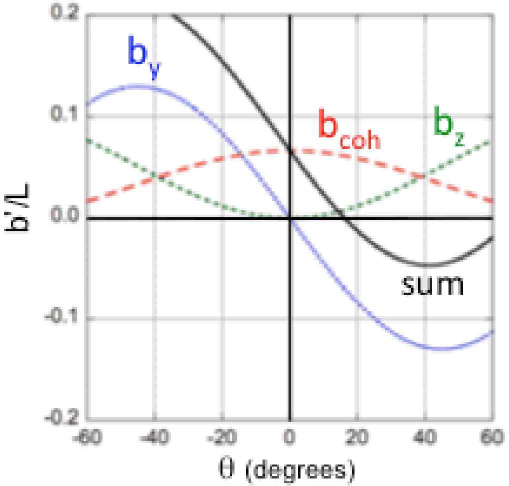
A Rocksalt/Tetradymite Interface with Large Misfit





+6/+5





Habit plane inclination:

Measured: 14.8°
Predicted: 16.2°

Defect spacing accommodates the (111)/(0001) coherency strain.

Heinz, Ikeda, Snyder, Medlin, Acta Materialia (2011)

Sandia National Laboratories

Conclusions

Key structural aspects layered chalcogenides are manifested in the detailed structures of extended defects in these materials.

Weak, van der Waals bonding across double chalcogenide layers

Ability to accommodate non-stoichiometry through altering the layer stacking

Close inter-relationship between the rocksalt and tetradymite structural types.

Attention to the topological properties and detailed structure of extended defects in the chalcogenides is critical.

Understanding interfacial formation and stability and, ultimately, interfacial electronic and thermal transport properties

Set of elementary "building blocks" for a general picture of dislocation and interfacial structure in layered chalcogenides

Sandia National Laboratories

Acknowledgements

Sandia/Livermore

K. Erickson, J.D. Sugar, N.Y.C. Yang, C.Spataru

Sandia/Albuquerque

M. Siegal, S. Limmer, W.G. Yelton

LBNL/NCEM

Q. Ramasse (present address, SuperSTEM Laboratory, Daresbury, UK)

California Institute of Technology

N.A. Heinz, T. Ikeda, G.J. Snyder (present address Northwestern Univ)

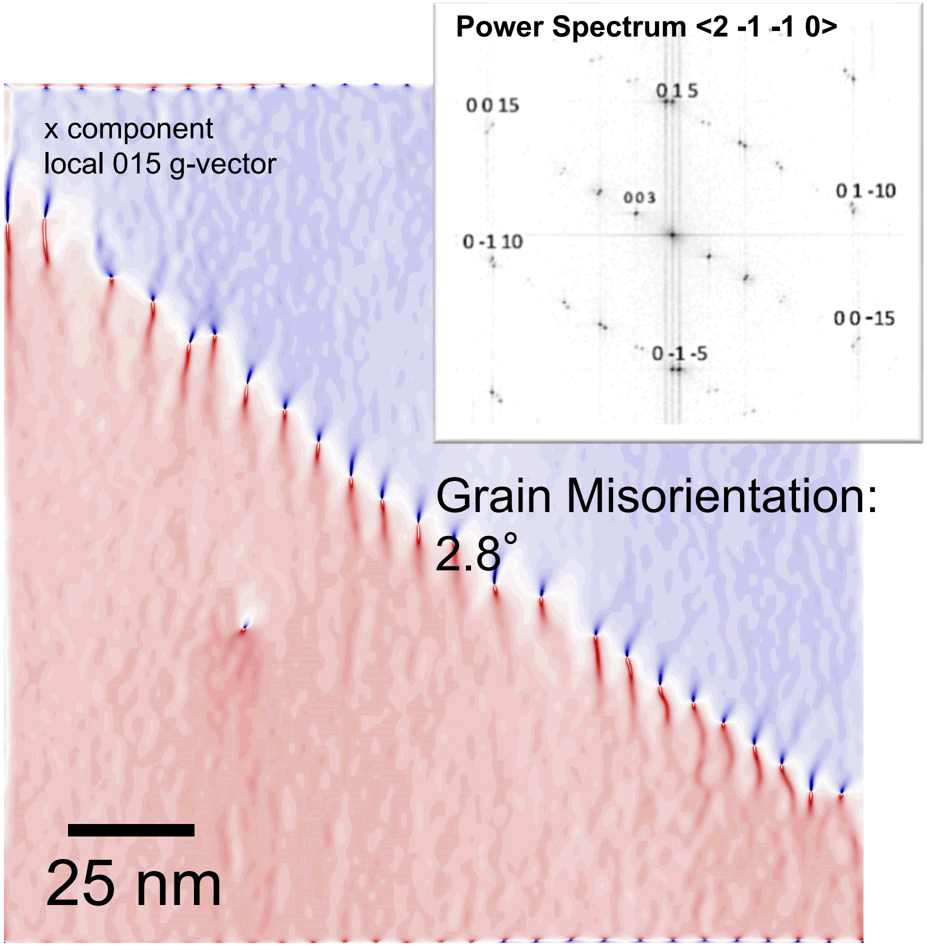
Sandia National Laboratories is a multimission laboratory managed and operated by National Technology and Engineering Solutions of Sandia, LLC., a wholly owned subsidiary of Honeywell International, Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA-0003525.

