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Atomic-Scale Investigations of Dislocations and Interfaces in Telluride-Based Thermoelectric Materials

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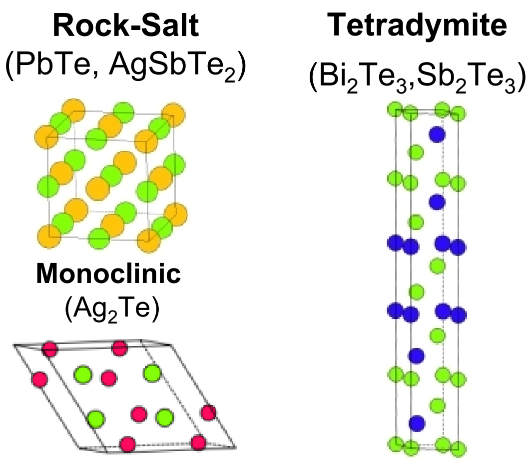
Our focus: Extended Defects in Tellurides



Rich set of structures and phase relations

<u>Longstanding importance as thermoelectrics</u>

-Bi_2Te_3-based alloys widely used for cooling and some low grade waste heat recovery applications

-p-type : $(Bi_{0.2}Sb_{0.8})_2Te_3$

-n-type $Bi_2(Te_{0.9}Se_{0.1})_3$

-PbTe and $(GeTe)_x(AgSbTe_2)_{1-x}$):

-higher T application

-unattended operation.

<u>Broader interest in Tellurides and related Chalcogenides</u>

-Topological insulators, catalysis,phase-change memory

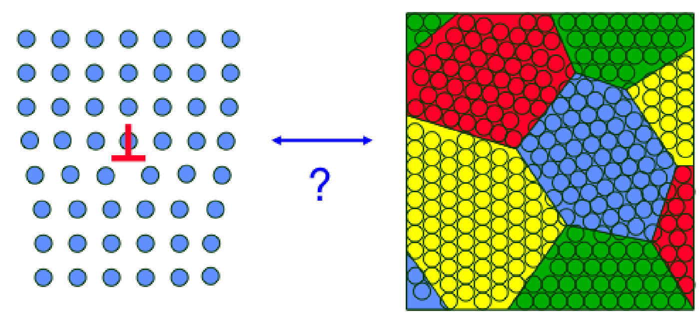
-2d materials, intergrowth compounds

<u>Interface control</u>: strategy for tailoring thermal and electronic transport.

Can we begin to make sense of interfaces and dislocations in these systems?

Our approach:

Understand structural relationships between chalcogenide phases.
Determine basic elements of interfacial structure.



Dislocations and Interfacial Line Defects:

Building blocks to general understanding of interface structure and behavior.

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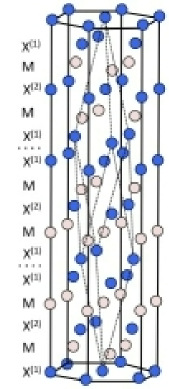
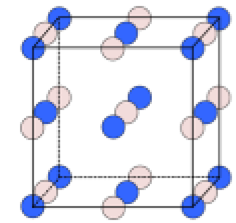
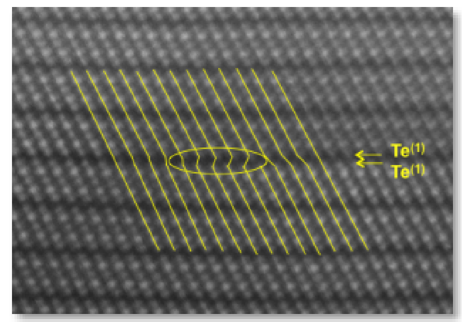
Outline

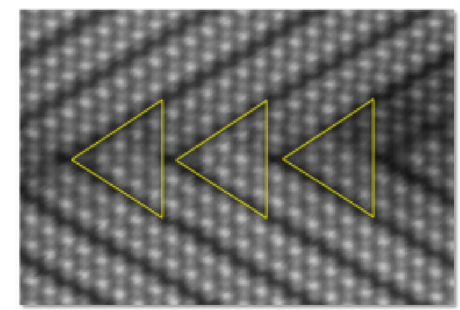
- ***Crystal structure in tetradymite-type compounds***
  - •Layered structure gives flexibility in accommodating compositional variations
  - •Close structural relationship to rock-salt chalcogenides





- ***Dislocation and Grain Boundary Structure in Bi_2Te_3***
  - •Impact of weak interlayer bonding
  - •local rock-salt coordination

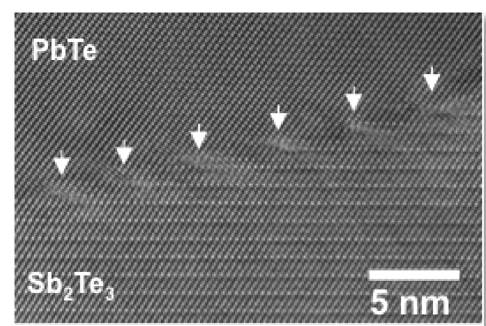


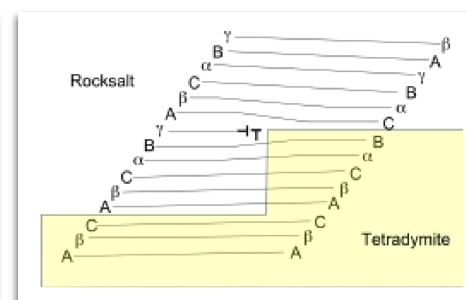


•Rocksalt/Tetradymite heterophase interfaces:

-Interfacial disconnections at Sb_2Te_3 precipitates in $AgSbTe_2$, and PbTe.

-Defect roles in mechanisms for phase transformation and strain accommodation





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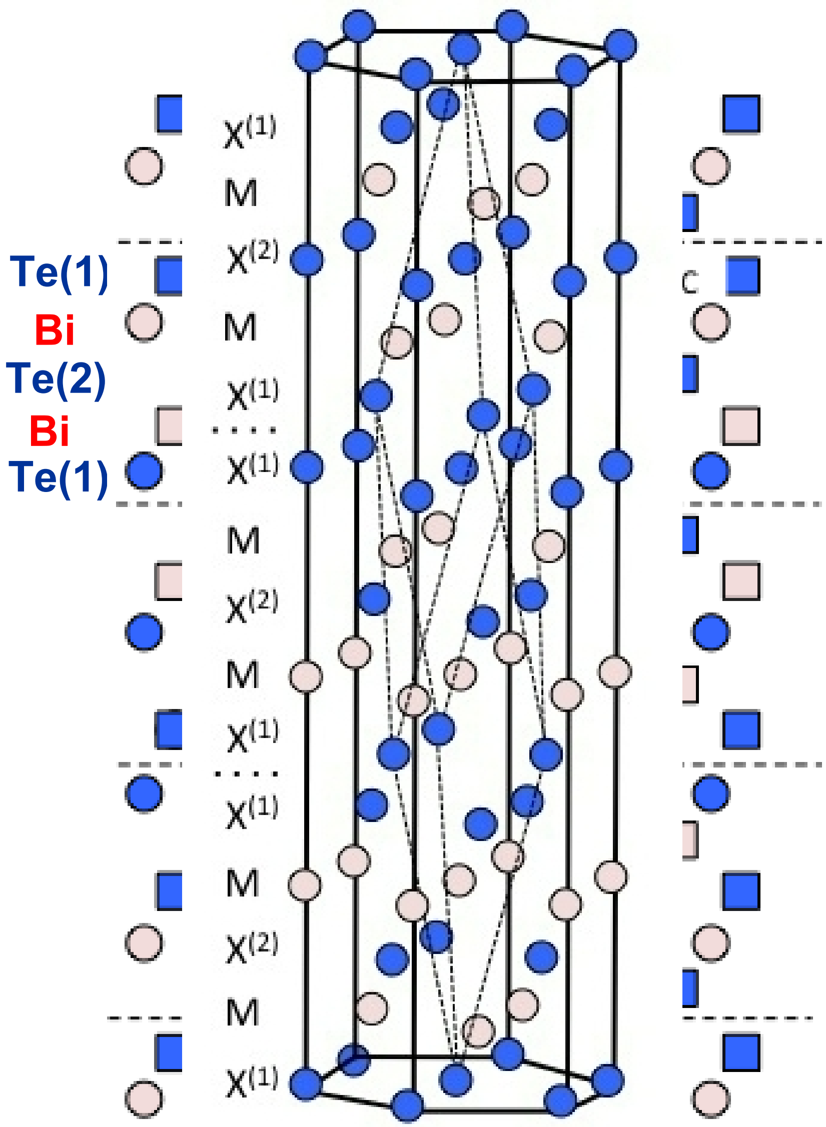
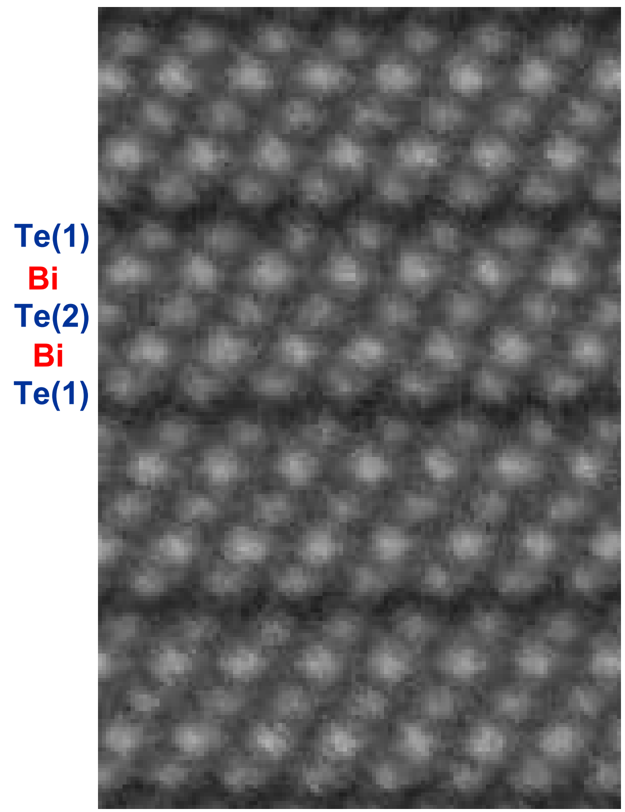
Bismuth Telluride (Bi_2Te_3): Crystal Structure



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

HAADF-STEM



Bi: Z=83
Te: Z=52

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

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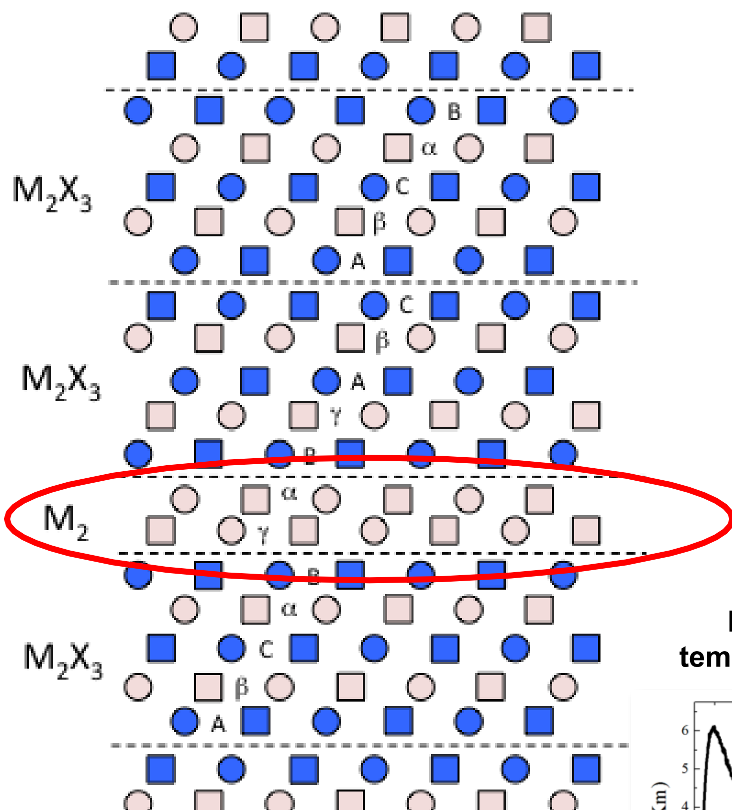
Layered structure allows flexibility in accommodating variations in composition

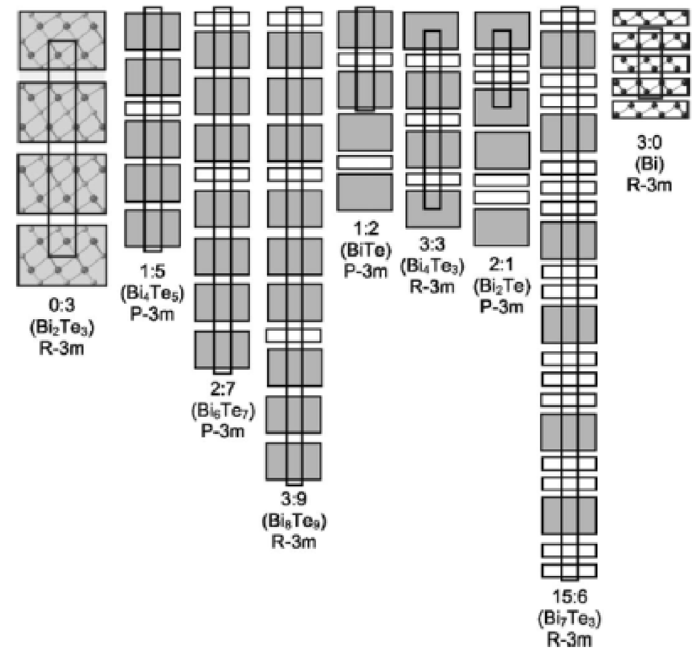
Insertion of metal bi-layers



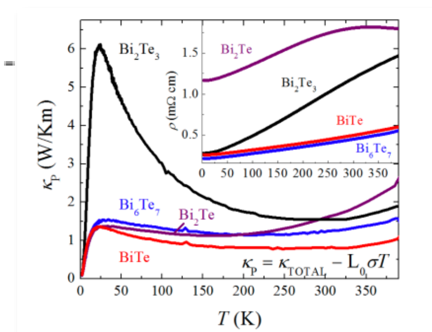
Example:
$(Bi_2)_m(Bi_2Te_3)_n$
homologous series

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

Increasing Bismuth →

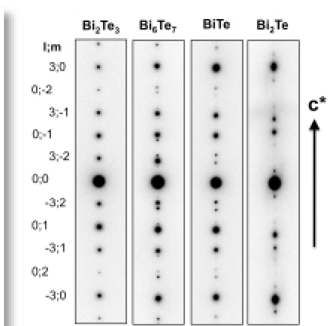


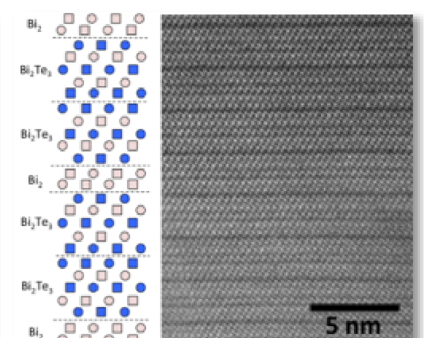
Dramatic reduction in low-temperature thermal conductivity



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

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



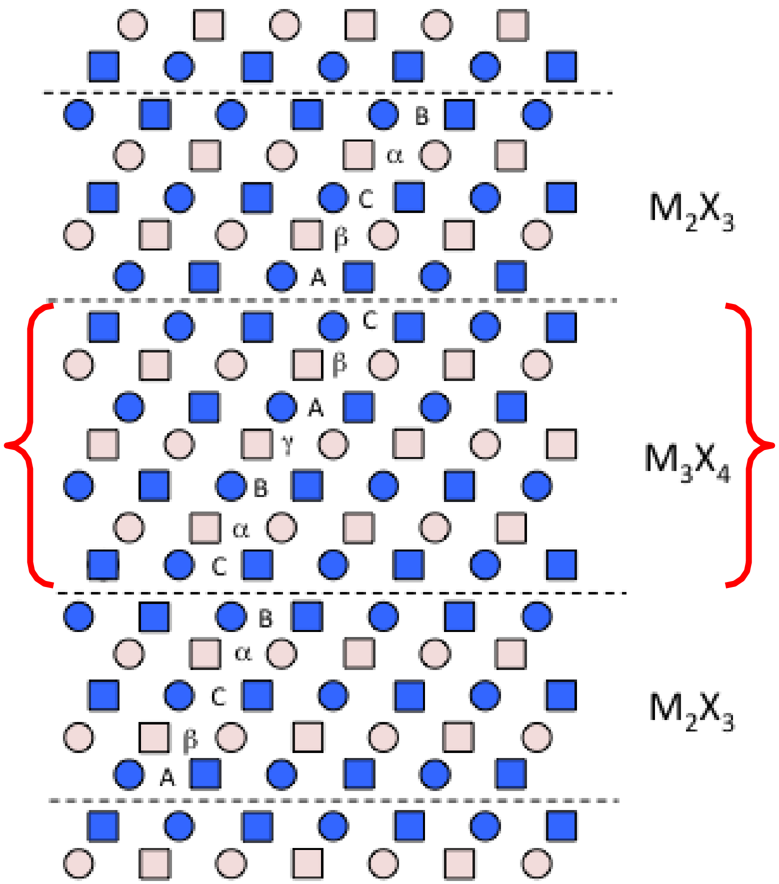


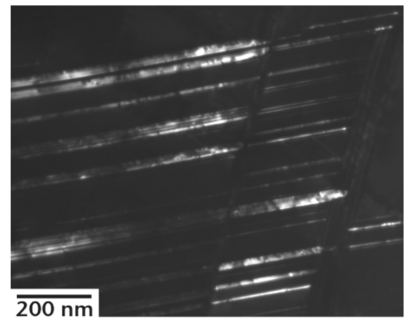
Medlin & Snyder, JOM 2013

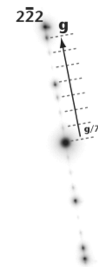
Layered structure allows flexibility in accommodating variations in composition

