Interfacial Structure in Telluride-Based Thermoelectric Materials

SAND2011-4856C

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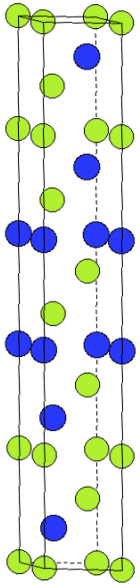
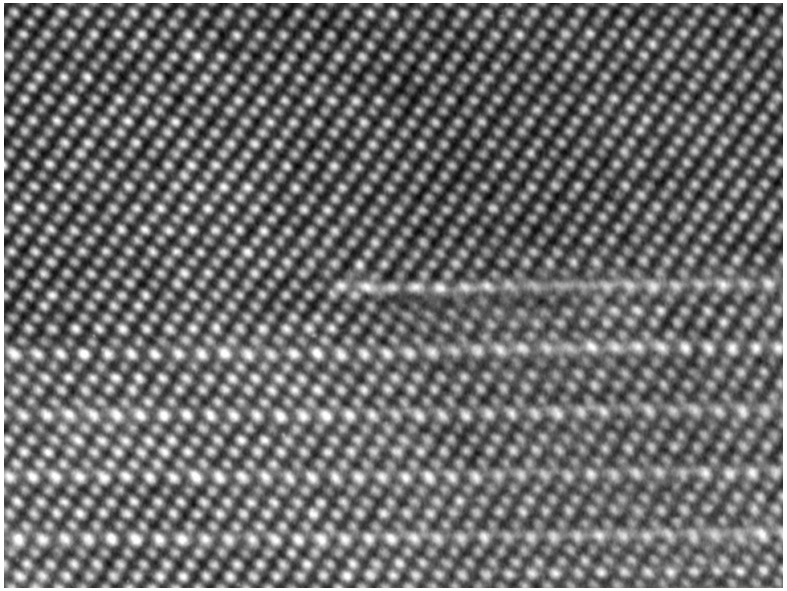
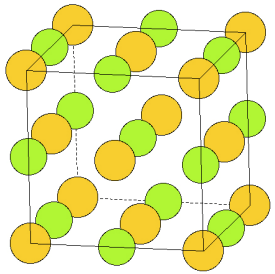
Tetradymite





Rock-Salt



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Microstructure in Bulk Thermoelectrics

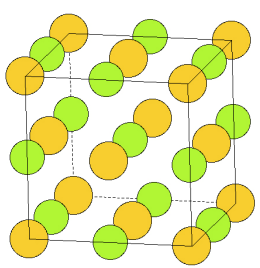
- Variety of microstructural strategies for bulk thermoelectrics employ embedded interfaces to decouple thermal and electronic transport

- Solid-state phase transformations provide one route to embedding interfaces

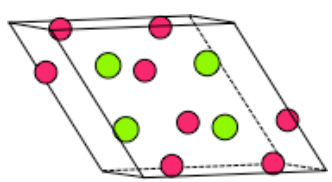
- *Our focus:*
  Establish the atomic mechanisms that govern formation and stability of embedded interfaces in nanostructured thermolectrics.

- *Thermoelectric Tellurides:*
  Rich set of structures and phase relations

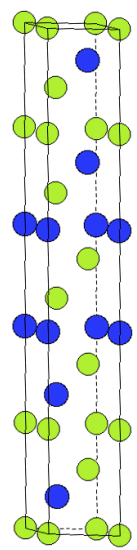
Rock-Salt
(PbTe, $AgSbTe_2$)



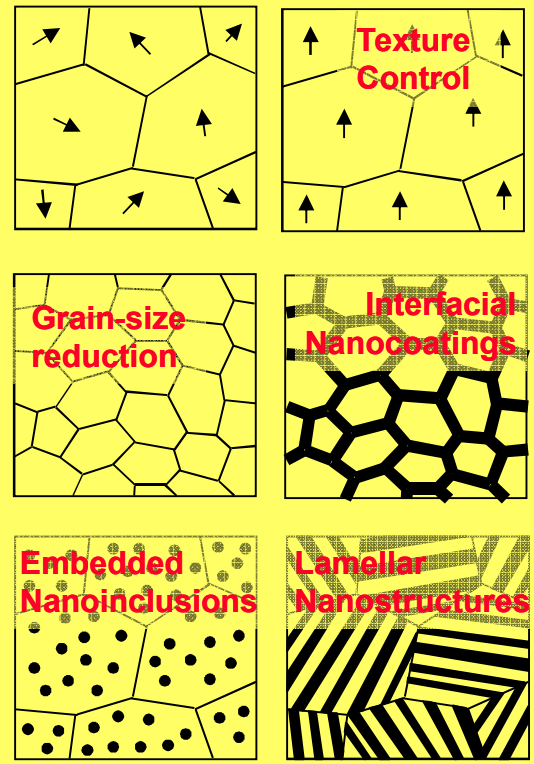
Monoclinic
(Ag_2Te)



Tetradymite
(Bi_2Te_3,Sb_2Te_3)



Microstructural Strategies for Nanostructured Bulk Thermoelectrics



Medlin and Snyder, Current Opinion in Colloid and Interface Science, 2009

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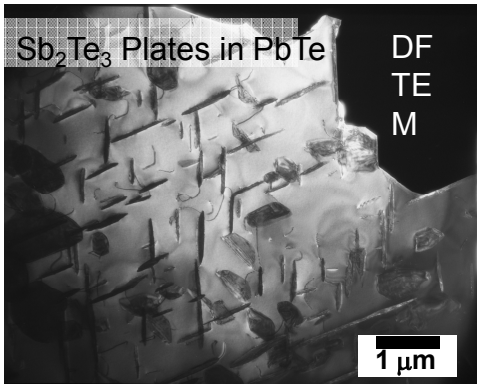
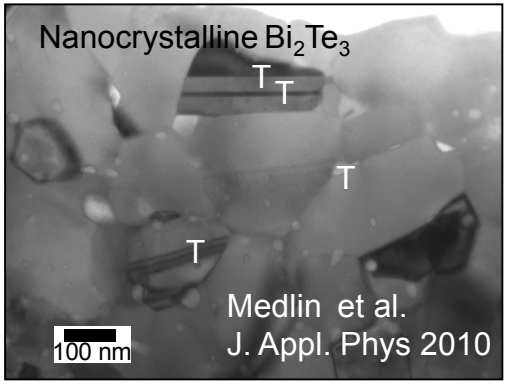
Outline

- **Rocksalt/Tetradymite Telluride Interfaces**
  - -$AgSbTe_2/Sb_2Te_3$
  - -$PbTe/Sb_2Te_3$
  - -Tetradymite plate formation.
  - - Interfacial strain accommodation.