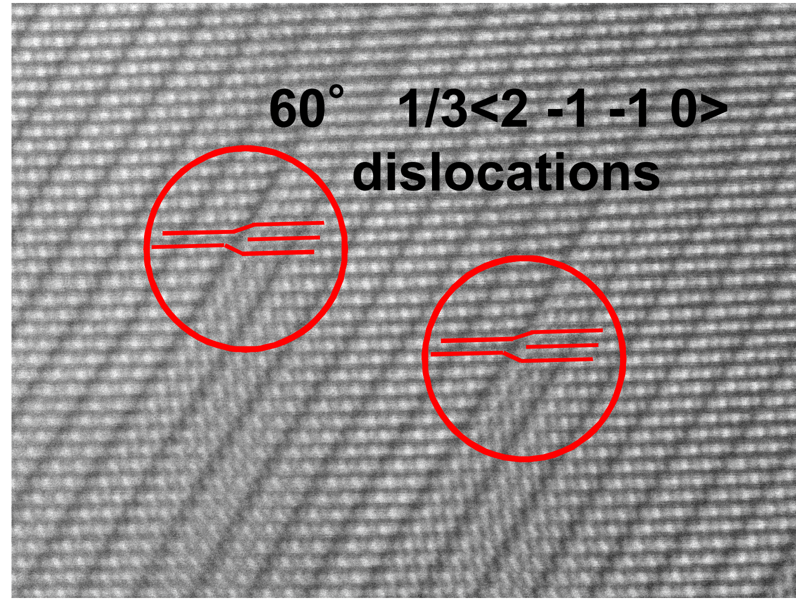
Sandia National Laboratories

extra

Array of 1/3<2-1-1 0> Dislocations

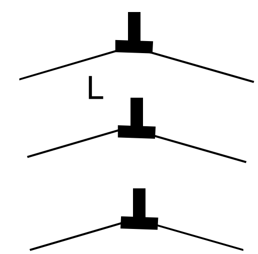
A Low Angle Tilt Boundary in Bi_2Te_3





Calculate tilt rotation from dislocation density

$$\theta = 2\sin^{-1}\left(\frac{b_{edge}}{2L}\right)$$



= 2.7° (calculated)
(2.8° measured)

L_{avg} = 8.0 nm
b_{edge} = 0.379 nm
(60° 1/3<2-1-10>
b=0.438 nm))

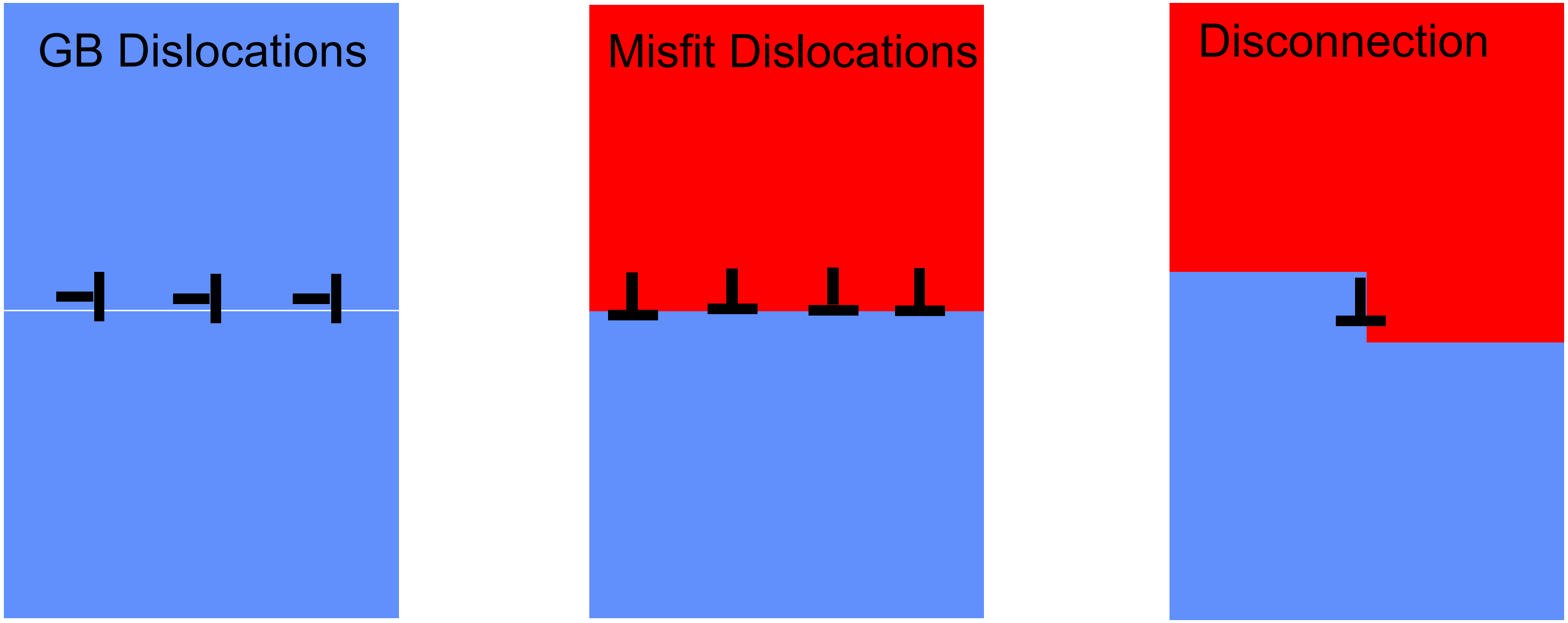
(for array of 60° dislocations, to be pure tilt, screw components must cancel)

HRSTEM
Analyzed using Geometric Phase Analysis method: Hÿtch,Snoek, Kilaas, Ultramicroscopy 1998

Sandia National Laboratories

Interfacial Defects:

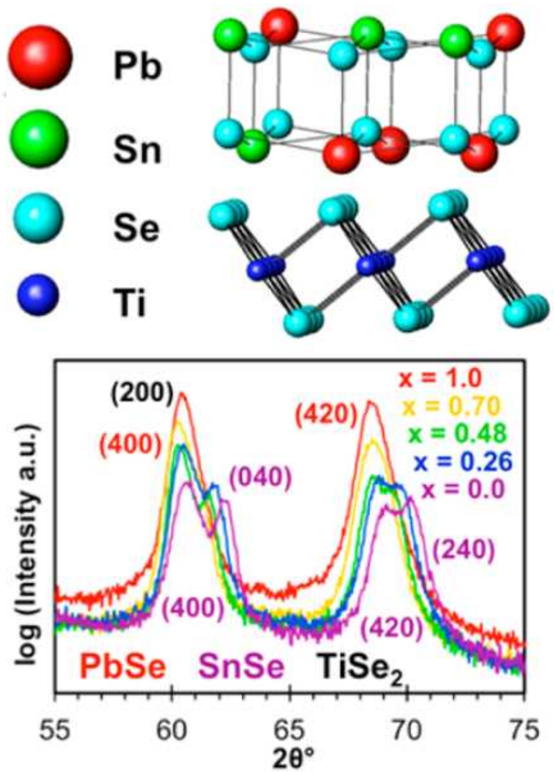
Some examples:

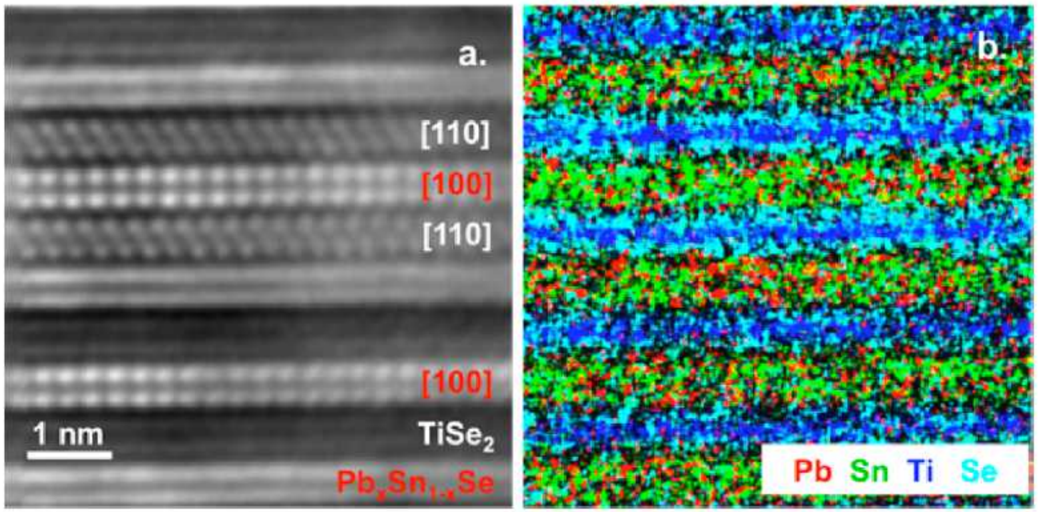


Anisotropic, layered structure of the chalcogenides, give rich interfacial defect behavior

Layered Chalcogenides: Diversity of Compositional and Structural Arrangements

Example: $(Pb_xSn_{1-x}Se)_{1+\delta}TiSe_2$ Intergrowth Compound





FEI-Titan 80-200
Chemistem

- Site specific alloying:
  - Sn, Pb on "rocksalt" bilayers
  - Separated by $TiSe_2$ tri-layers
- Crystalline sheets, but rotational, "turbostratic," disorder between layers
  - -a "ferecrystal"

D.R. Merrill, D.R. Sutherland, J. Ditto, S.R. Bauers, M.Falmbigl, D.L. Medlin, D.C. Johnson, Chemistry of Materials 27 (2015) 4066-4072.