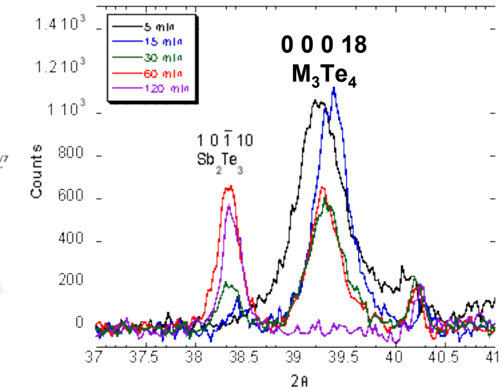
Metal rich, 7-Layer M_3X_4 fault

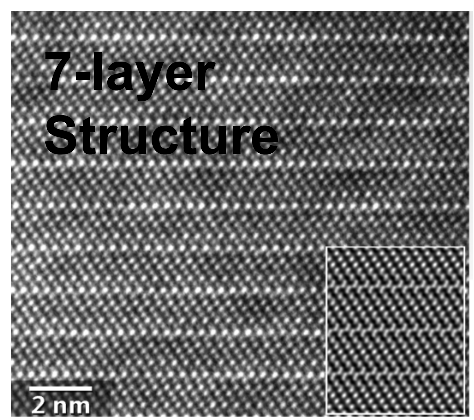
Example: $(Ag,Sb)_3Te_4$ transition phase during nucleation of Sb_2Te_3 precipitates in $AgSbTe_2$

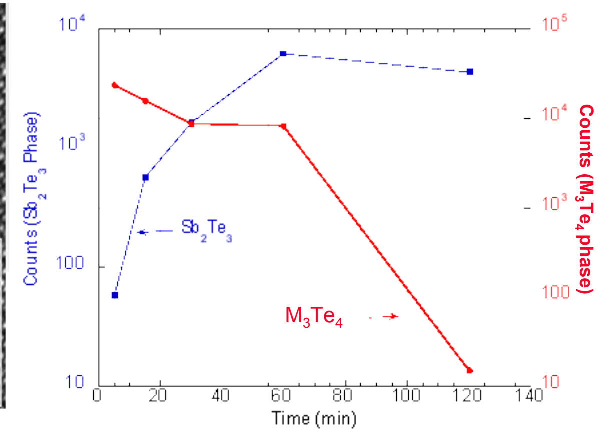












Sharma, Sugar, & Medlin, Journal of Applied Physics (2010).
Sugar and Medlin, Journal of Materials Science (2011)

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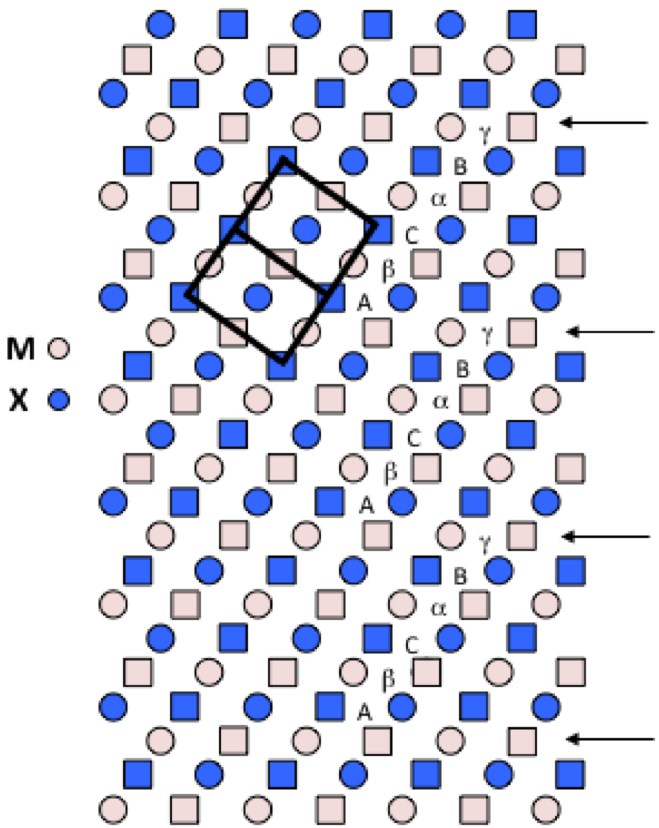
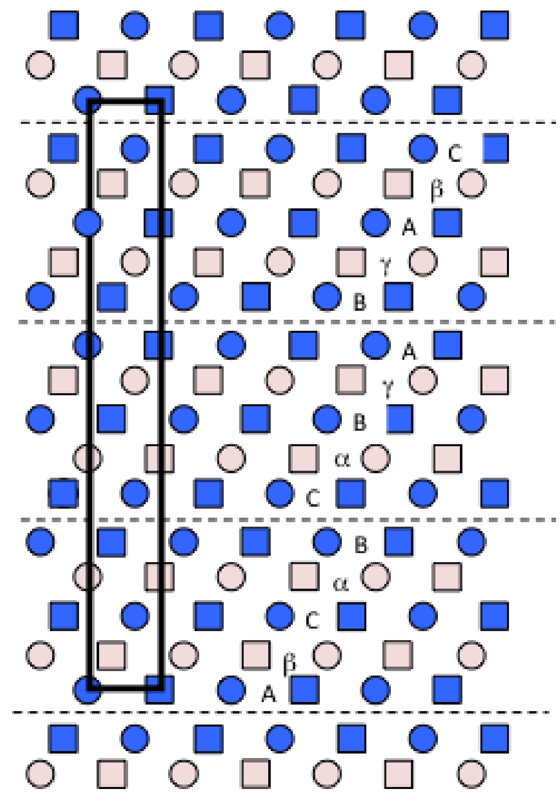
Tetradymite and Rocksalt structures are closely related

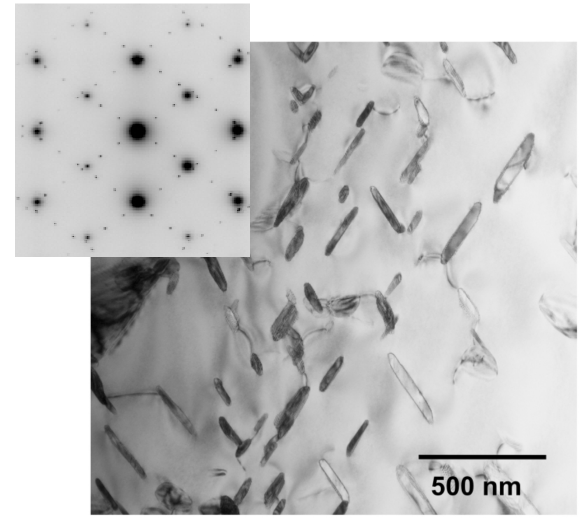
Rocksalt (MX) Structure



Tetradymite (M_2X_3) Structure



Example: Crystallographically Aligned Sb_2Te_3 precipitates in PbTe

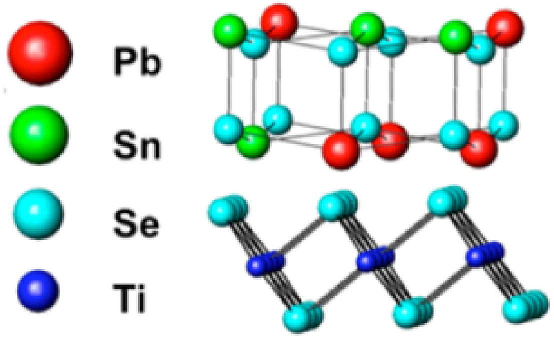


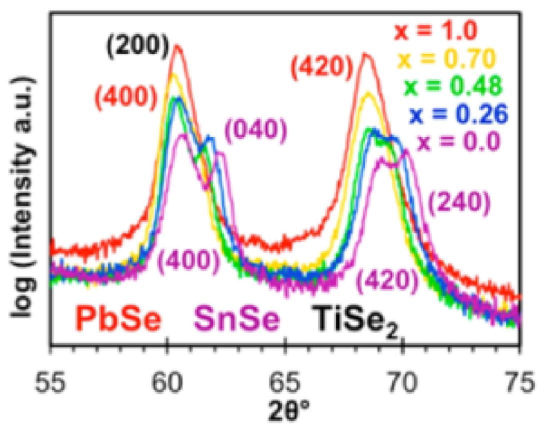
Heinz, Snyder, Ikeda, and Medlin, Acta Mat. 2011

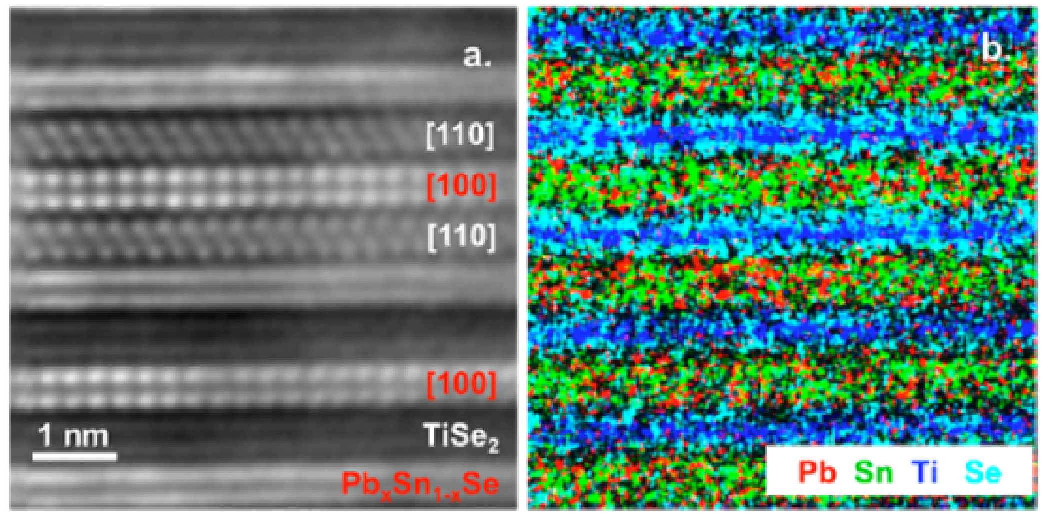
- Solid-state phase transformations in chalcogenides
- Structural interpretation of extended defects

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.

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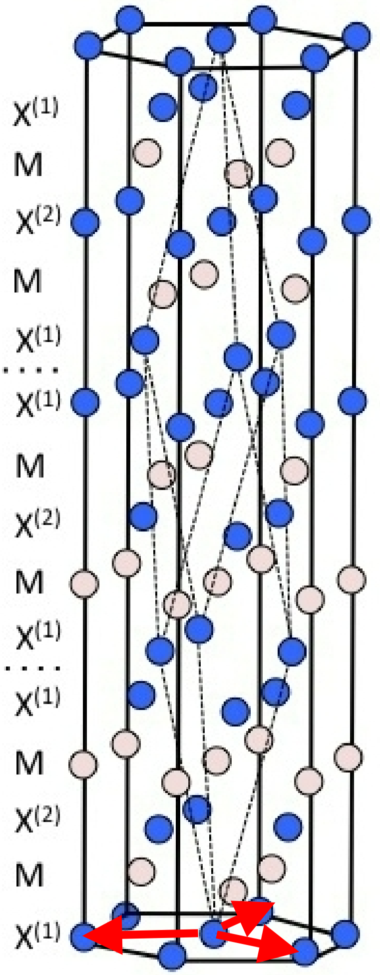
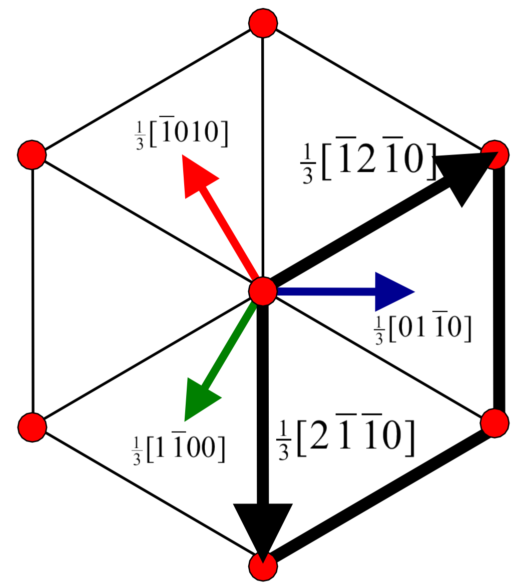
How do these structural considerations impact Dislocations and Interfaces?

Dislocations in Bismuth Telluride

Burgers vectors lying in 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

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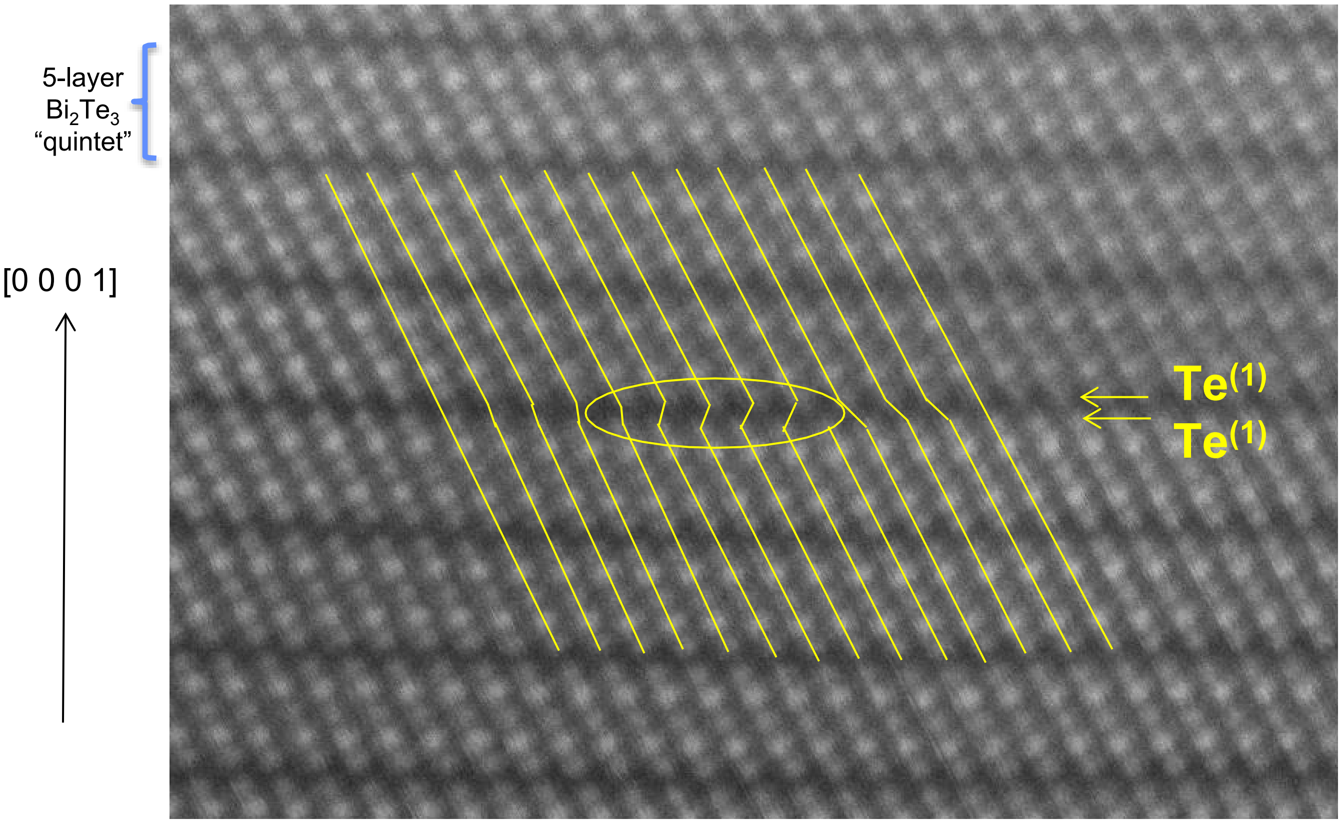
Dislocation Core structure: termination at $Te^{(1)}$-$Te^{(1)}$ layer, core spreading



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

60° mixed dislocation

Dissociated?

30° mixed partial

Stacking Fault

90° edge partial

1/3<1 0 -1 0> partial dislocations.