- **Structure of the basal twin in Bi_2Te_3**
  - -What is the compositional termination?
  - -Structural relaxations?
  - -Formation mechanism?



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Collaborators

Sandia:

Josh Sugar
Jessica Lensch-Falk
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Caltech:

Nick Heinz
Teruyuki Ikeda
G. Jeffrey Snyder

LBNL:

Quentin Ramasse

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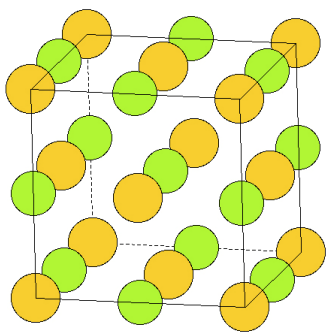
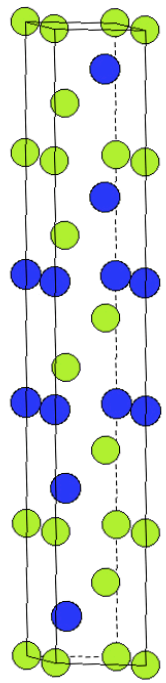
Heterophase Rock-Salt/Tetradymite Telluride Interfaces

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:

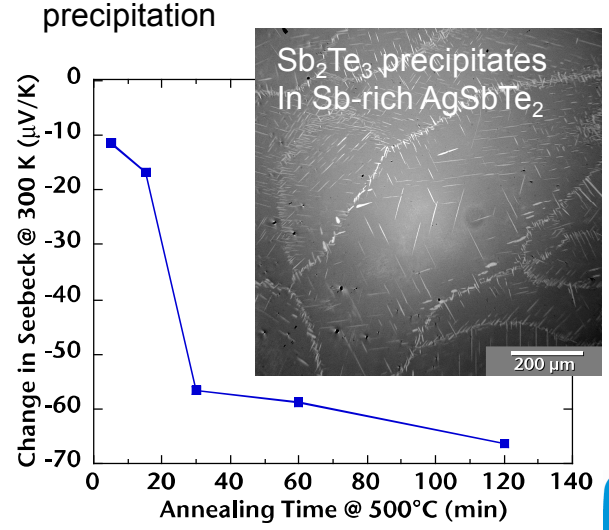
-Possibility for well ordered interfaces.
-Transformations provide bulk route to synthesis.
Ikeda, et al., Chem Mater. 2007
Snyder and Toberer, Nature Materials 2008

-$AgSbTe_2$:

-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

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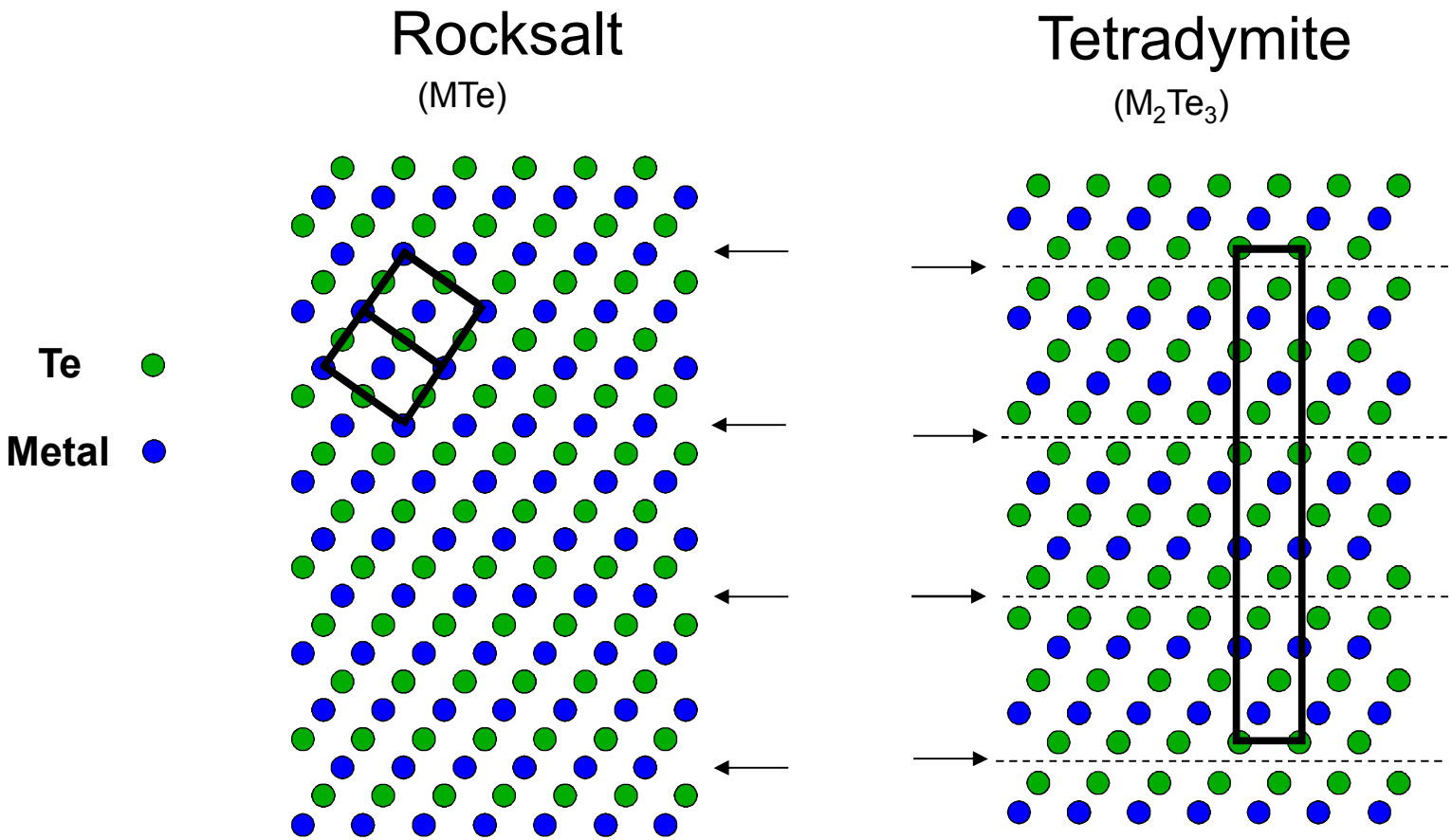
Rocksalt and Tetradymite-structured Tellurides are Closely Related



-Remove metal plane every 6 layers
-Shear blocks by 1/3<10-10>
(or 1/6<112> relative to cubic coordinates)