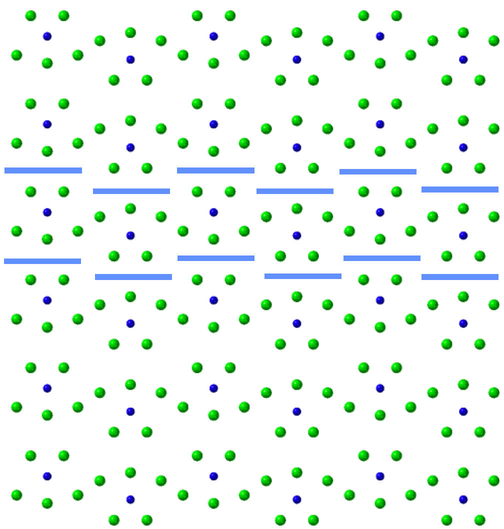
Sandia National Laboratories

$ZrTe_5$: A complex, layered chalcogenide

Material of interest as a Dirac Semimetal

Corrugated layering structure

Orthorhombic, *Cmcm*

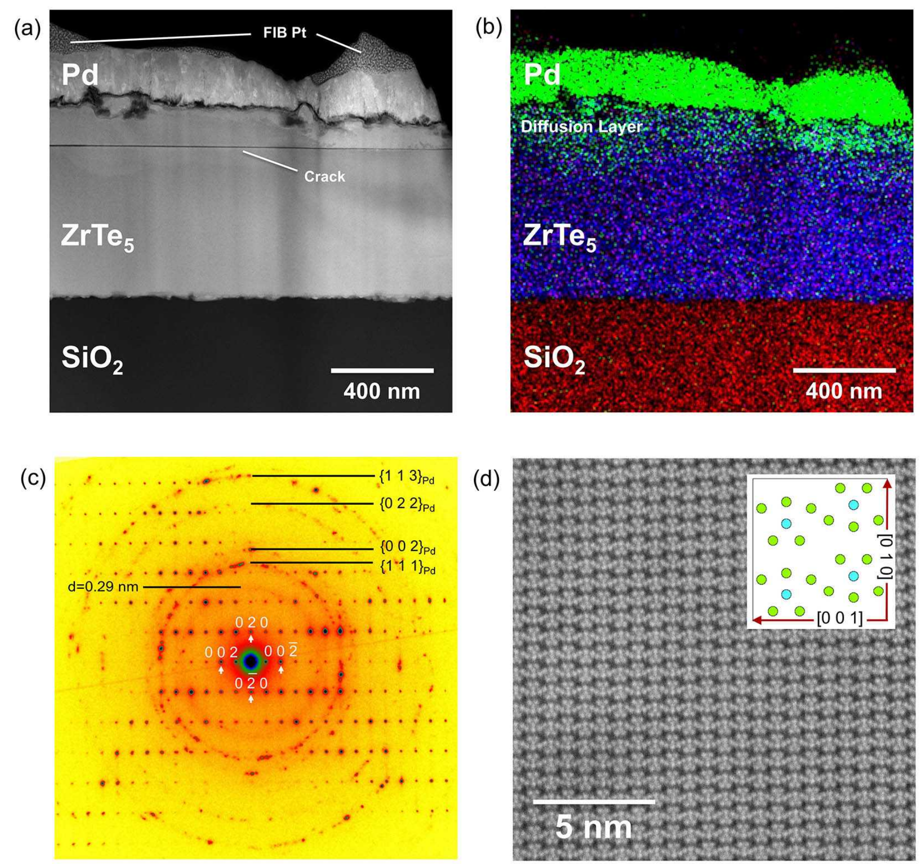


[1 0 0] projection

a=3.9875Å, b=14.530Å, c=13.724Å

H. Fjellvåg, A. Kjekshus, Solid State Communications, 60 (2) (1986) 91-93

Interdiffusion of contact metallization causes large strains

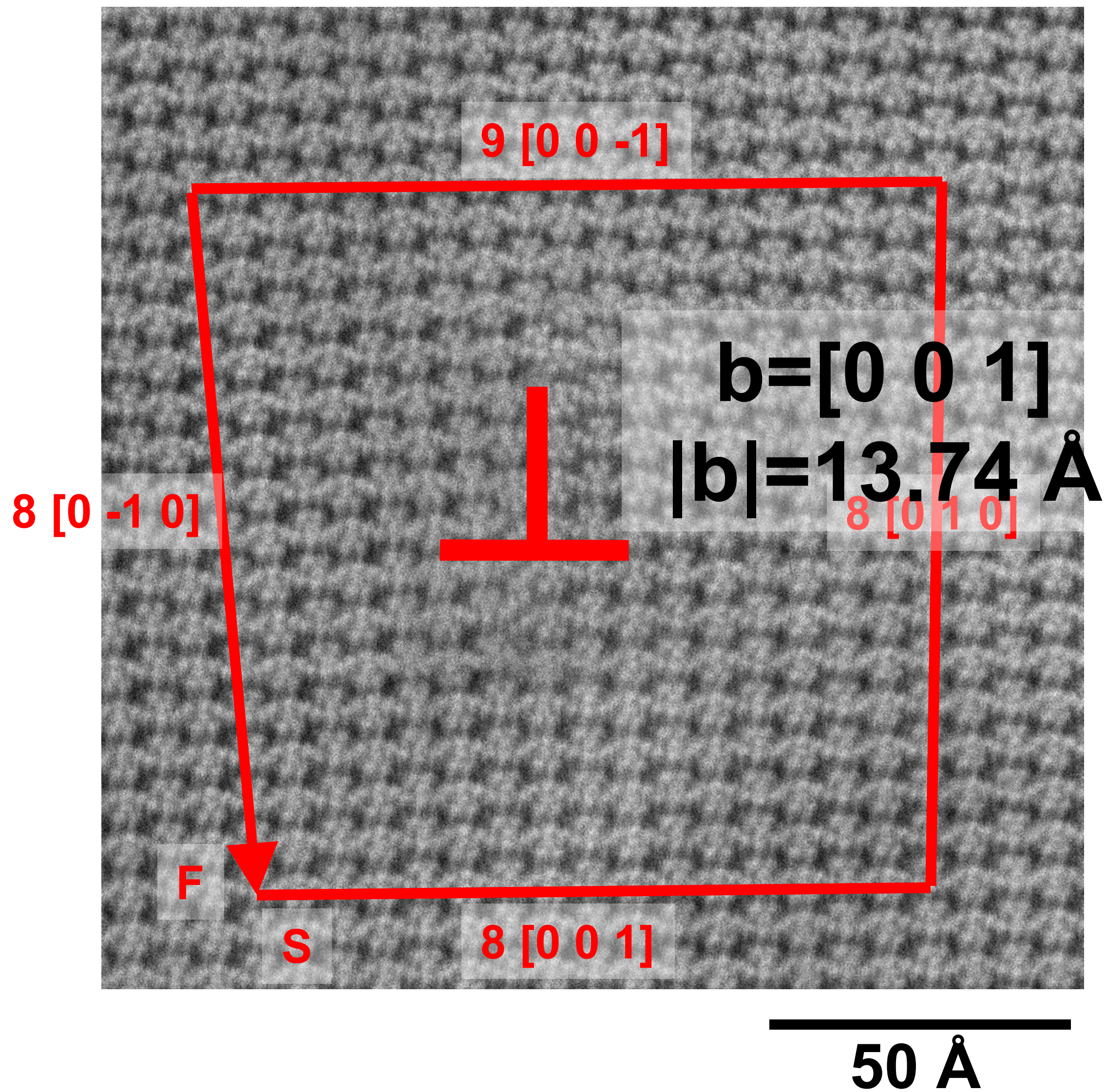


F. Léonard, W.L. Yu, K.C. Collins, D.L. Medlin, J.D. Sugar, A.A. Talin, W. Pan
ACS Applied Materials and Interfaces 9 (42) (2017) 37041-37047