FEI-Titan
HAADF-STEM
300 keV

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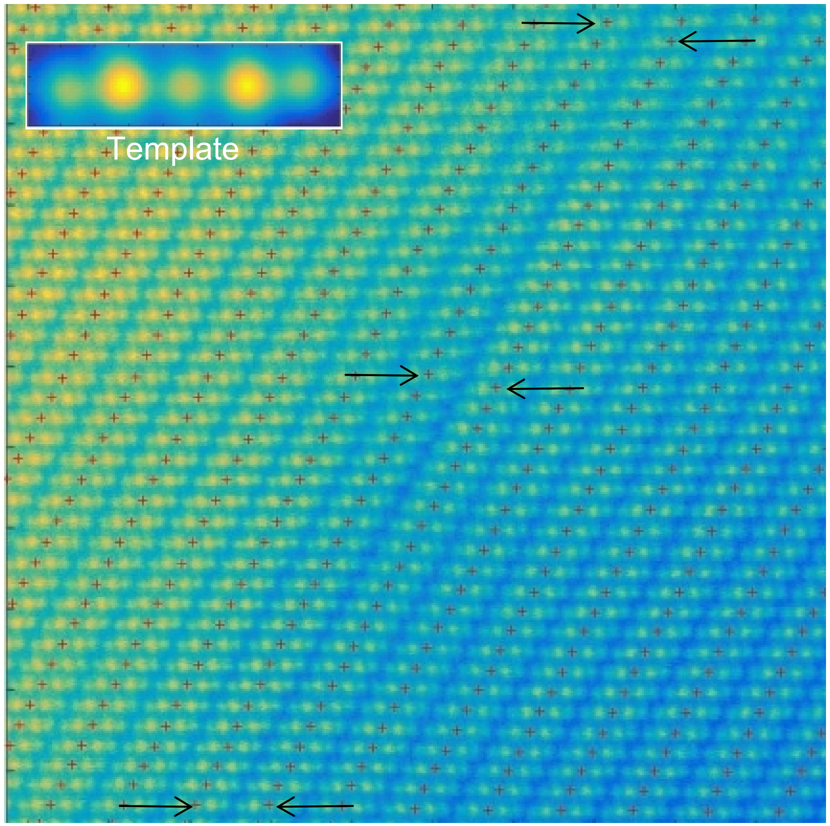
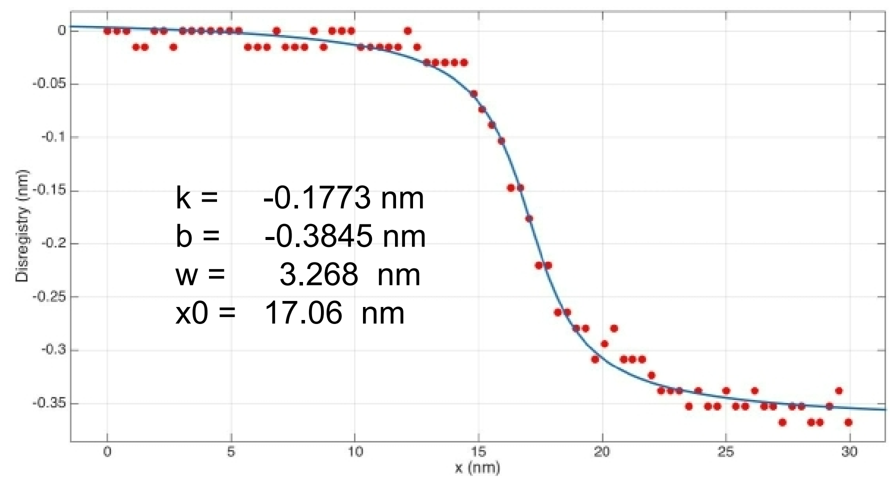
Quantify Disregistry on Slip Plane using Peierls-Nabarro Dislocation Model

Disregistry of {1 0 -1 5} planes across slip plane measured through template matching



$$u_+ - u_- = k + \frac{b_{edge}}{\pi} \tan^{-1}\left(\frac{x - x_0}{w/2}\right)$$

Disregistry — Burgers vector — core-width



w=3.7 nm ± 0.6 nm

6 dislocations
2-4 measurements each

Core-spreading on basal plane, but no localized partial dislocations or well defined stacking fault.

Working with modelers to extract energetics of gamma-surface.

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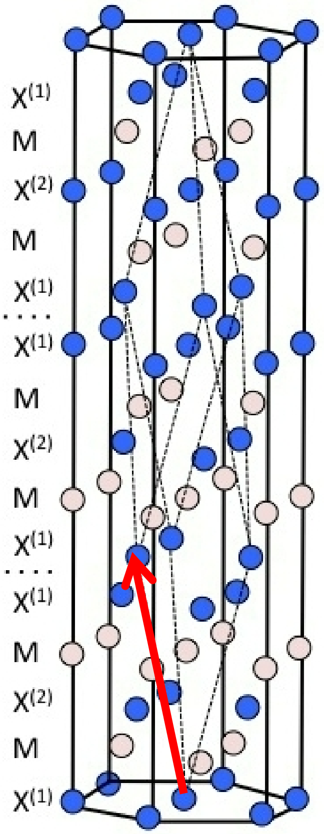
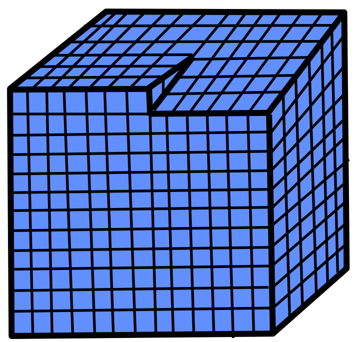
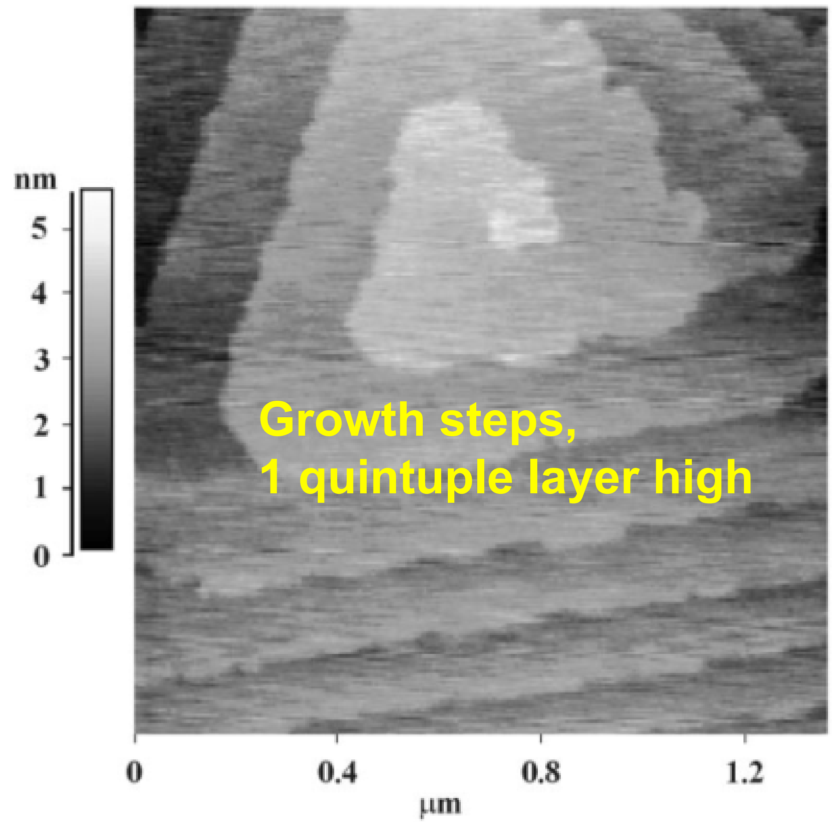
Non-basal dislocations:
Screw dislocations important to crystal growth





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

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?

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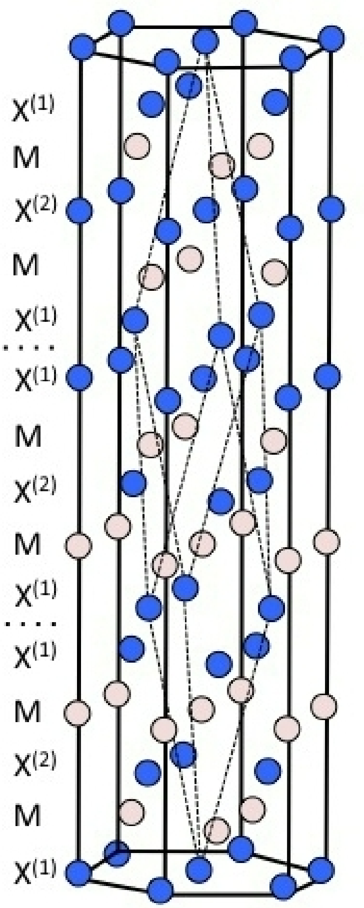
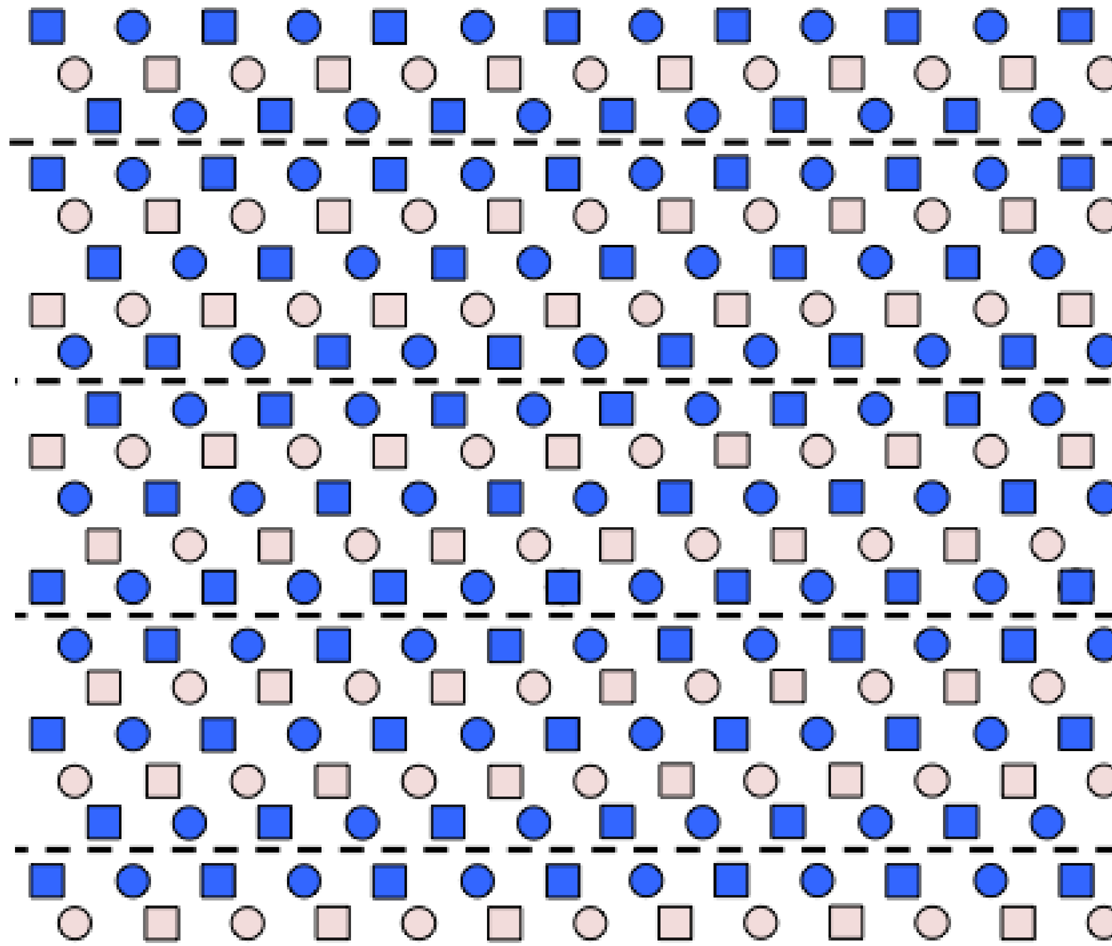
Non-basal edge dislocations: What happens if we pull out a quintuple unit?





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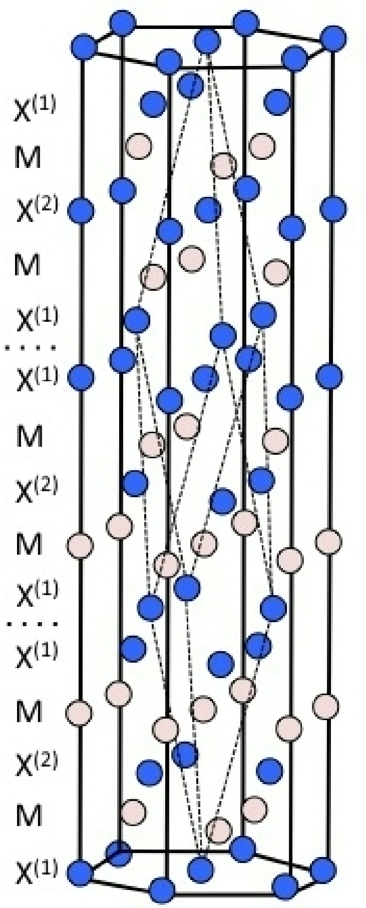
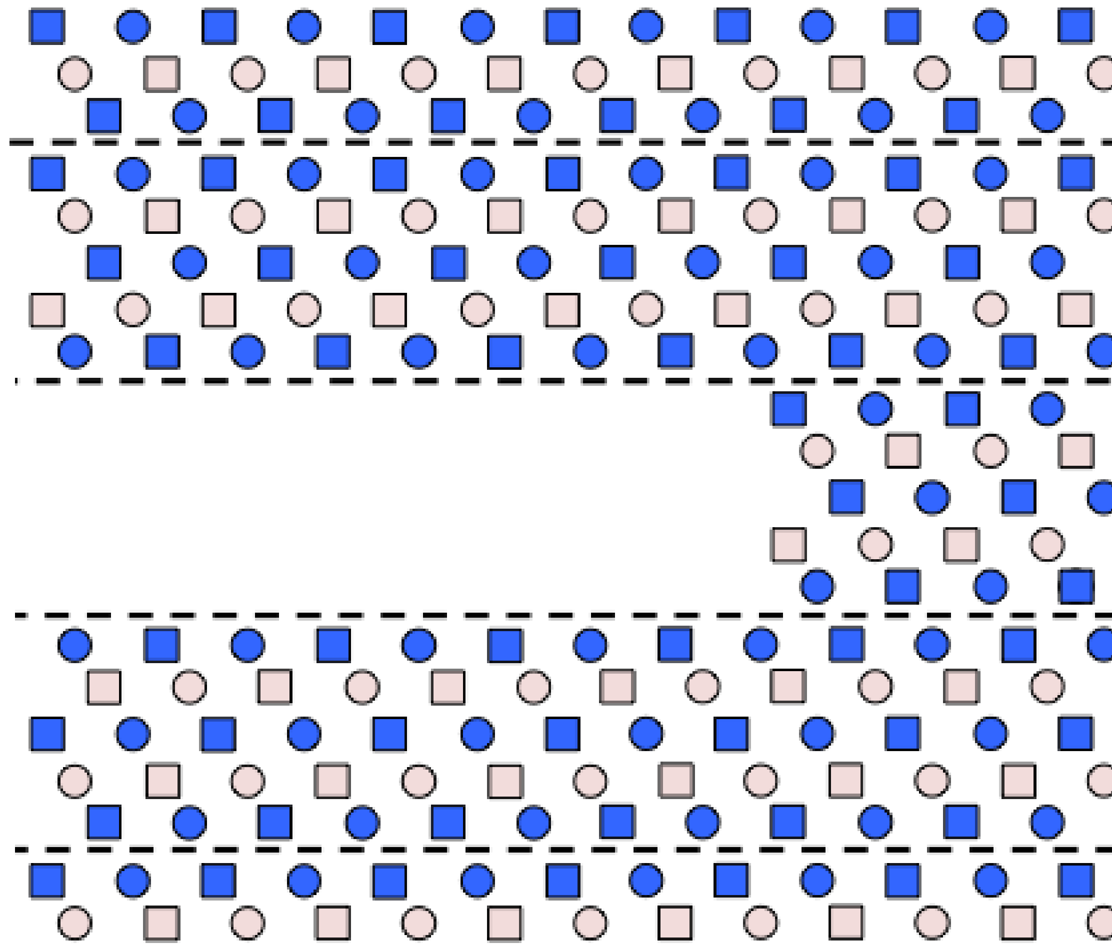
Non-basal edge dislocations: What happens if we pull out a quintuple unit?