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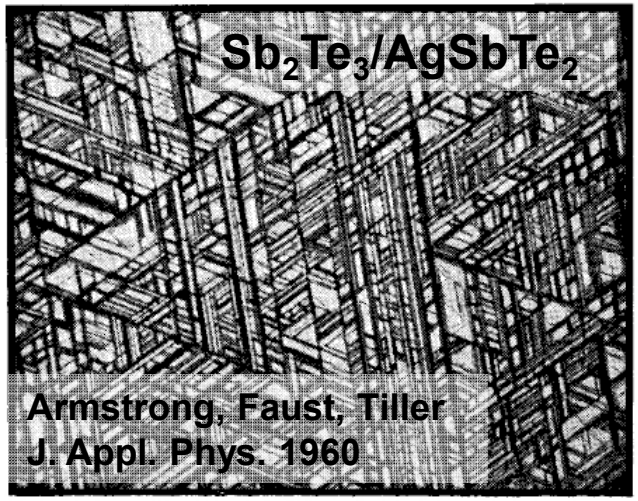
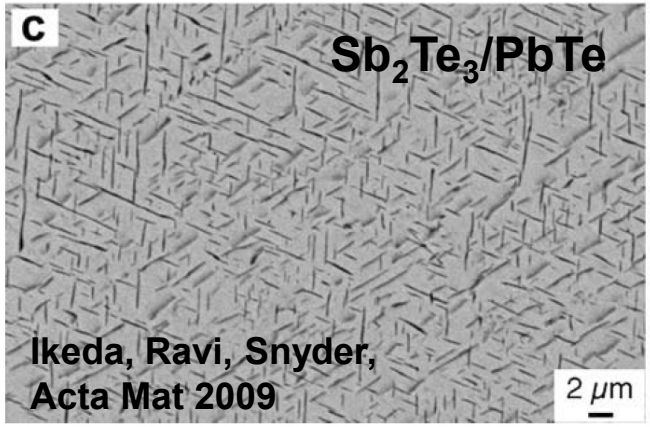
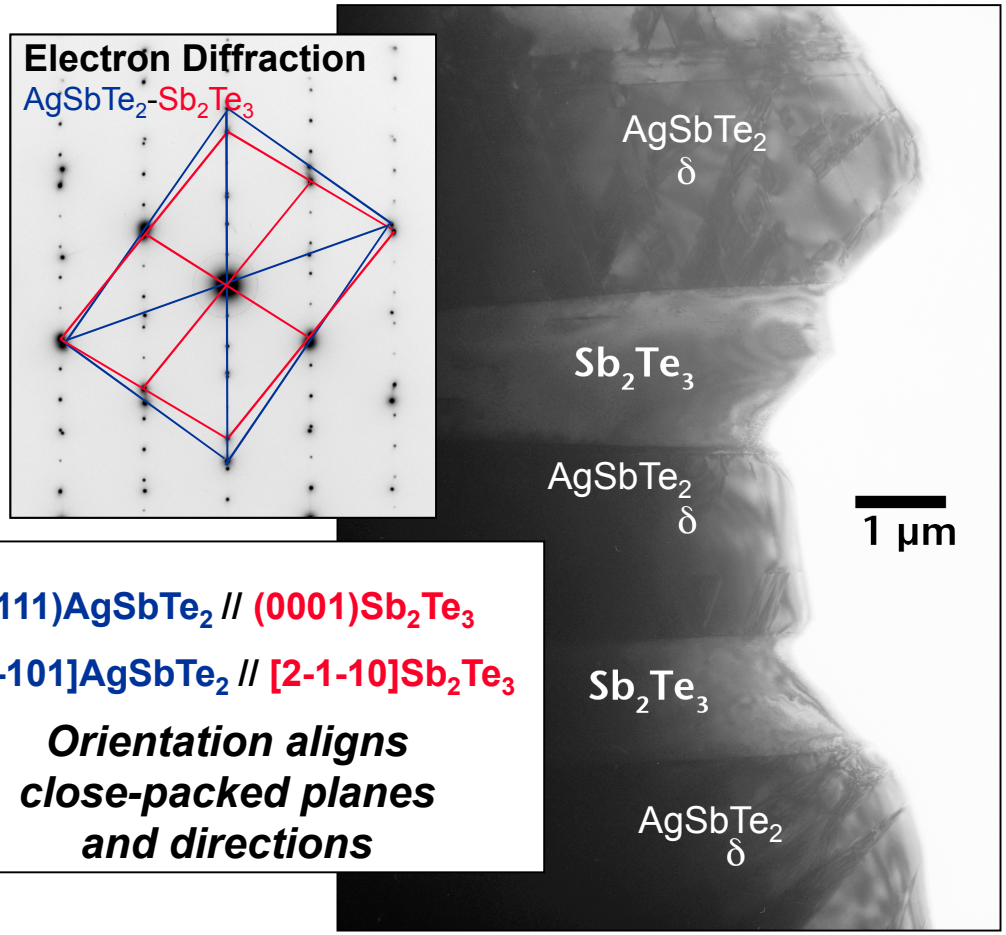
Tetradymite Precipitates in rock-salt structured tellurides

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

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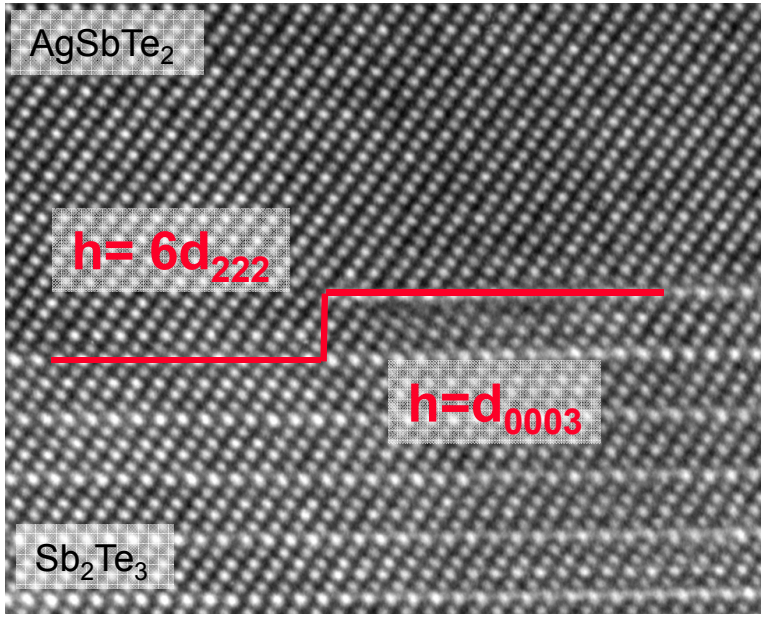
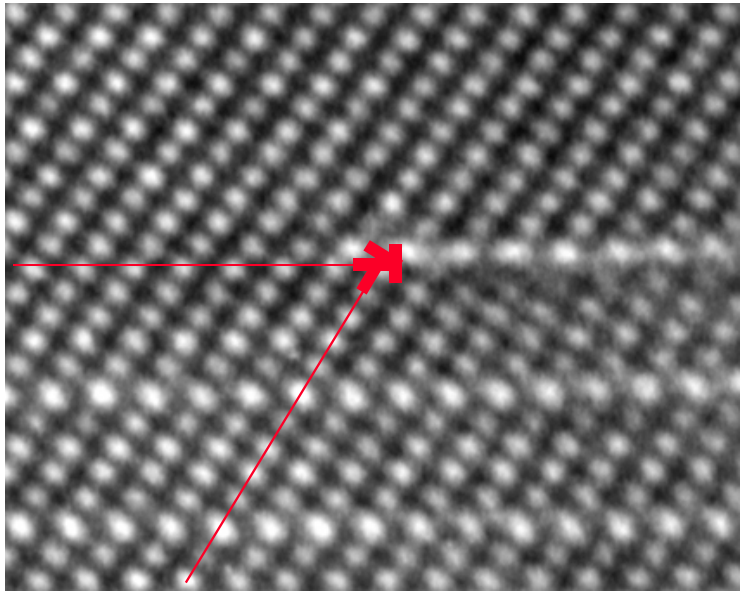
HRTEM : Step at $AgSbTe_2/Sb_2Te_3$ Interface