Sandia National Laboratories

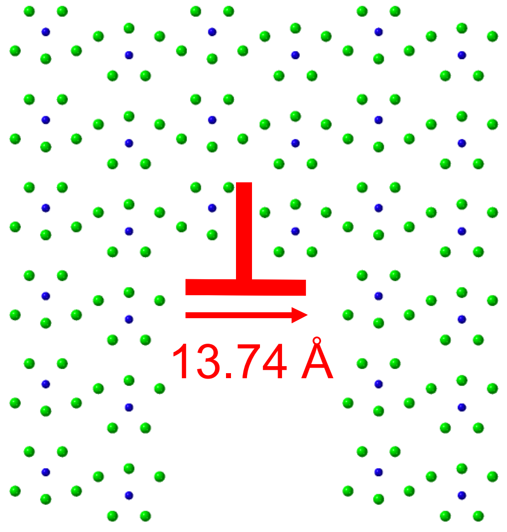
Dislocation Structure in Zirconium Telluride

HAADF-STEM



$ZrTe_5$ Crystal structure

Orthorhombic, *Cmcm*



[1 0 0] projection

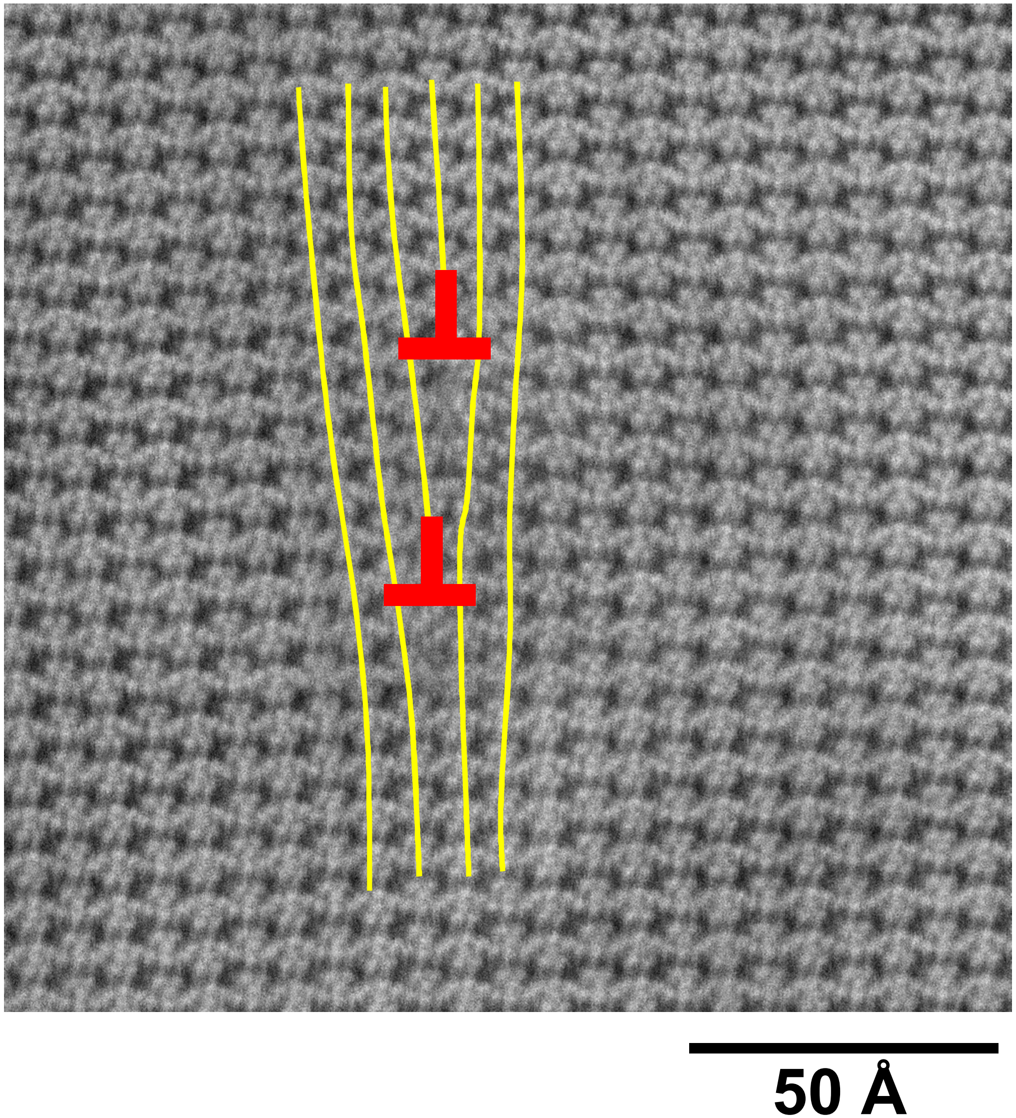
a=3.9875Å, b=14.530Å, c=13.724Å

H. Fjellvåg, A. Kjekshus, Solid State Communications, 60 (2) (1986) 91-93

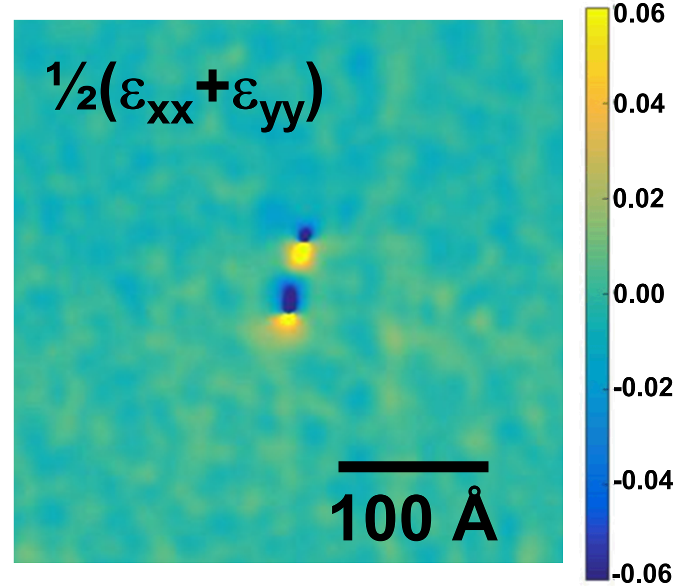
Sandia National Laboratories

Dislocation Structure in Zirconium Telluride

HAADF-STEM



GPA Strain Map



Climb dissociation into two ½[0 0 1] partial dislocations

Why care Dislocations in Layered Chalcogenides

– **Impact on transport properties**

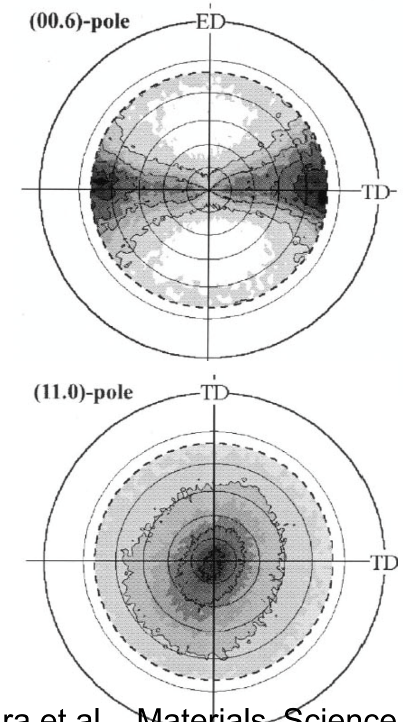
– **Processing:**

- Deformation processing is common for bulk thermoelectrics:
  – hot pressing, extrusion
- Thin film nanostructure growth, epitaxy,
  – coherency strains accommodated by interfacial defects.
  – non-stoichiometric defect cores.

– **Elementary interest:**

- Weak van der Waals bonding and complex crystal structures yield rich variety of defect configurations.

Example: Texture Control in Bi_2Te_3 via Hot-Extrusion



Miura et al., Materials. Science and Engineering. A (2000)

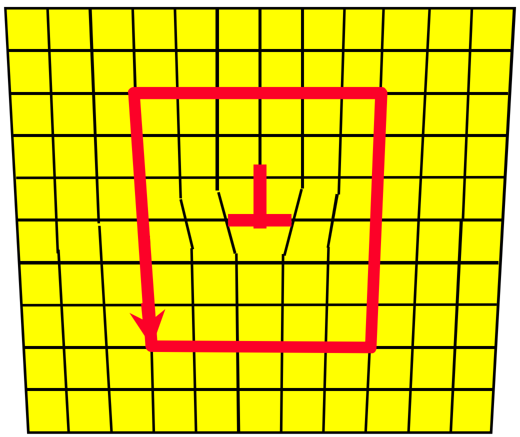
Focus for this presentation:

-Application of atomic resolution microscopy and dislocation/interface theory to understand structure of crystal defects in layered chalcogenides

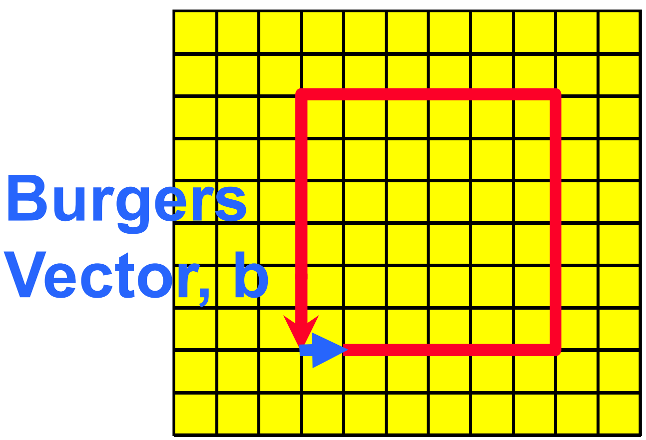
Sandia National Laboratories

How do these structural considerations impact Dislocations and Interfaces?