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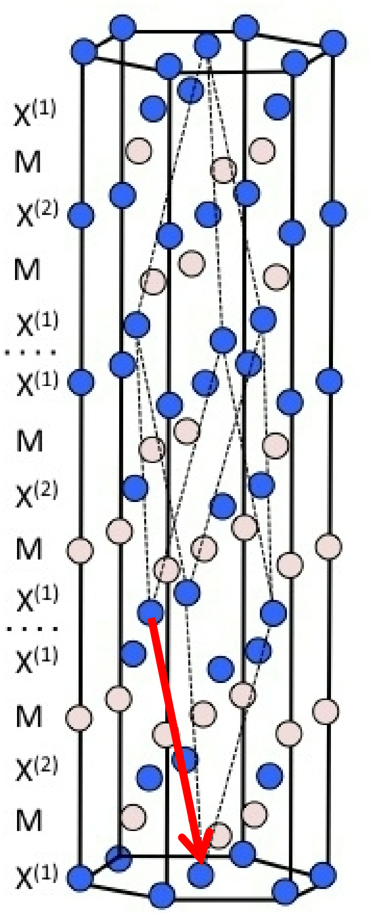
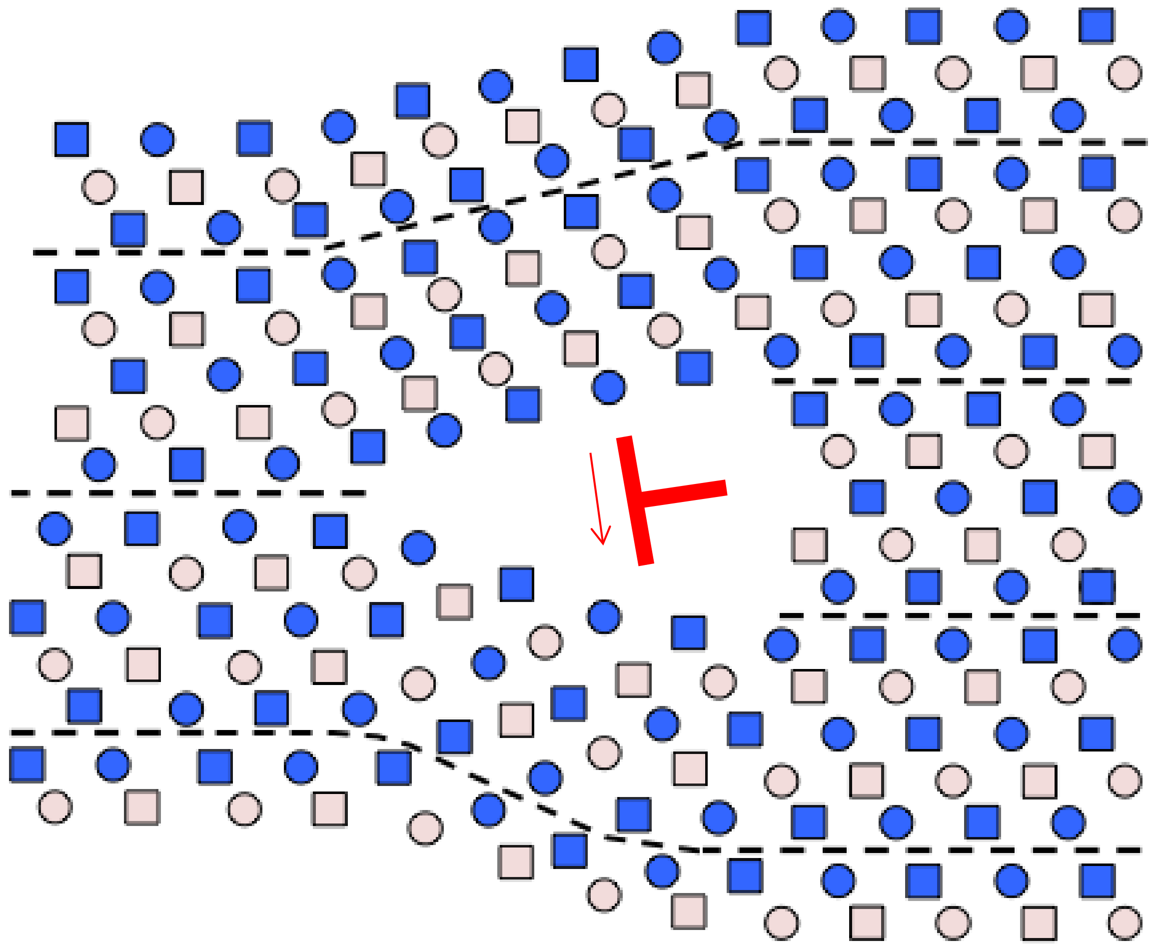
Non-basal edge dislocations: What happens if we pull out a quintuple unit?





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

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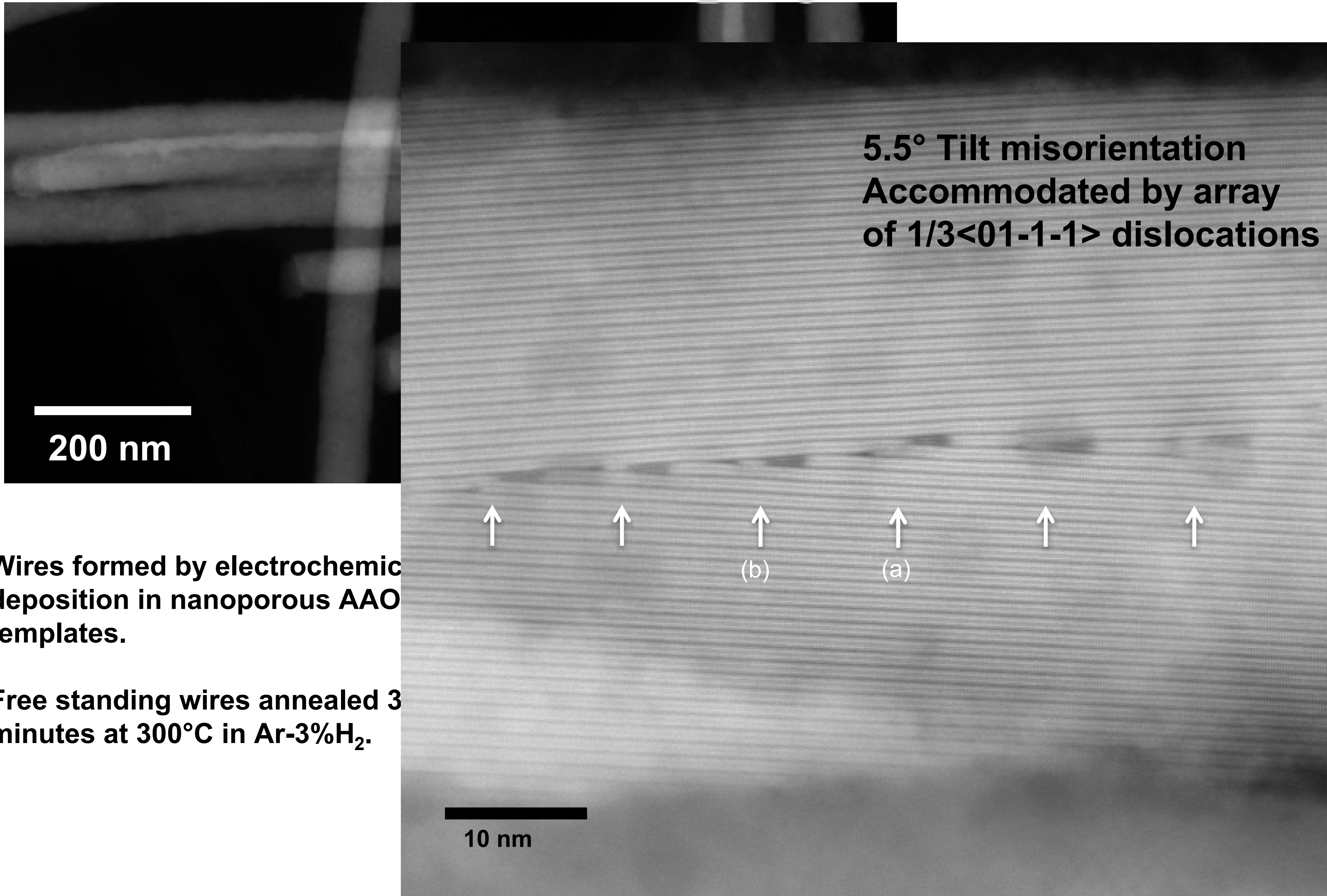
Dislocations in Bi_2Te_3 Nanowires

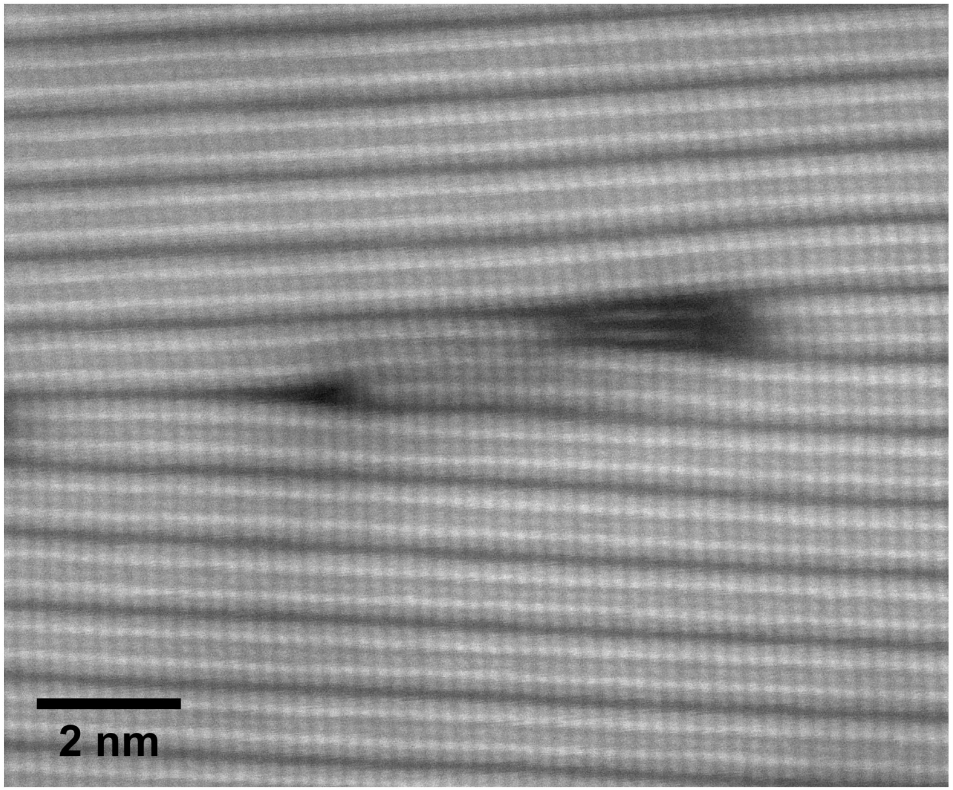


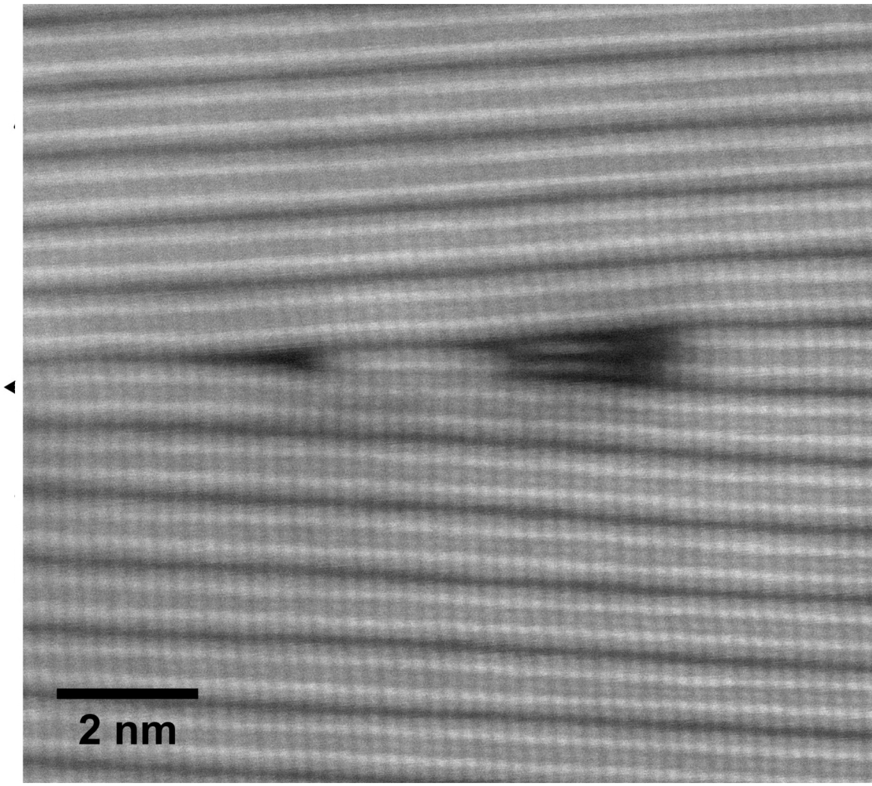
Wires formed by electrochemic deposition in nanoporous AAO templates.

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

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

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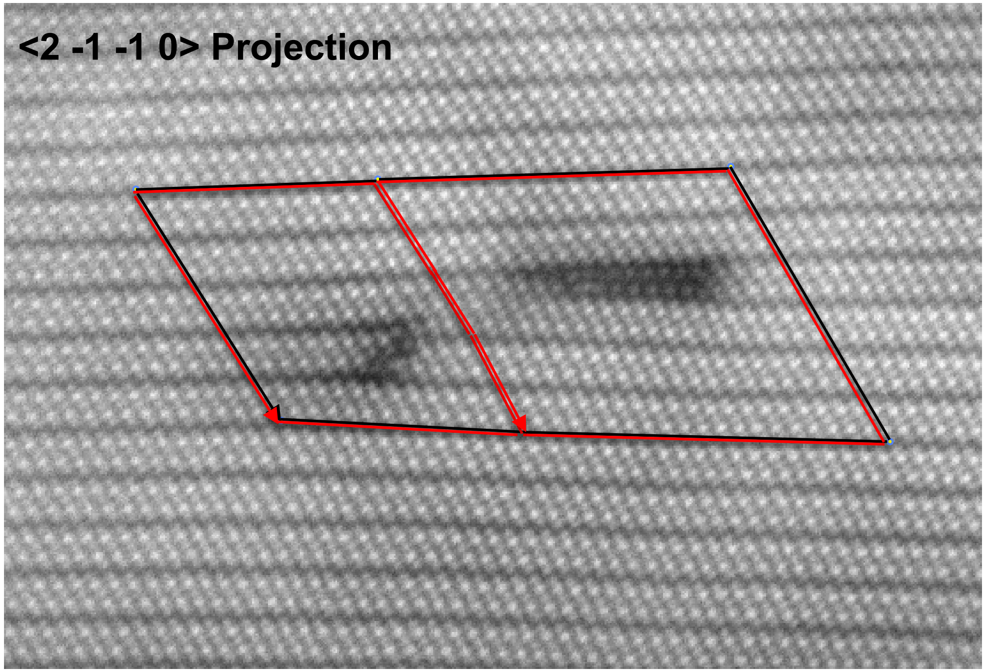
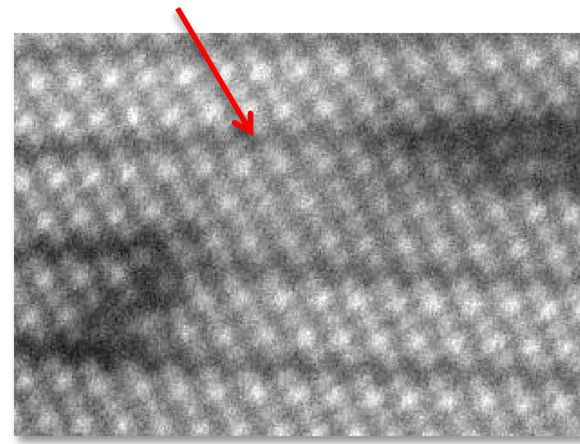
(1/3)[0 1 -1 -1] Dislocation in Bi_2Te_3:



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

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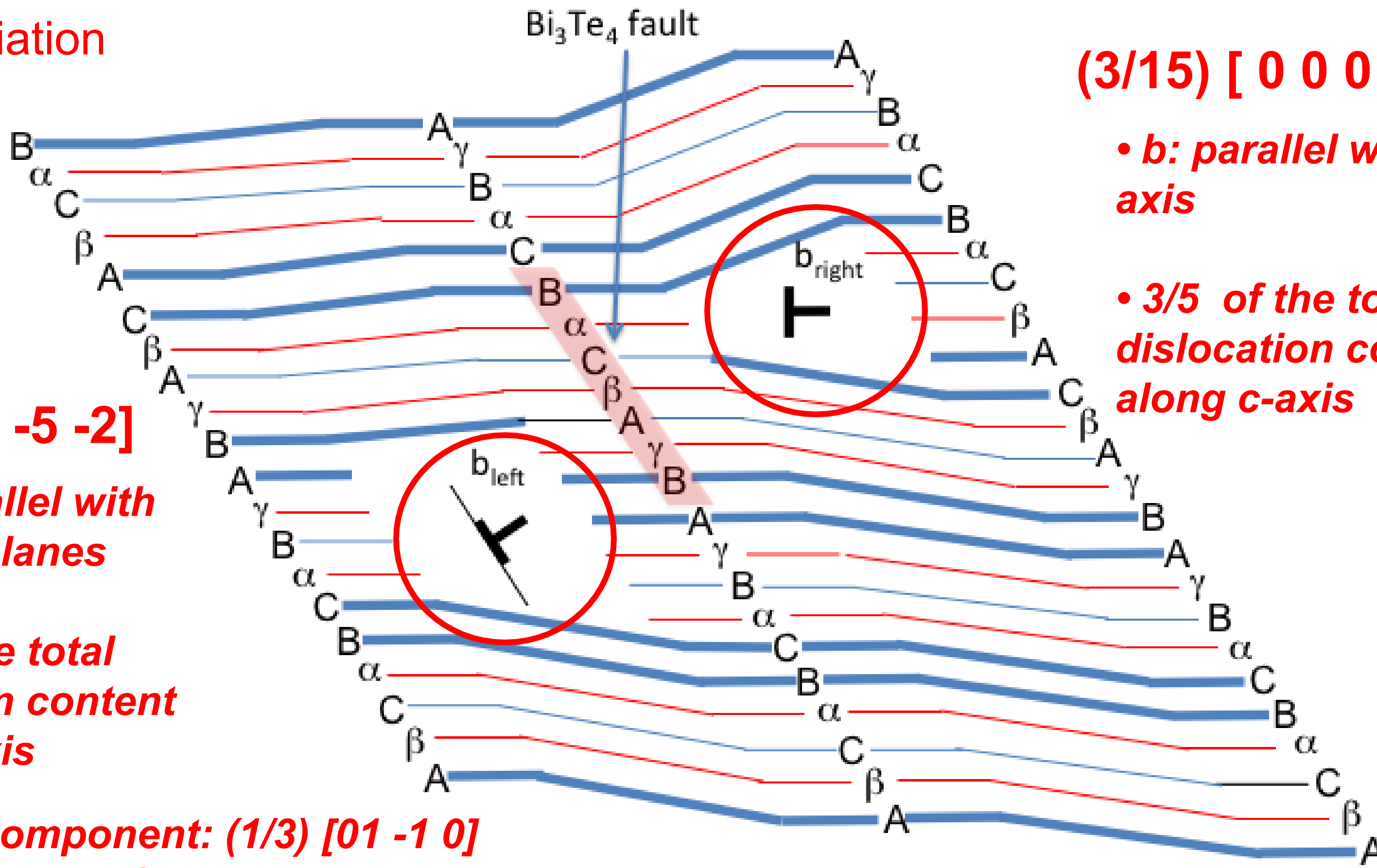
7-Layer Bi_3Te_4 faults: Mechanism to accommodate Te loss during annealing