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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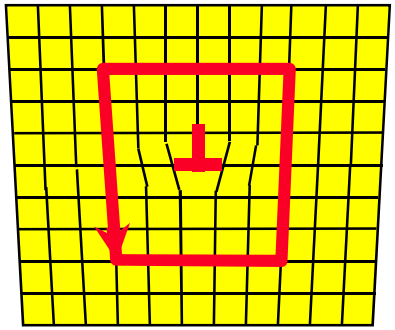
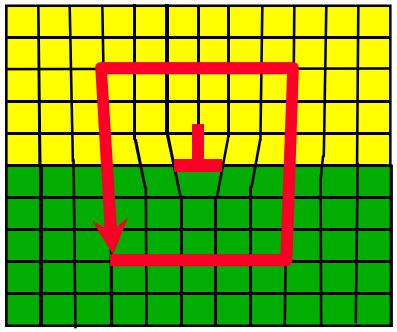
Defining the topological properties of line defects requires a reference frame

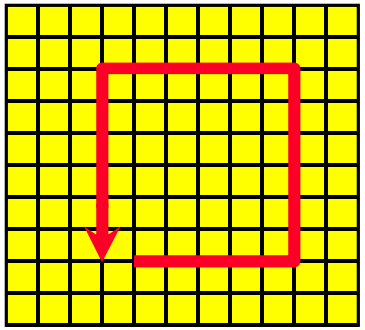
Bulk Lattice Dislocation.



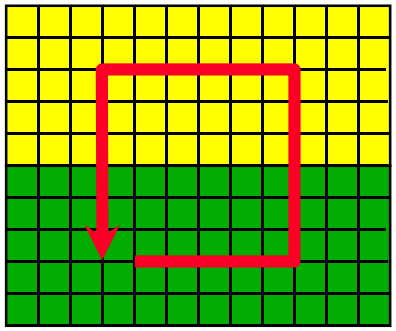
Heteroepitaxial Misfit Dislocation.



Reference Frame:
Perfect Crystal



Reference Frame:
Coherently Strained Interface



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Circuit analysis to quantify defect character

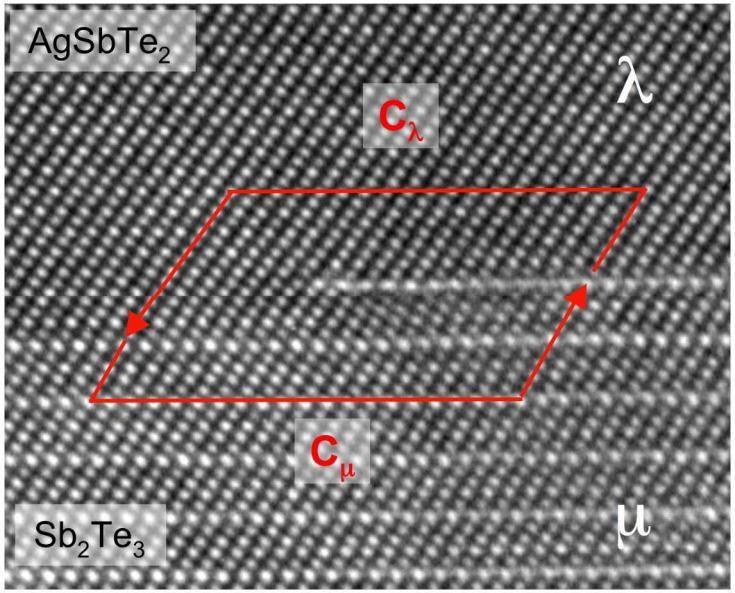
Burgers vector:

Upper crystal circuit

Lower crystal circuit

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

Crystal coordinate transformation



Referenced to Coherent Frame:

Strain to bring μ and λ into coherency

$$P = LAM = \begin{pmatrix} \frac{1}{2} & \frac{-1}{2} & \frac{c_{hex}}{a_{cub}\sqrt{3}} \\ 0 & \frac{1}{2} & \frac{c_{hex}}{a_{cub}\sqrt{3}} \\ \frac{-1}{2} & 0 & \frac{c_{hex}}{a_{cub}\sqrt{3}} \end{pmatrix}$$

Converts from orthonormal to λ crystal coordinates

Converts from μ crystal coordinates to orthonormal coordinates

Misfit: 0.79%

$$r = \frac{1}{\sqrt{2}} \frac{a_{cub}}{a_{hex}} = 1.0079$$

Sb_2Te_3: a=4.264 Å
c=30.458Å

$AgSbTe_2$: a=6.078Å

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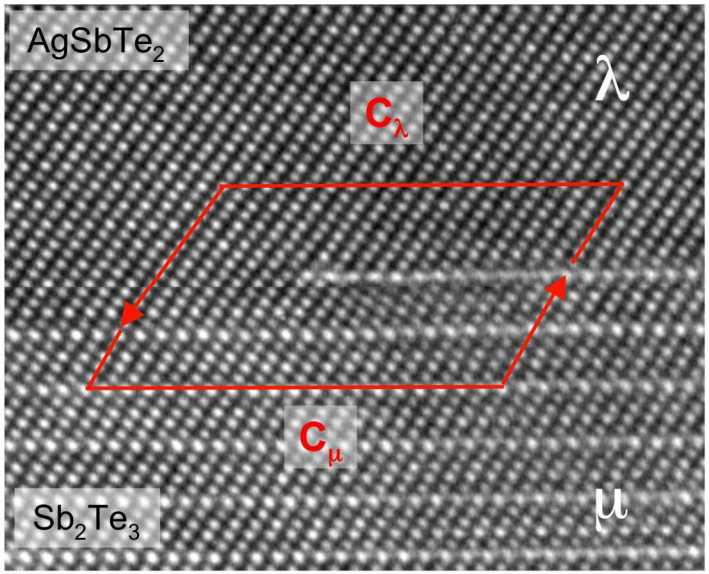
Role of defect in precipitate growth:

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 reference frame

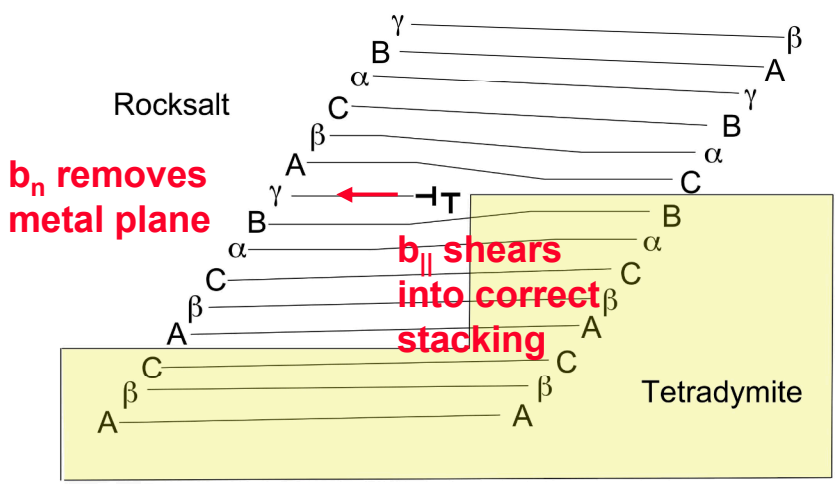
Resolve b into components normal and parallel to interface

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

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

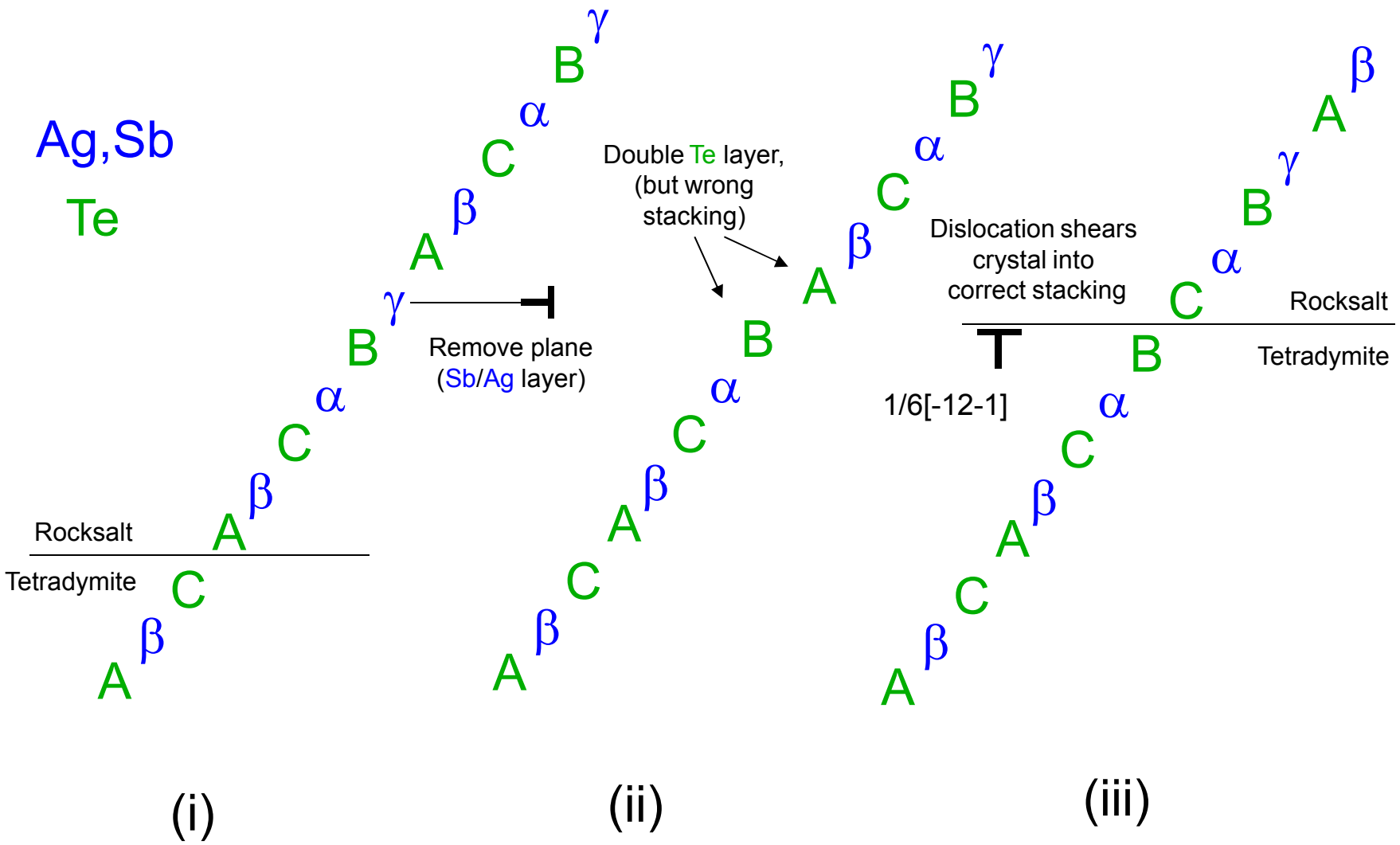
$$\mathbf{b}_{\parallel} = \frac{a_{cub}}{6}[\bar{1}2\bar{1}]$$

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



Medlin and Sugar, Scripta Materialia, 2010.

Schematic of Transformation Sequence



Medlin and Sugar, Scripta Materialia, 2010.