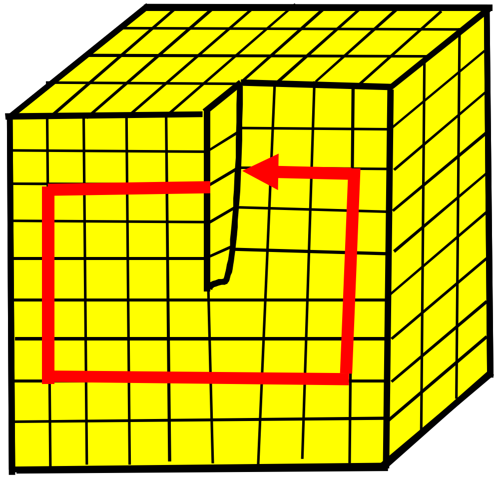
Edge Dislocation



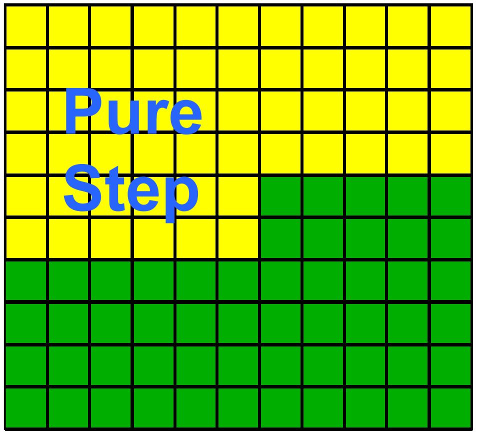
Reference Frame:
Perfect Crystal

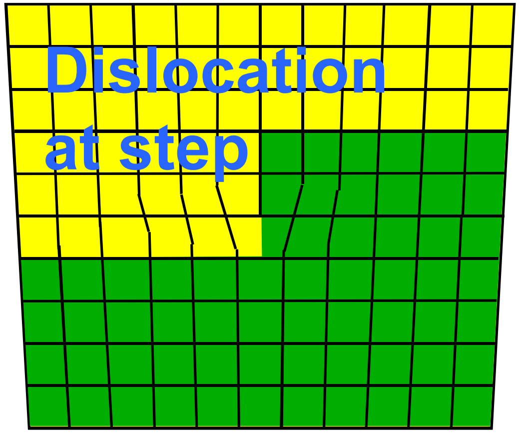


Screw Dislocation



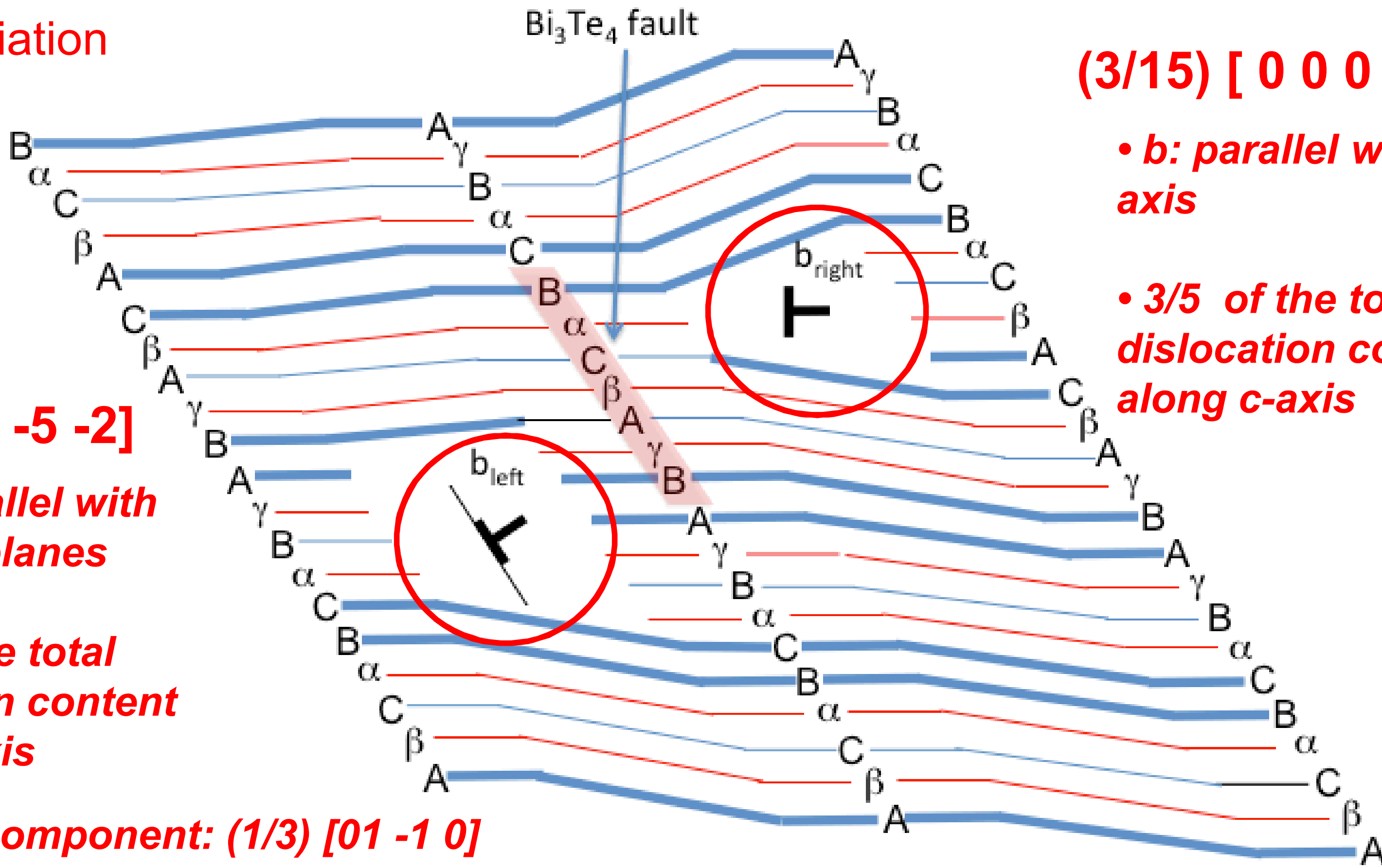
Interfacial Disconnection





7-Layer Bi_3Te_4 faults: Mechanism to accommodate Te loss during annealing

Climb dissociation



(3/15) [0 0 0 -1]

- ***b: parallel with c-axis***
- ***3/5 of the total dislocation content along c-axis***

(1/15) [0 5 -5 -2]

- ***b is parallel with (0 1 -1 5) planes***
- ***2/5 of the total dislocation content along c-axis***

Horizontal component: (1/3) [01 -1 0]

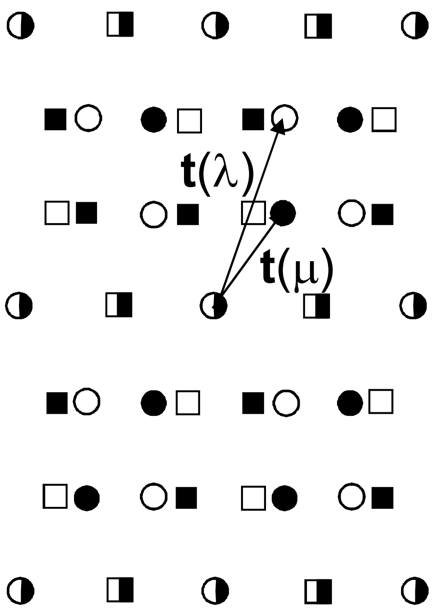
- ***analogous to Shockley partial.***
- ***avoids fault in stacking resulting from additional 2 planes at Bi_3Te_4 fault***

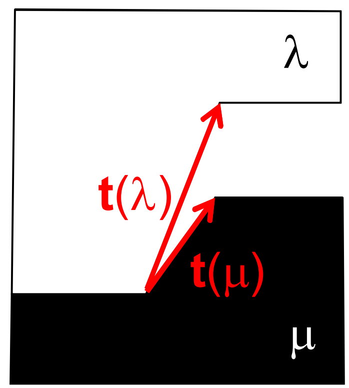
Medlin, Erickson, Limmer, Yelton, Siegal, J. Mat. Sci. 2014