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***

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

Interfaces in the Tellurides

- Grain Boundaries:
  - Bi_2Te_3
- Heterophase interfaces
  - Rock salt / tetradymite

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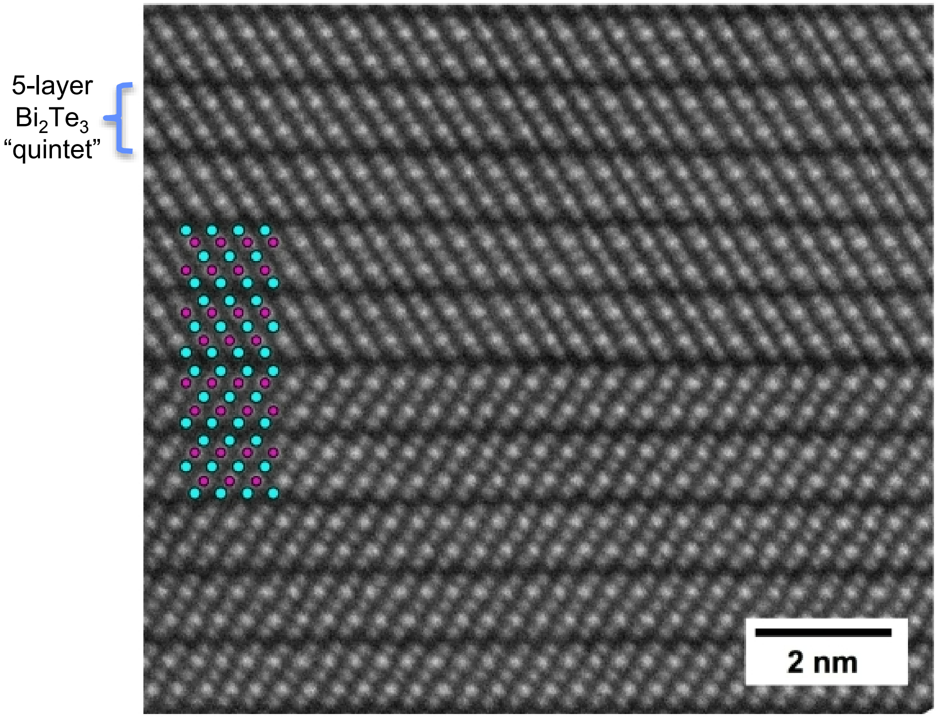
Atomic Structure of the Bi_2Te_3 Basal Twin:
Energetic preference for termination at $Te^{(1)}$ sites

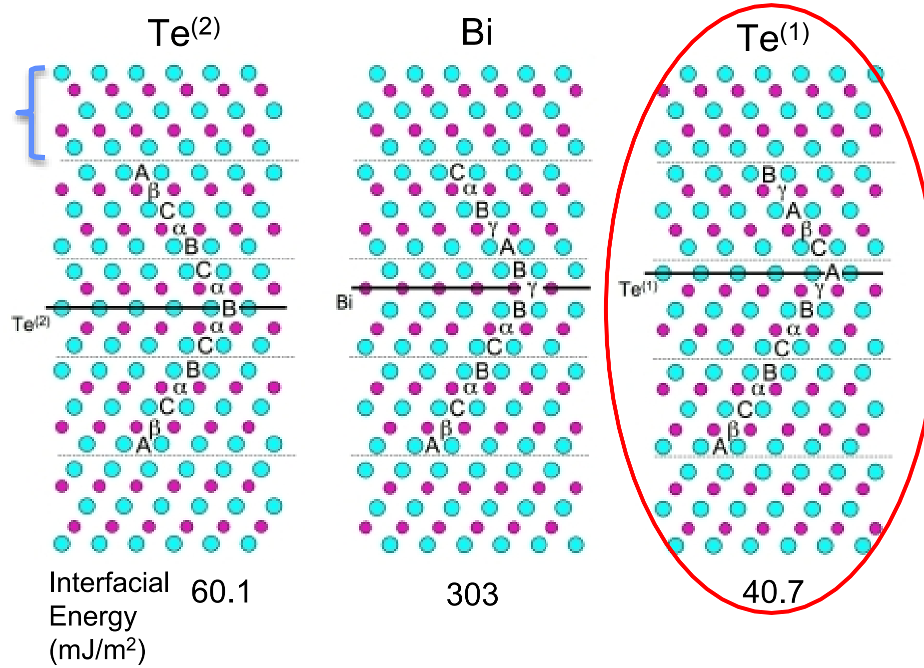
HAADF-STEM Imaging:

Twin Boundary Terminated at $Te^{(1)}$ layer



DFT Calculations:

Three Possible Compositional Terminations



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

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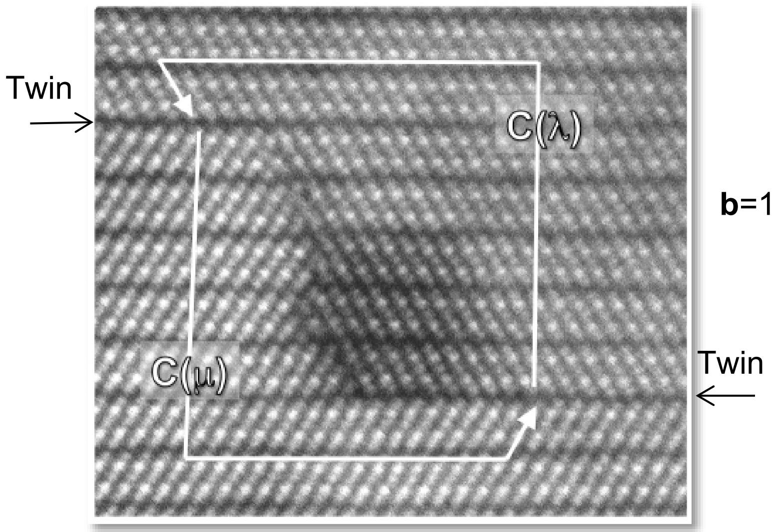
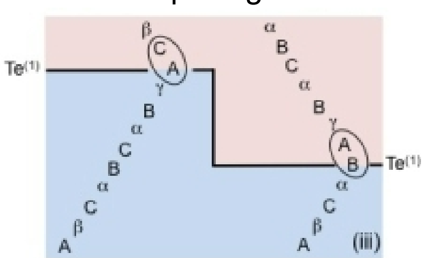
Preferential termination at $Te^{(1)}$ layers: Impact on boundary steps

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

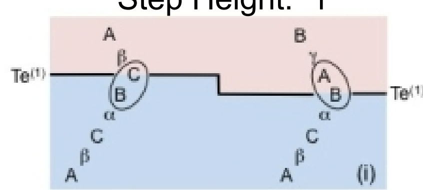


b=1/3<10-10>

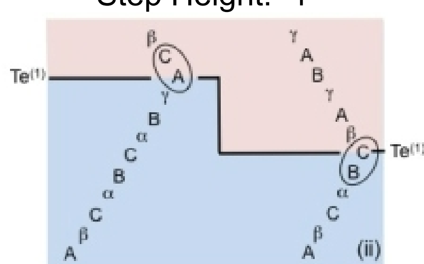
Step Height: 5



Step Height: 1



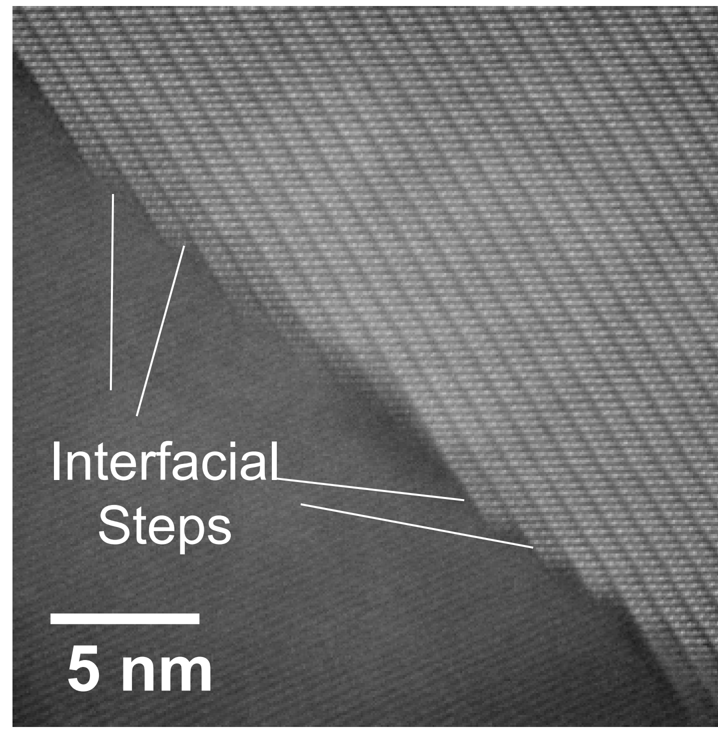
Step Height: 4



b=1/3<10-10>

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

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



Medlin and Snyder, JOM (2013).

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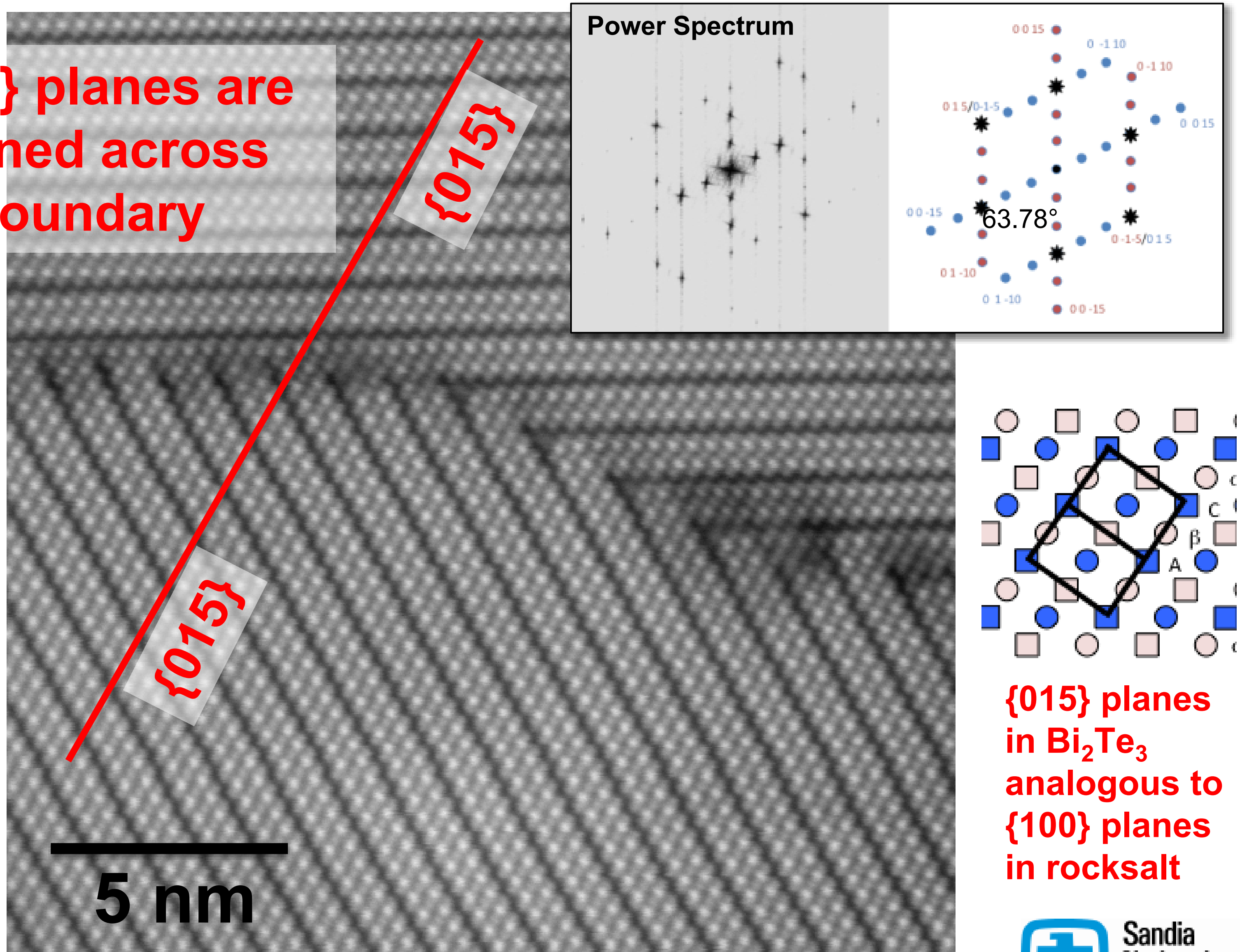
Bi_2Te_3 <2-1-1 0>//<-2 1 1 0> 63.78° Boundary



Electrodeposited
Bi_2Te_3 nanowire
Annealed 300°C

{015} planes in Bi_2Te_3 analogous to {100} planes in rocksalt

FEI-Titan
HAADF-STEM
300 keV

D.L. Medlin, S. Limmer, G. Yelton, M.P. Siegal, in preparation.

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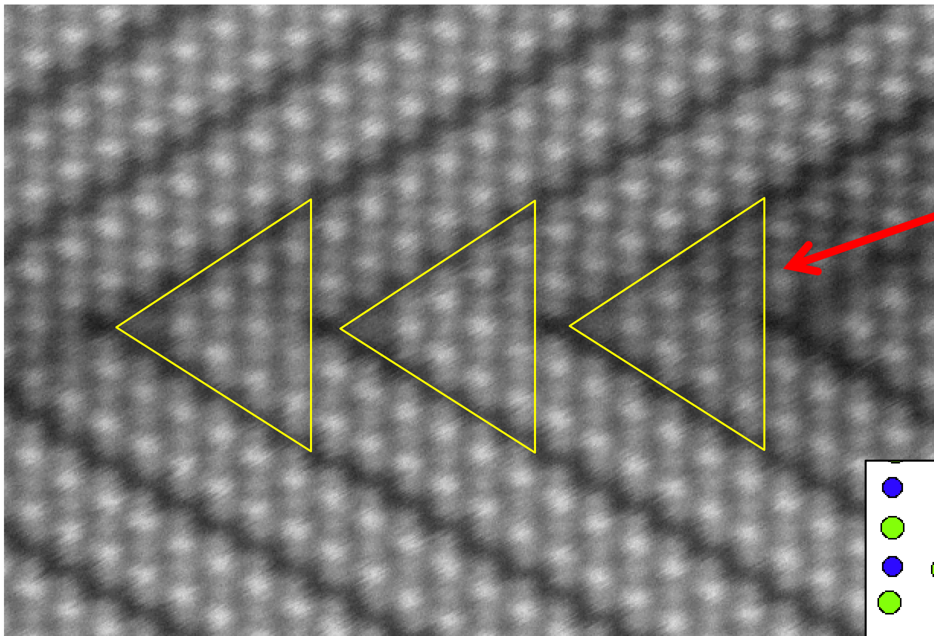
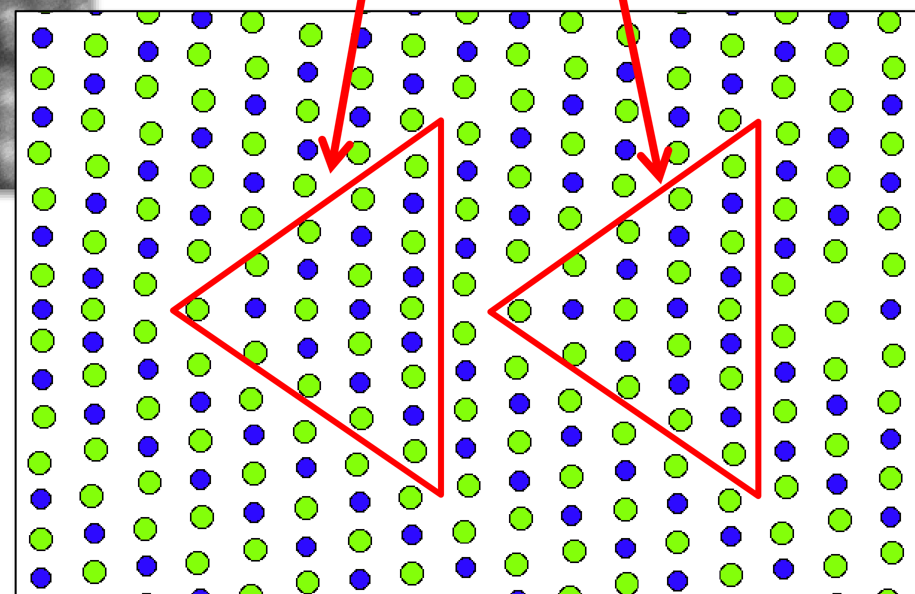
Symmetrical Interface Configuration

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



Rocksalt coordinated grain boundary units



Each triangular unit:
10 Bi 15 Te

2:3 ratio of Bi and Te maintained at interface

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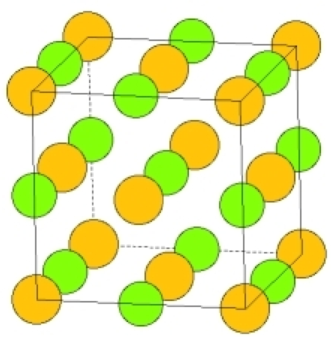
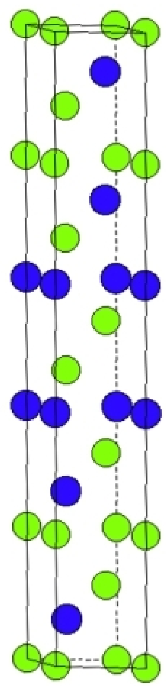
Heterophase Rocksalt/Tetradymite Telluride Interfaces

Rock-Salt
(PbTe, $AgSbTe_2$)



Fm-3m

Tetradymite
(Bi_2Te_3, Sb_2Te_3)



R-3m

What happens at interface?
How do transformations occur?
Misfit accommodation?