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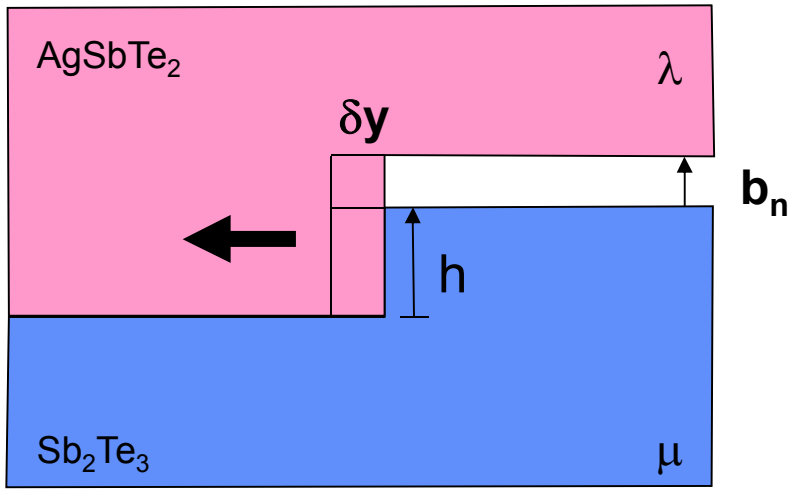
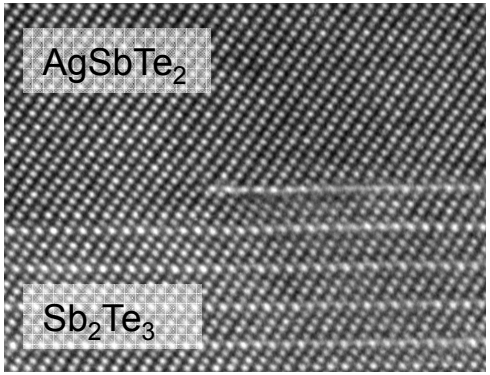
Defect properties give local mass flux required for transformation

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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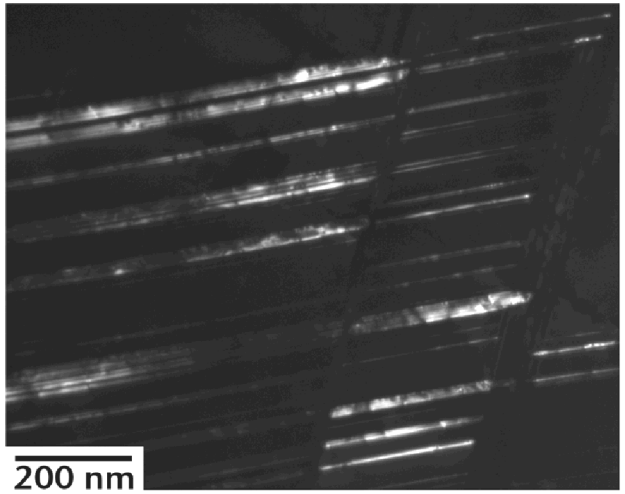
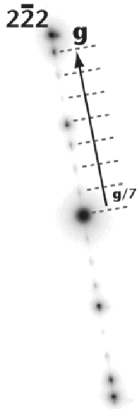
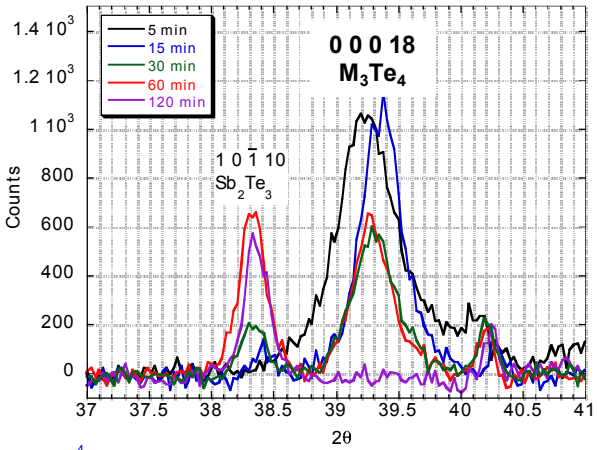
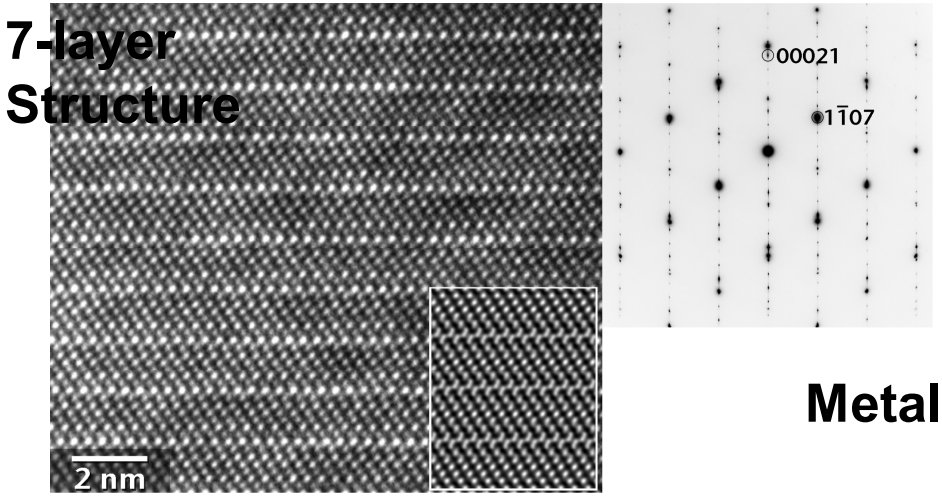
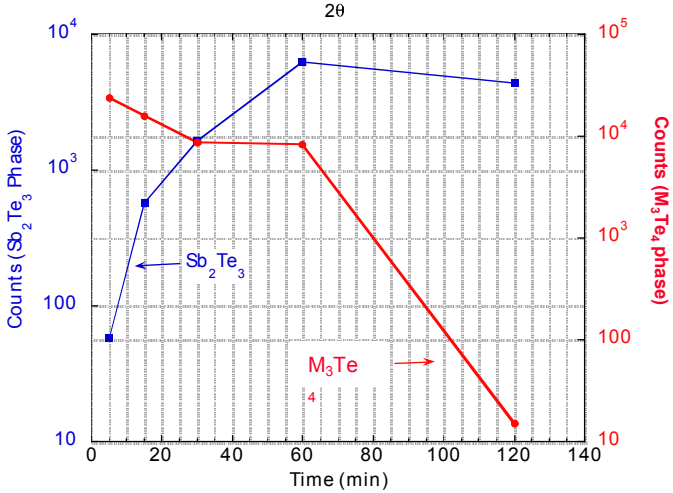
Initial Stages of Precipitation: Transition Phase: $(Ag,Sb)_3Te_4$