Sandia National Laboratories

Interfacial Line defects: in general have both dislocation and step content

Dichromatic Pattern





$$t(\lambda) = \tfrac{1}{2}[1\bar{2}1]_\lambda$$

$$t(\mu) = \tfrac{1}{2}[101]_\mu$$

$$\mathbf{b} = \tfrac{1}{3}[1\bar{1}1]_\lambda$$

Crystal lattice translation vectors

$$\mathbf{b}_{ij} = \mathbf{t}(\lambda)_{ij} - \mathbf{P}\,\mathbf{t}(\mu)_{ij}$$

Burgers vectors of the set of "admissible" defects

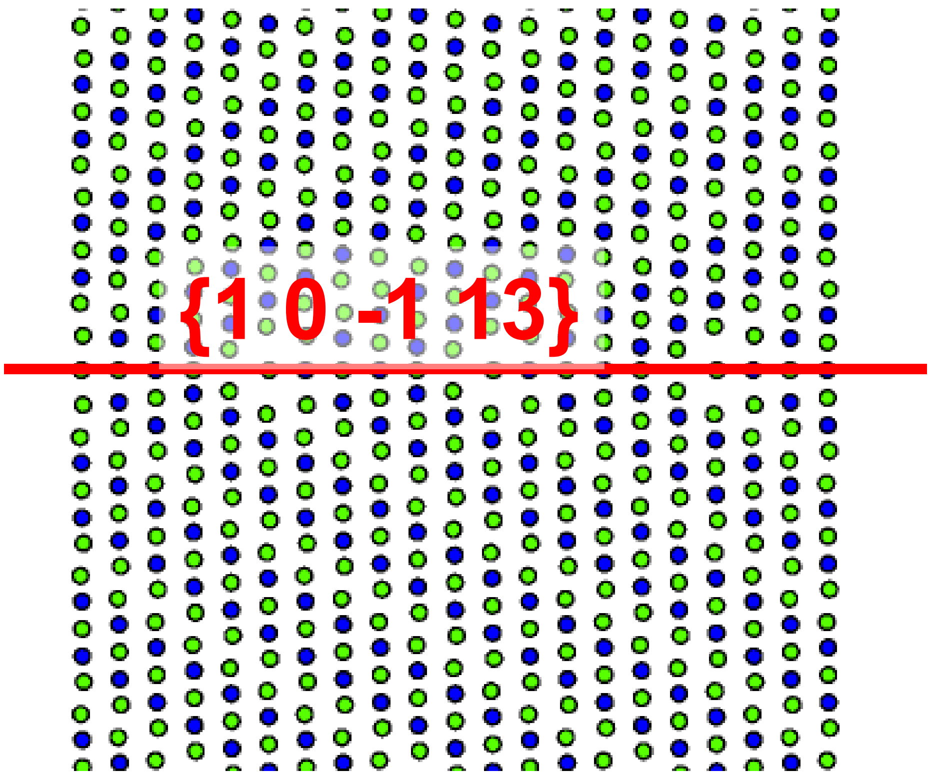
Matrix converts from μ to λ crystal coordinates

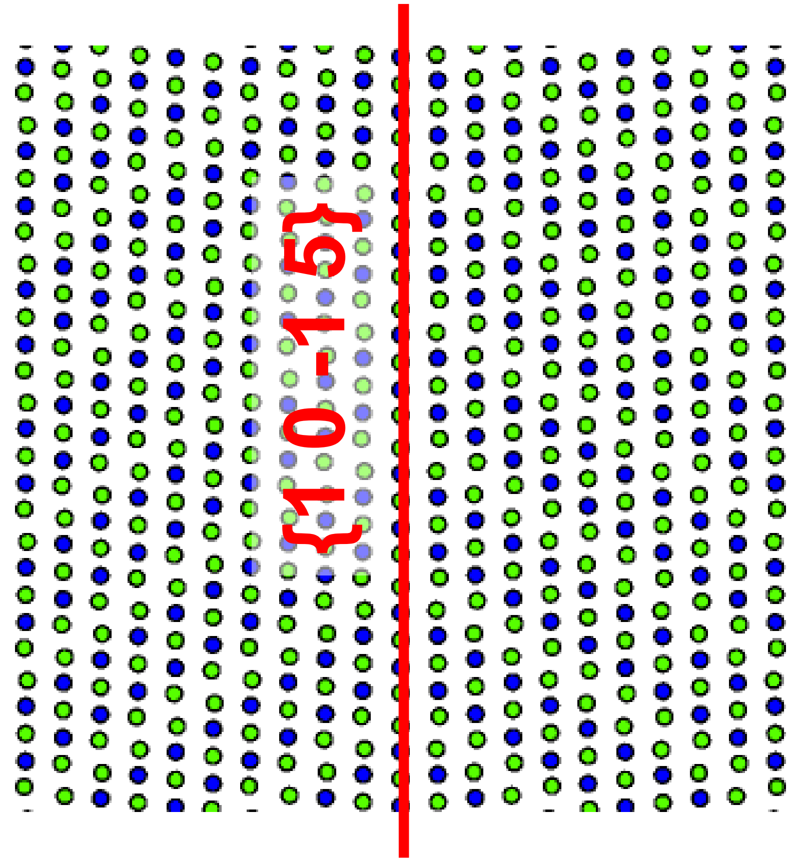
"disconnection" = both step and dislocation content

R.C. Pond, Dislocations in Solids, Chapter 38 (1989)
J. Hirth & R.C. Pond, Acta Materialia (1996)

Sandia National Laboratories

Observed Symmetric Interface: Inclination 90° from {1 0 -1 5}





Sandia National Laboratories

Observed Symmetric Interface: Configuration: close to {1 0 -1 10} twin