-Interest in forming thermoelectric nanocomposites of rock-salt and tetradymite tellurides:

-Possibility for well ordered interfaces.

-Transformations provide bulk route to synthesis.

Ikeda, et al., Chem Mater. 2007

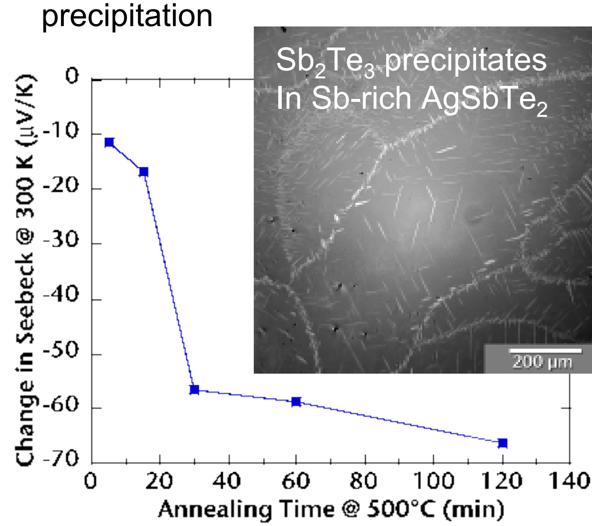
Snyder and Toberer, Nature Materials 2008

-$AgSbTe_2$:

-Constituent of TAGS $(GeTe)_x(AgSbTe_2)_{1-x}$ and LAST $(PbTe)_x(AgSbTe_2)_{1-x}$ zT ~ 1.8

-High performance TE material: zT > 1.2

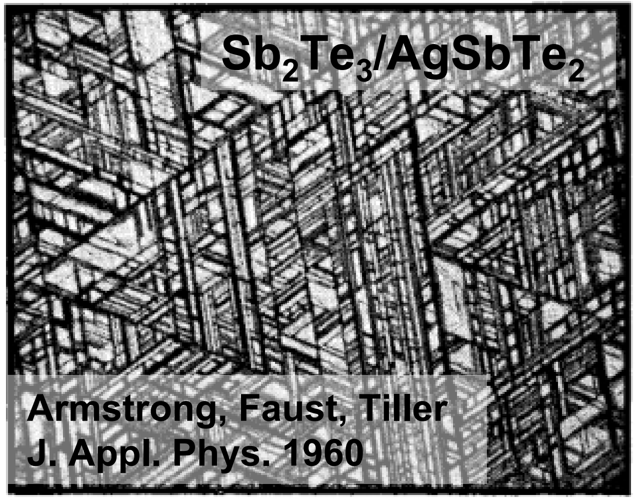
-Degradation of Seebeck coefficient with Sb_2Te_3 precipitation

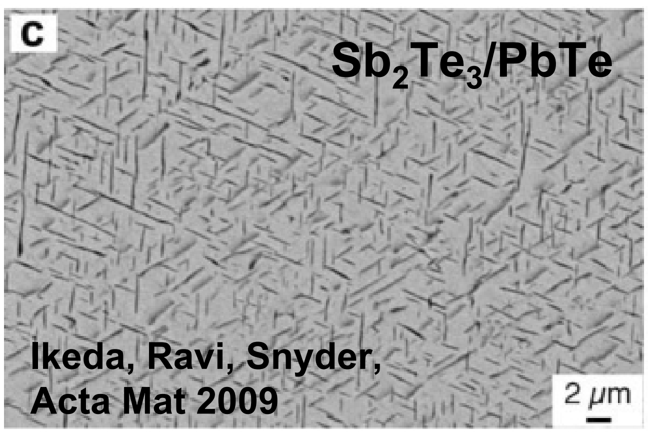


Sharma, Sugar, Medlin J. Appl. Phys. 2010

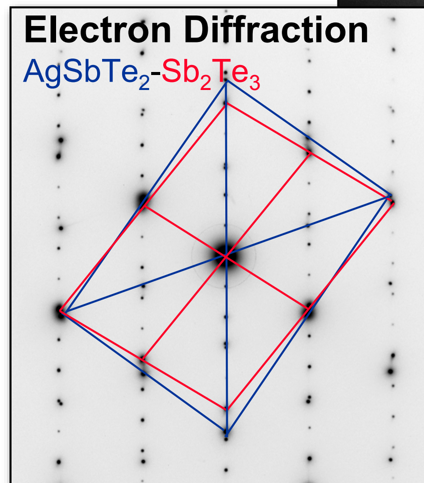
Crystallographic alignment between rocksalt and tetradymite phases

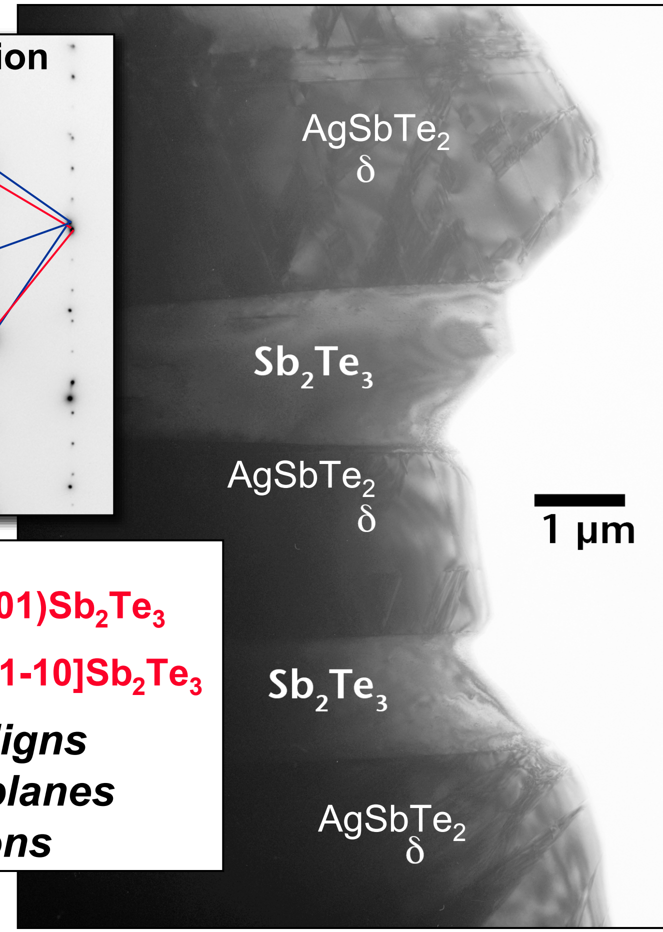
Widmanstätten plates





TEM $Sb_2Te_3/AgSbTe_2$





(111)$AgSbTe_2$ // (0001)Sb_2Te_3

[-101]$AgSbTe_2$ // [2-1-10]Sb_2Te_3

Orientation aligns close-packed planes and directions

Medlin and Sugar,
Scripta Mat 2010

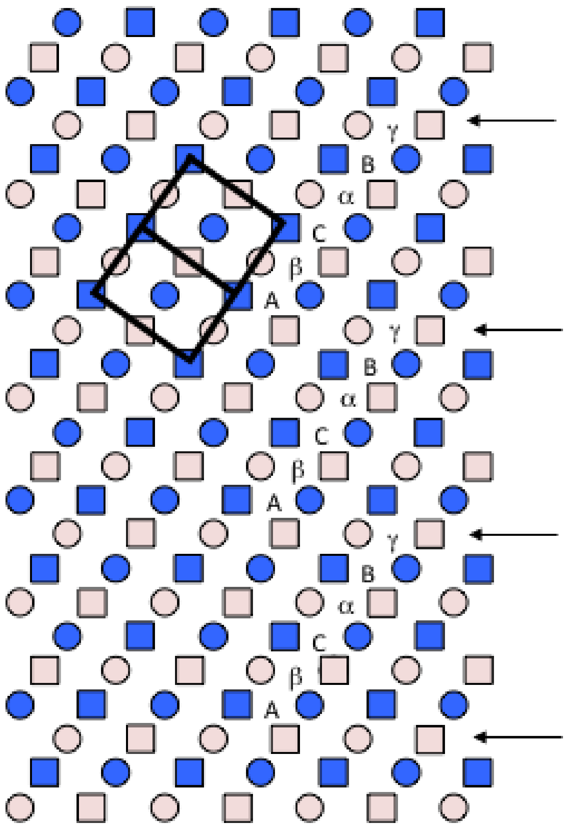
How to convert between the rocksalt and tetradymite structures?

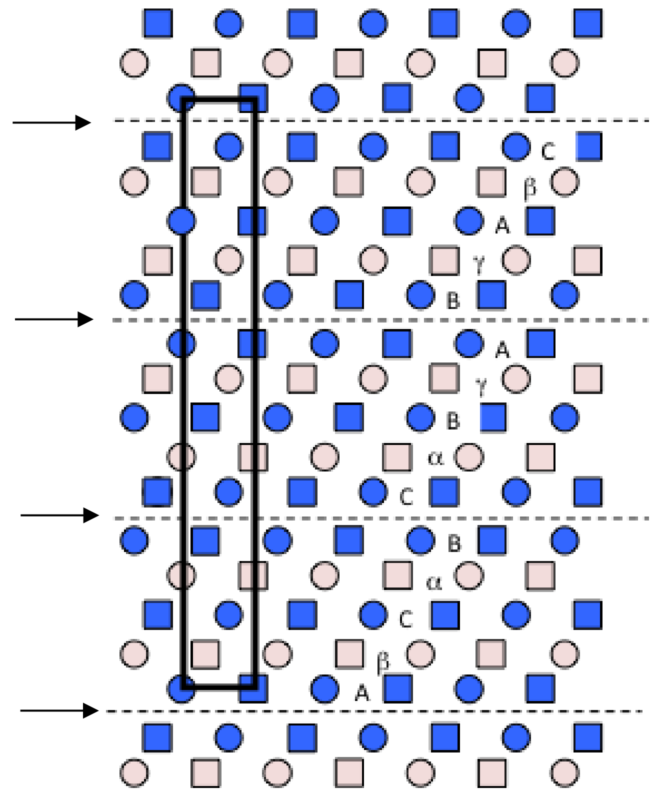
Rocksalt (MTe)

Tetradymite (M_2Te_3)

Te ●

Metal ○





-Remove metal plane every 6 layers

-Shear blocks by 1/3<10-10> (or 1/6<112> relative to cubic coordinates)

N. Frangis et al., J. Solid State Chemistry 84 (1990)

Transformation can be accomplished by motion of disconnections (steps with dislocation content)

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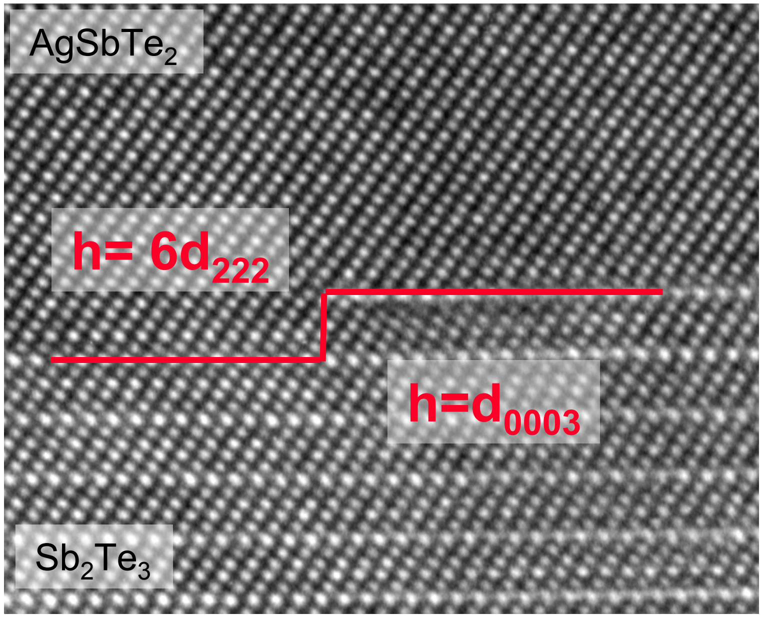
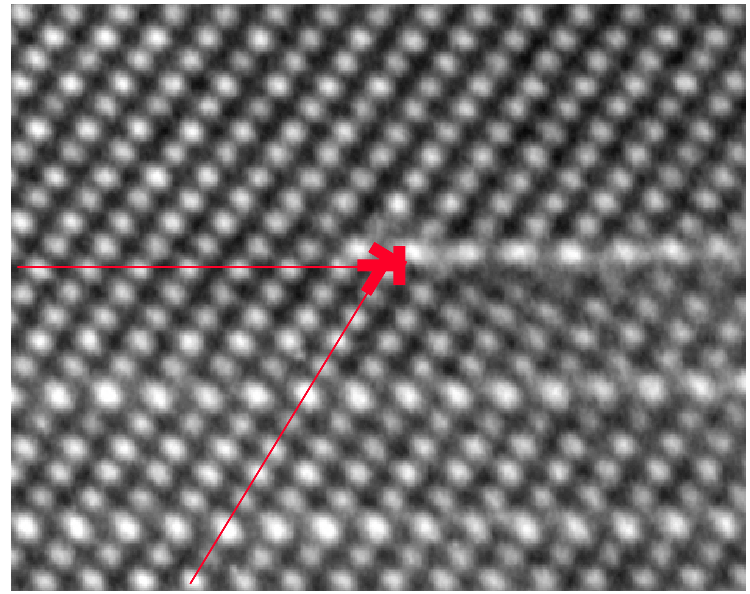
HRTEM : Step at $AgSbTe_2/Sb_2Te_3$ Interface





JEOL 4000EX HRTEM

Defect has both step and dislocation character.

-Interfacial "Disconnection" (e.g. Hirth and Pond, Acta Mat 1996).

-Geometric properties of disconnections control mass flux and structural rearrangements of phase transformations.

Step joins 6 {222} planes in $AgSbTe_2$ with 5 {000 15} planes in Sb_2Te_3

Complex dislocation configuration.

Medlin and Sugar, Scripta Materialia, 2010.

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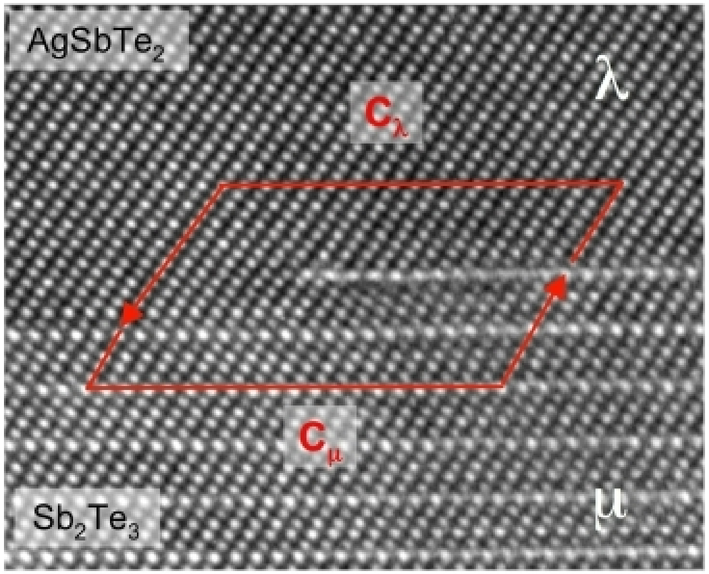
Role of defect in precipitate growth:

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

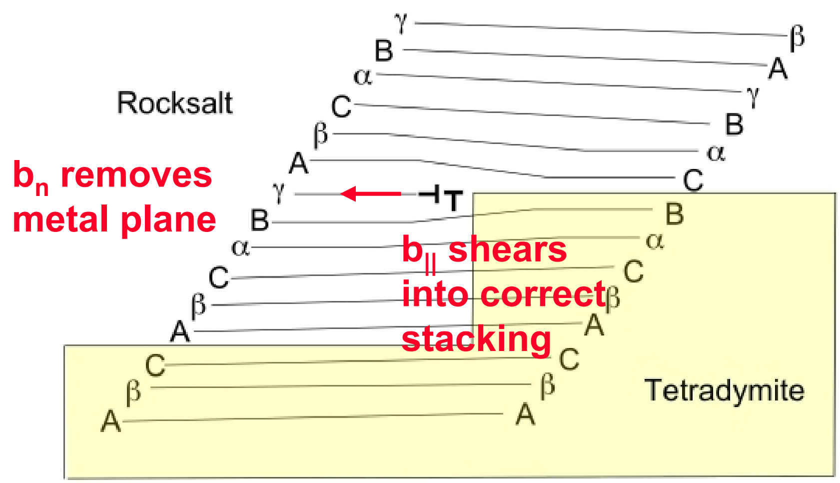
Resolve b into components normal and parallel to interface

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

- ***mismatch of step heights.***
- ***$|b_n|=0.3747$Å***

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

- ***Analogous to Shockley partial Dislocation***
- ***$|b_{||}|=2.48$Å***



Medlin and Sugar, Scripta Materialia, 2010.