Metal rich intermediate phase

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

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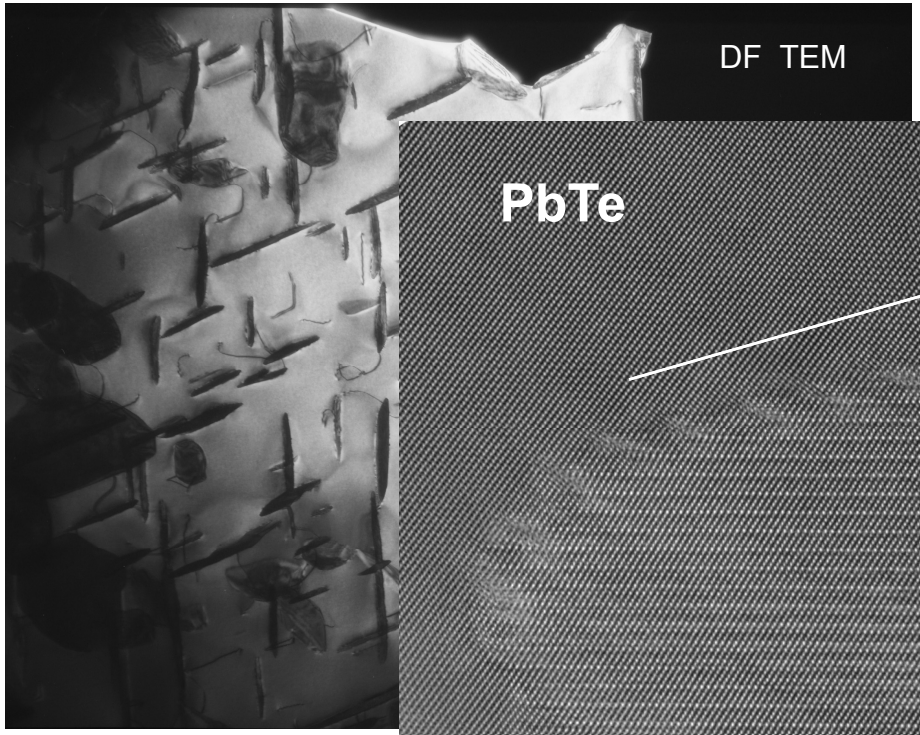
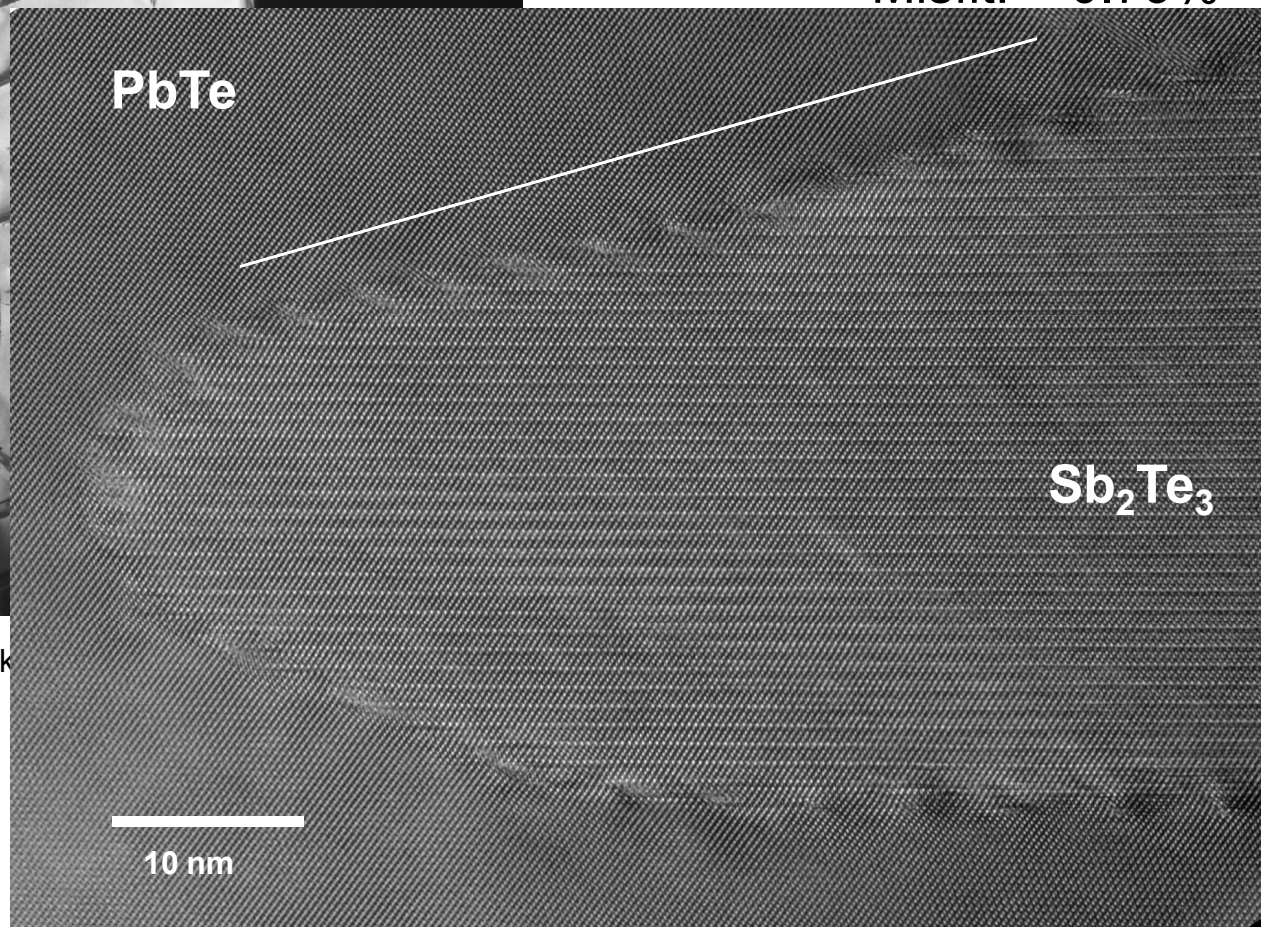
A system with larger misfit: $PbTe/Sb_2Te_3$