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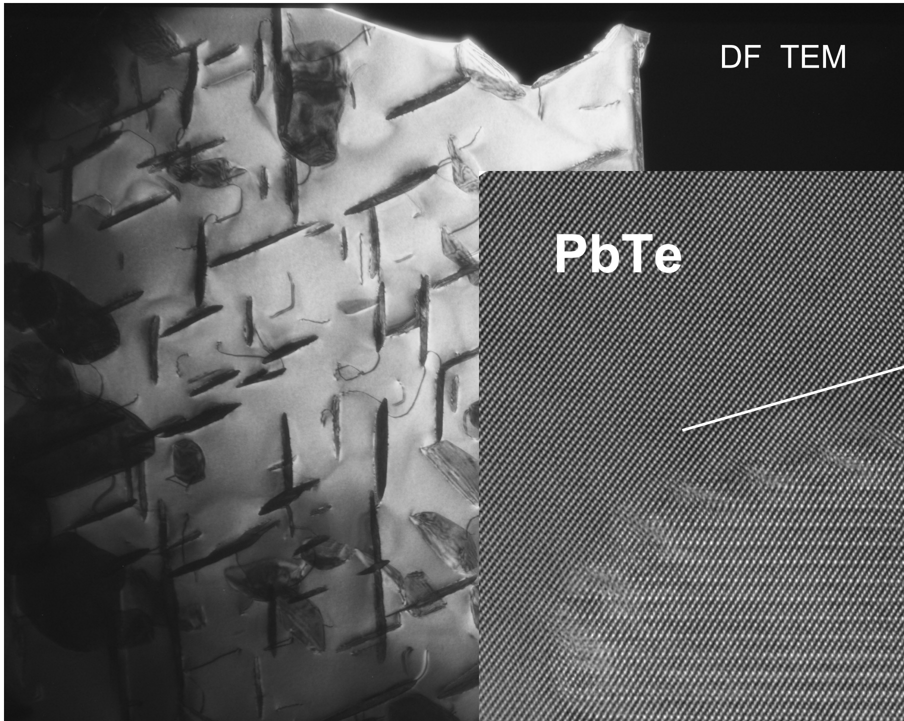
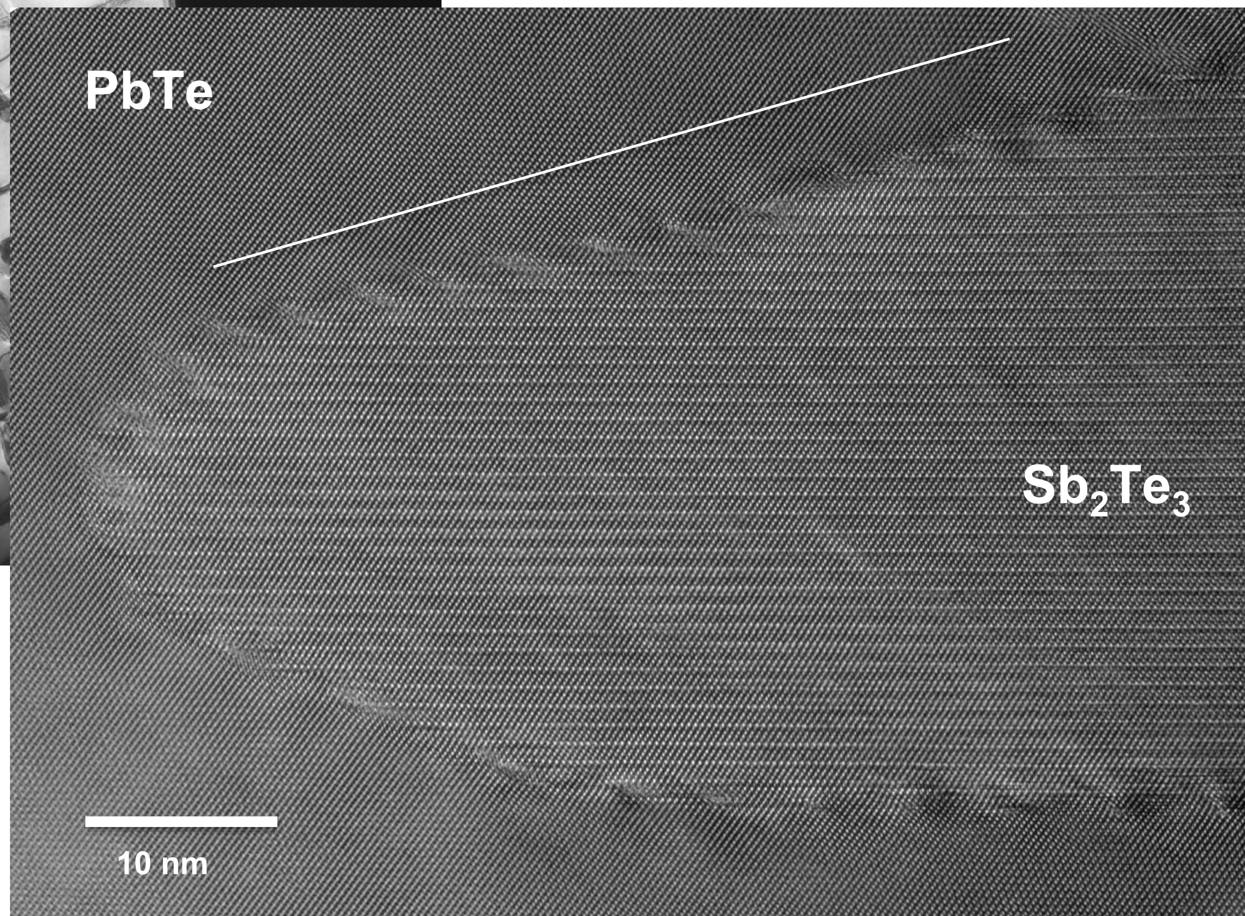
A system with larger misfit: $PbTe/Sb_2Te_3$

Sb_2Te_3 Precipitates in PbTe

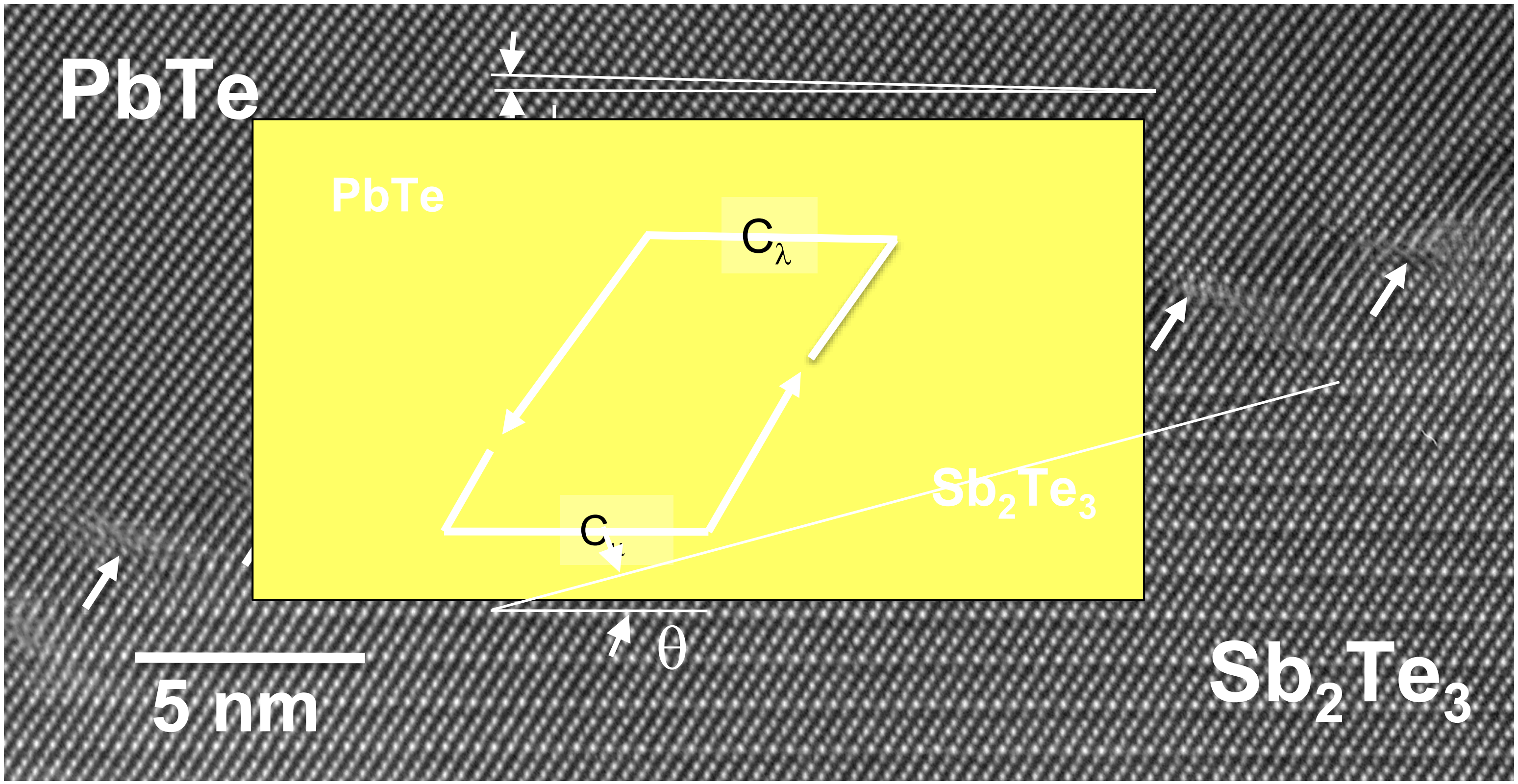


$AgSbTe_2(111)/Sb_2Te_3(0001)$
Misfit: +0.79%



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

Inclined Section of interface Composed of Disconnections



HRTEM JEOL 4000EX

Circuit Analysis:

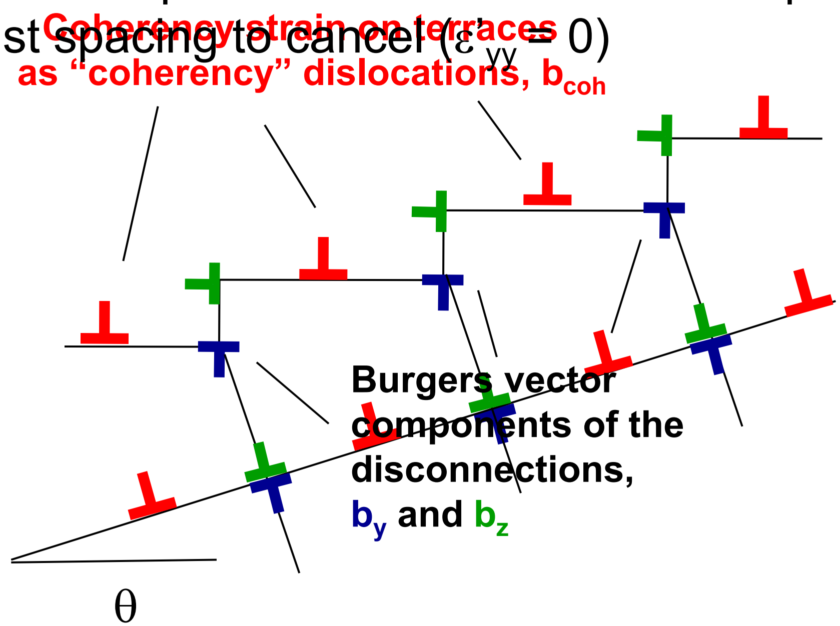
Defects identical to the “6/5” disconnections observed in $AgSbTe_2/Sb_2Te_3$

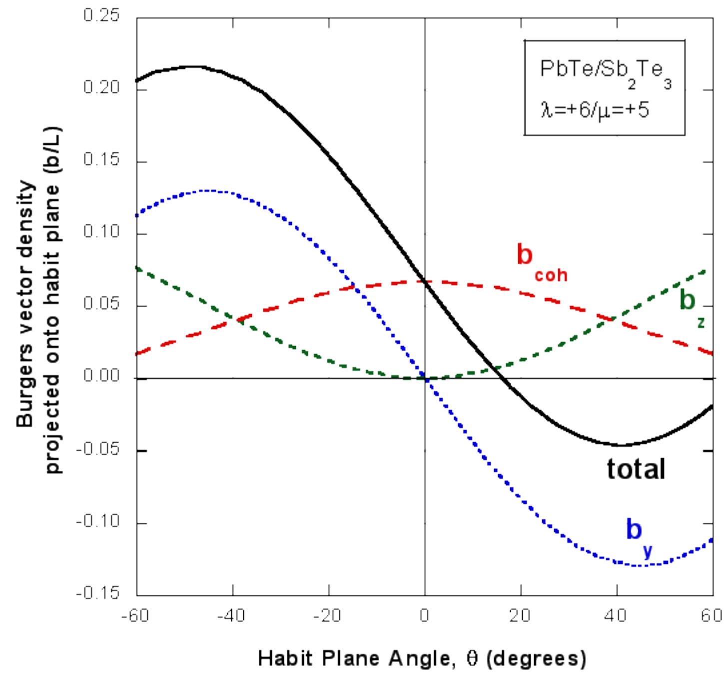
Interface Geometry:

Inclination: θ =14.8° Lattice rotation: ϕ = 1.1° to 1.4°

Interplay between Misfit Accommodation and Interface Inclination

Project components on inclined interface plane
Adjust spacing to cancel ($\varepsilon'_{yy} = 0$)





$$-\varepsilon = (b_y \tan\theta + b_z \tan^2\theta)h^{-1}$$ ➔ θ=16.2°

Pond, Celotto, Hirth, Acta Mater. 2003

Out of plane **b** components produce small rigid body crystal rotation,

$$\phi = 2\sin^{-1}[(b_z \cos\theta - b_y \sin\theta - \varepsilon h \cos\theta)\sin\theta / 2h]$$ ➔ φ=1.7°

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

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Conclusions

Key structural aspects of the tetradymite-type 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 transport properties in nanostructured bulk thermoelectrics.

Set of elementary "building blocks" for a general picture of interfacial structure in chalcogenide thermoelectrics

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Acknowledgements

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Sandia/Albuquerque

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LBNL/NCEM

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California Institute of Technology

N.A. Heinz, T. Ikeda, G.J. Snyder

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-LBNL: User program, National Center for Electron Microscopy
-UCD: Z. Zhang and E. Lavernia, for assistance with bulk Bi_2Te_3 processing

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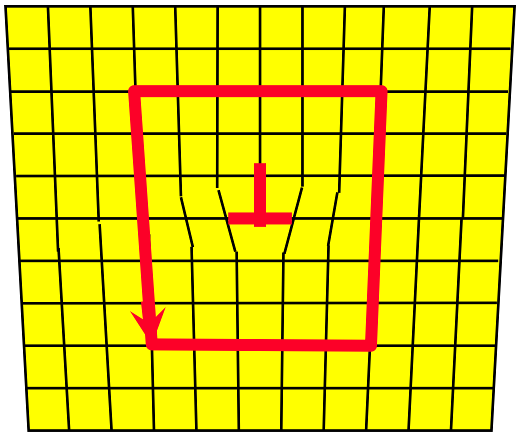
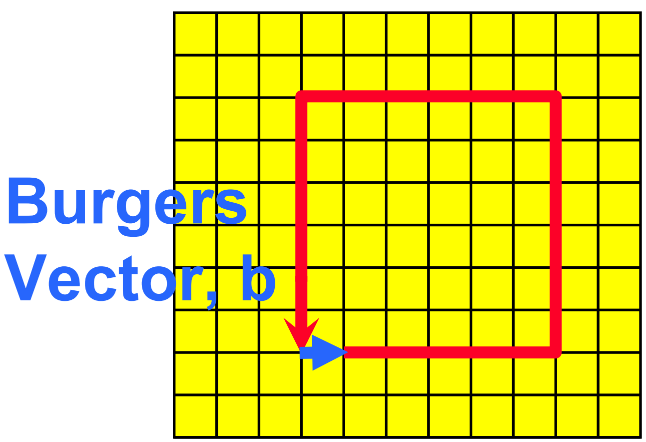
How do these structural considerations impact Dislocations and Interfaces?

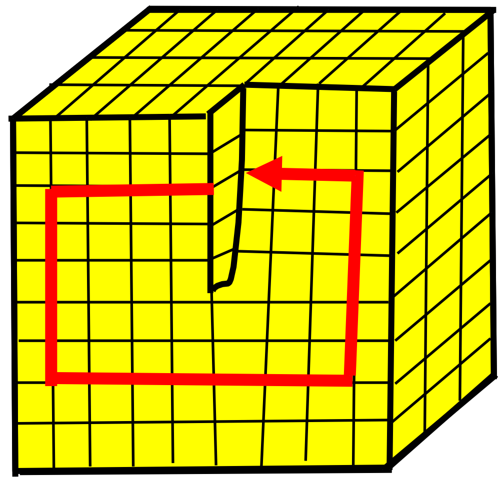
Edge Dislocation



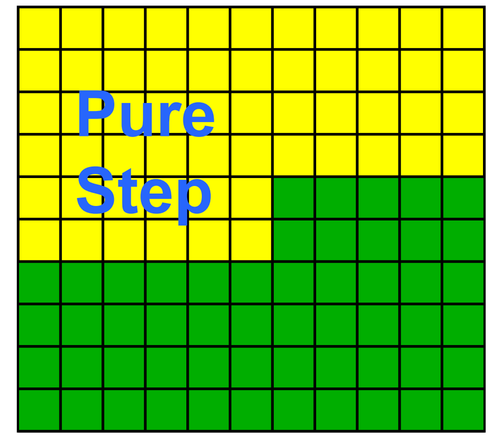
Reference Frame:
Perfect Crystal

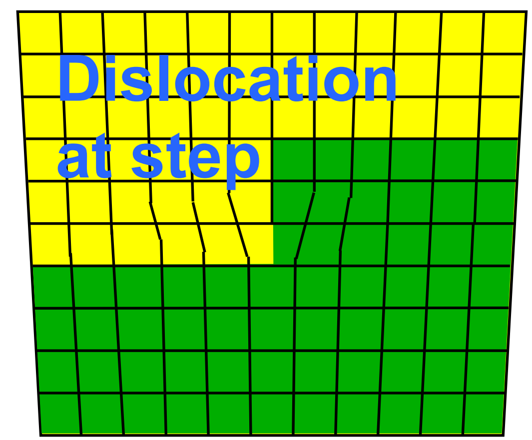


Screw Dislocation



Interfacial Disconnection





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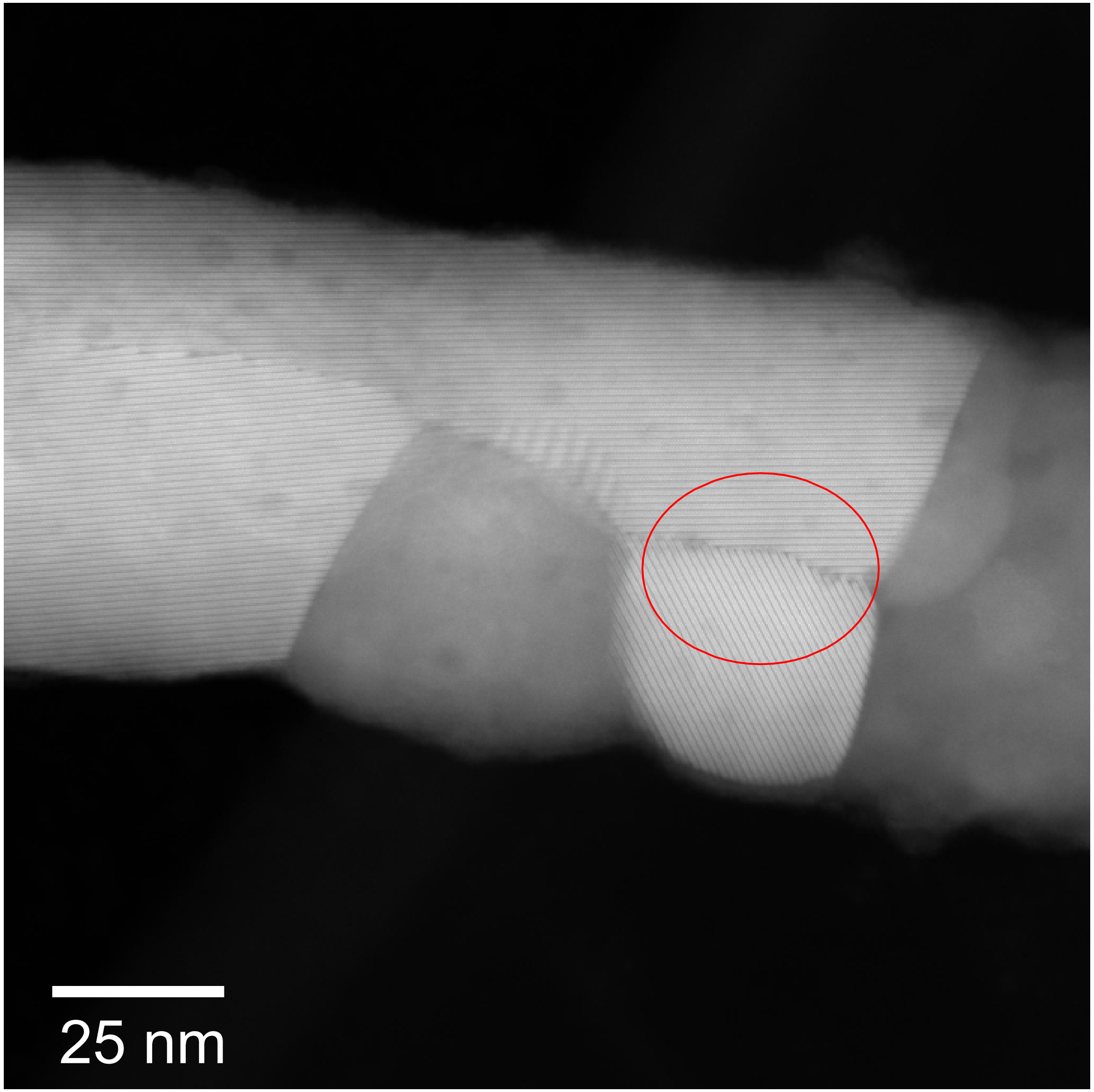
Bi_2Te_3 <2-1-1 0>//<-2 1 1 0> 63.78° Boundary

Electrodeposited
Bi_2Te_3 nanowire
Annealed 300°C



FEI-Titan
HAADF-STEM
300 keV

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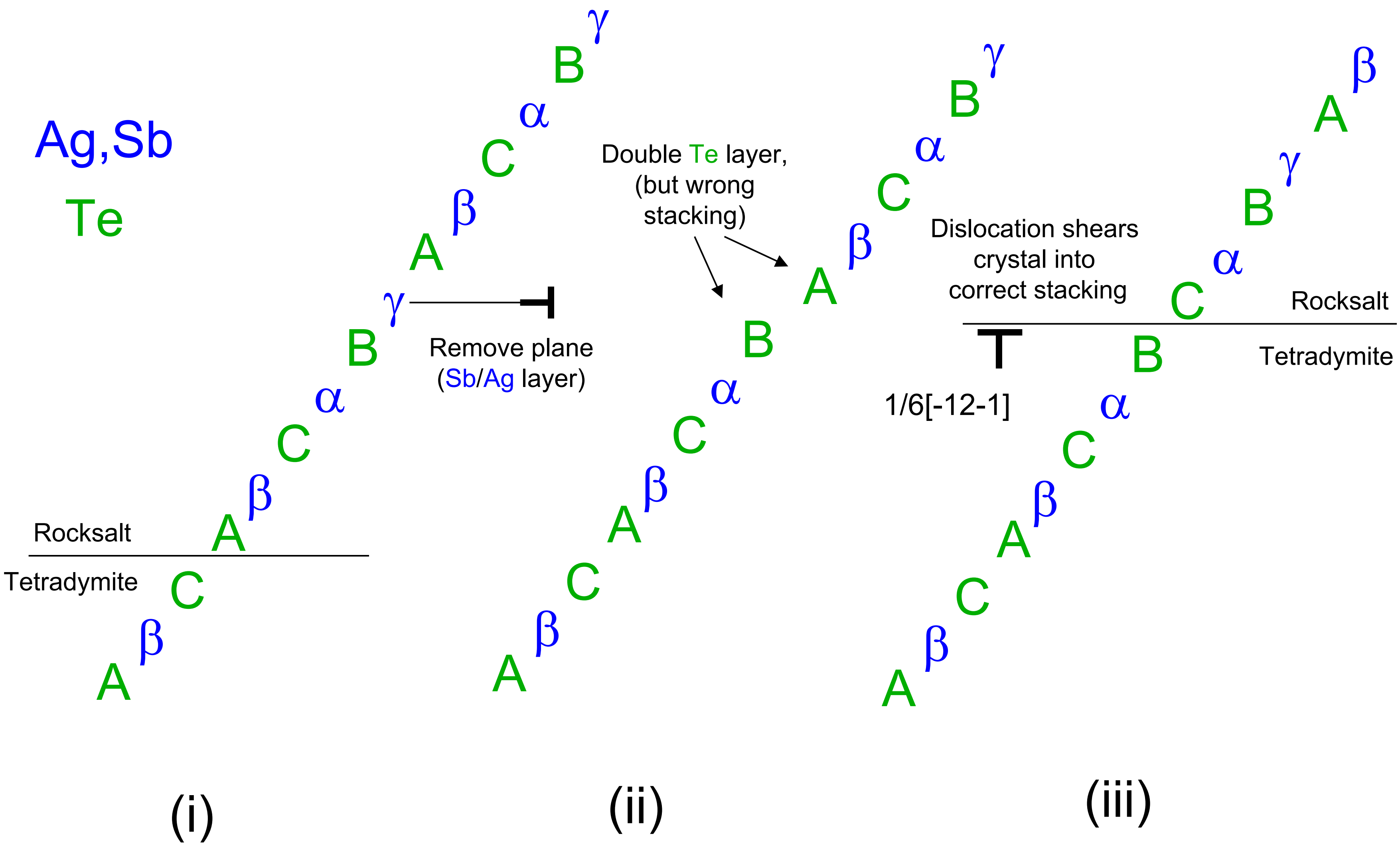
Schematic of Transformation Sequence



Medlin and Sugar, Scripta Materialia, 2010.

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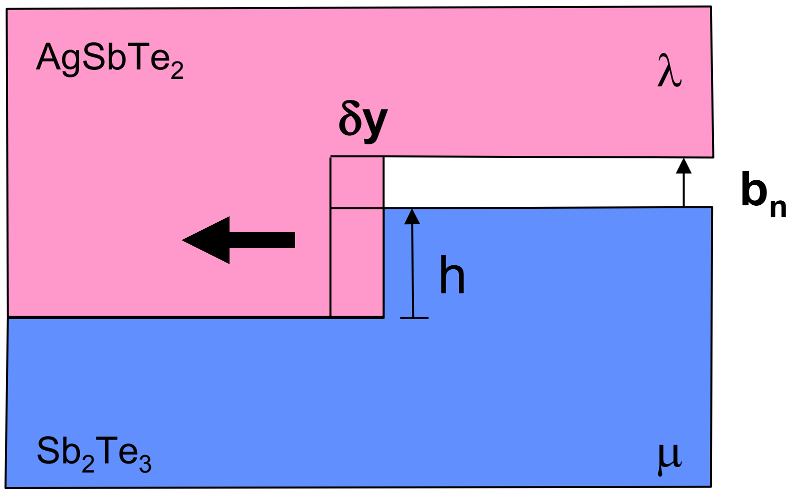
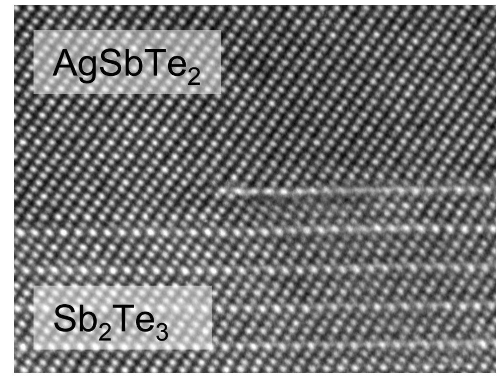
Defect properties give local mass flux required for transformation

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.

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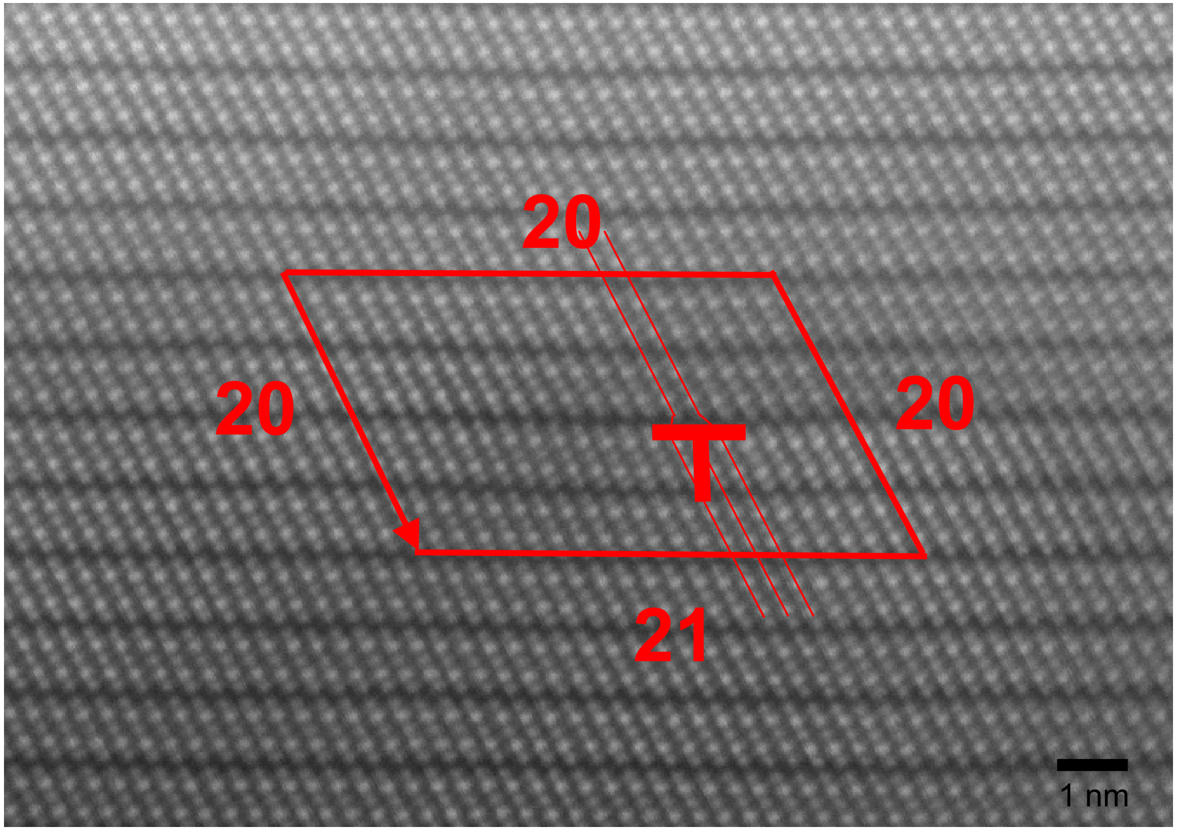
Dislocation Core structure: termination at Te$^{(1)}$-Te$^{(1)}$ layer, dissociation

5-layer
Bi_2Te_3
"quintet"

[0 0 0 1]



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

60° mixed dislocation

FEI-Titan
HAADF-STEM
300 keV

<2 -1 -1 0 > projection

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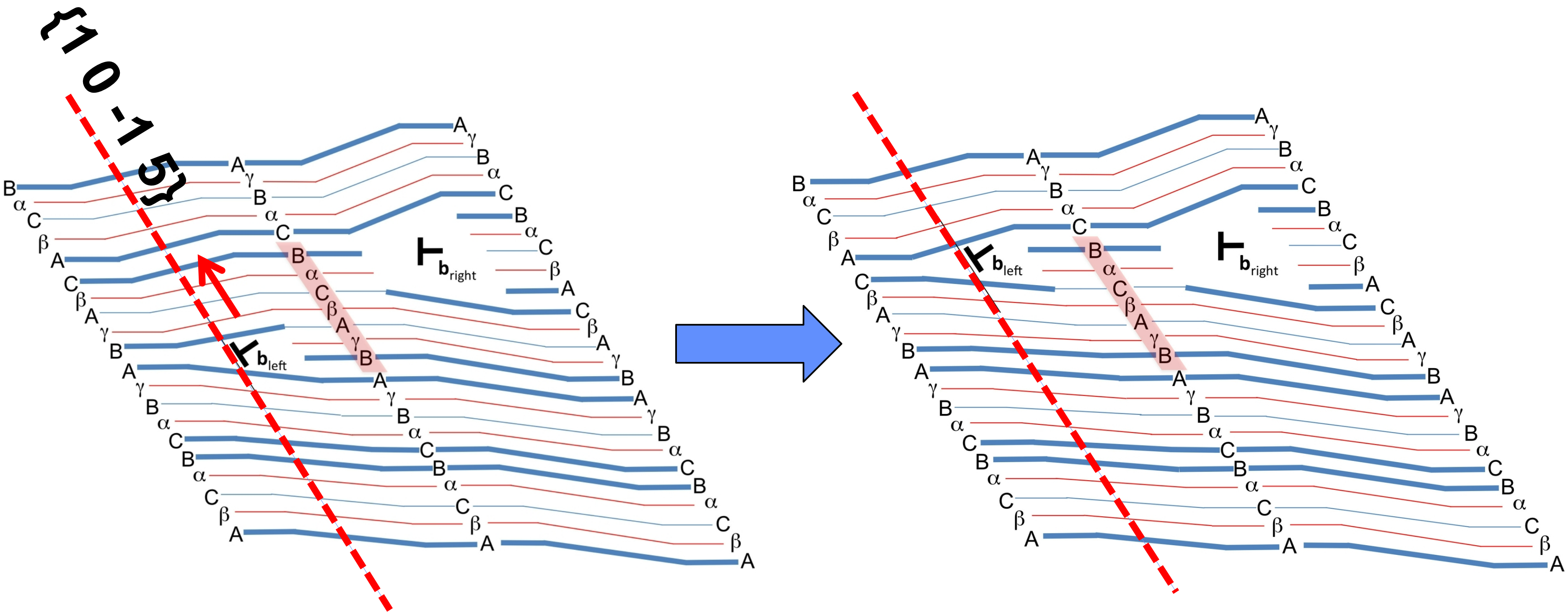
Core can re-configure via glide of the left partial dislocation on {1 0 -1 5} plane



-{1 0 -1 5} is most densely packed plane in tetradymite structure
-Analogous to {001} plane in rock-salt structure.

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