Sb_2Te_3 Precipitates in PbTe



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



Work with N. Heinz, T. Ik

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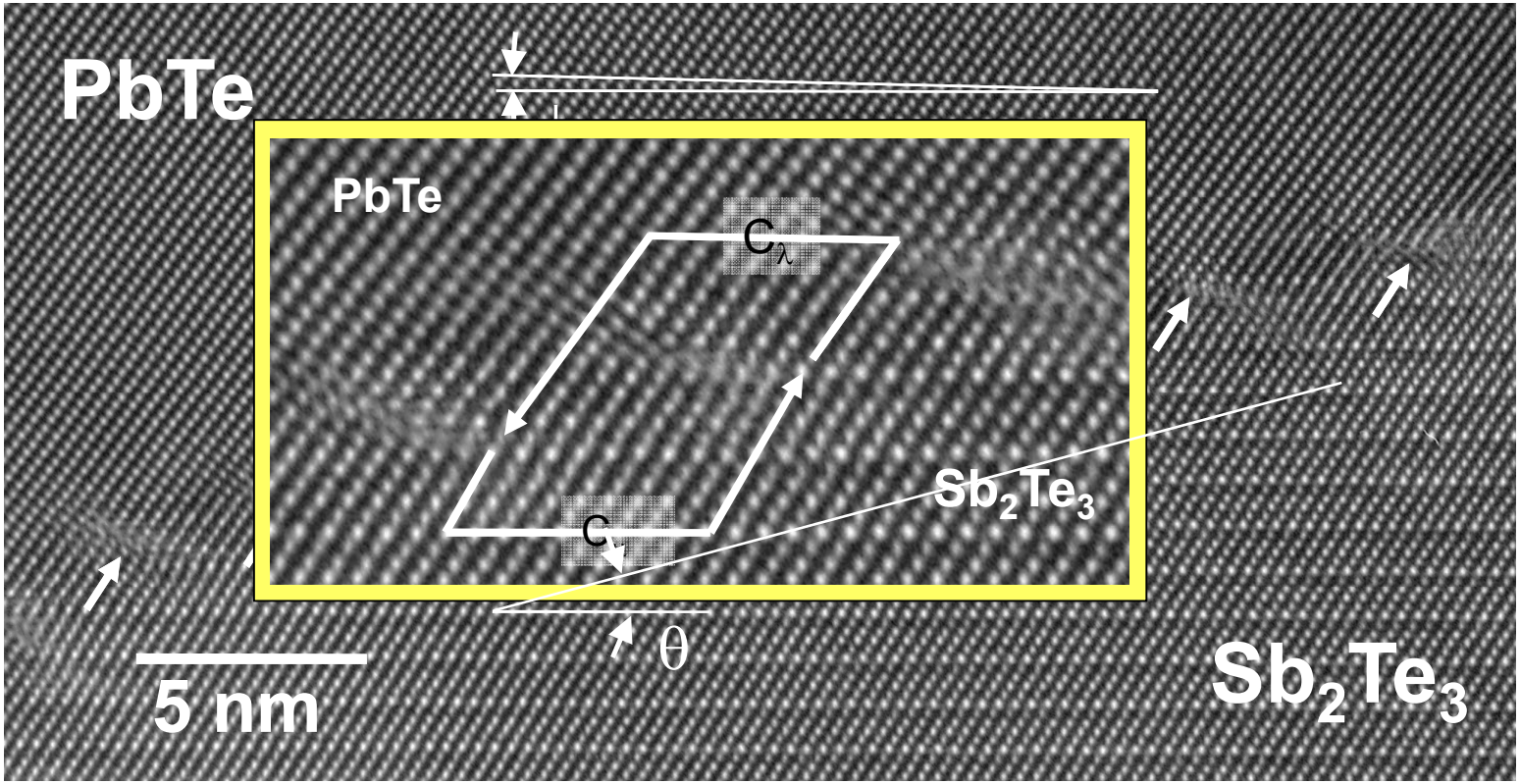
Inclined Section of interface Composed of Disconnections



Circuit Analysis:
Defects identical to the disconnections observed in $AgSbTe_2/Sb_2Te_3$

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

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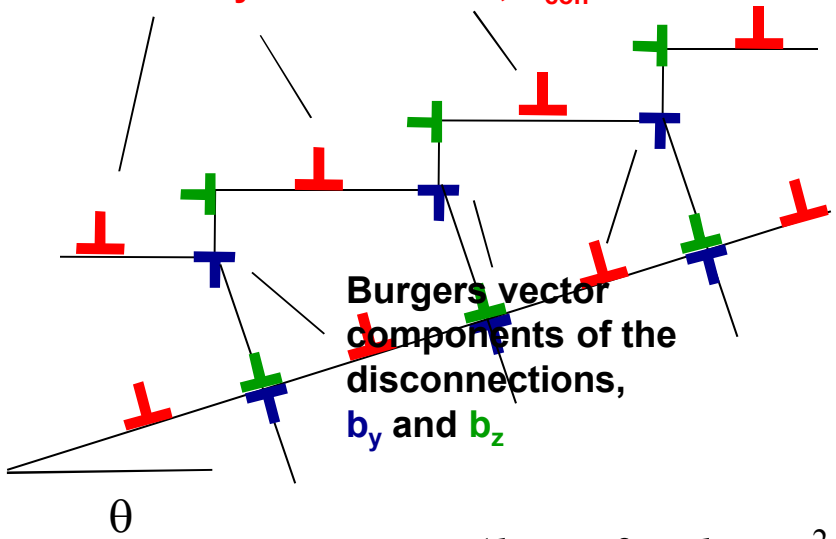
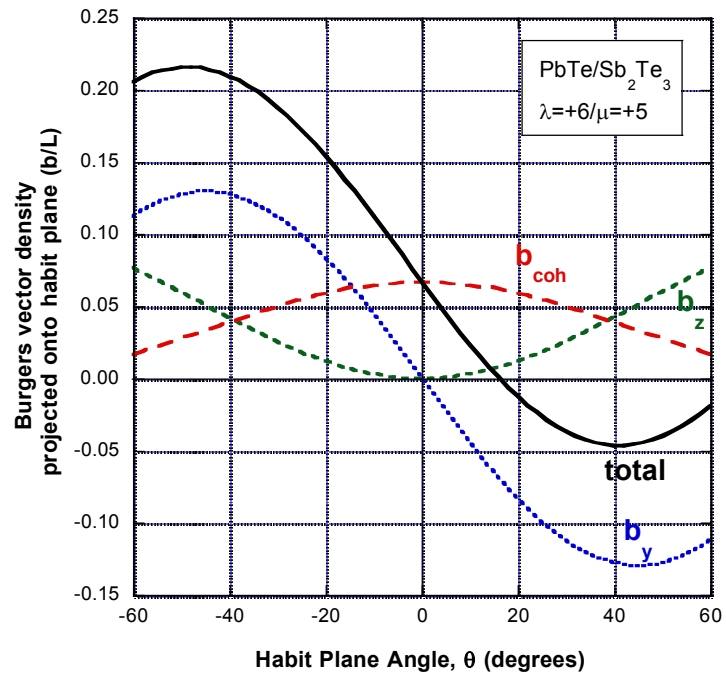
Defect Spacing Controlled by Misfit Strain

Project components on inclined interface plane

Adjust spacing to cancel (ε_{yy} = 0)

Coherency strain on terraces as "coherency" dislocations, b_{coh}





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

➔ θ=16.2°

Pond, Celotto, Hirth, Acta Mater. 2003

Out of plane **b** components produce small rotation,

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

➔ ϕ=1.7°

Steps cannot move independently:
Must be coupled through strain interaction

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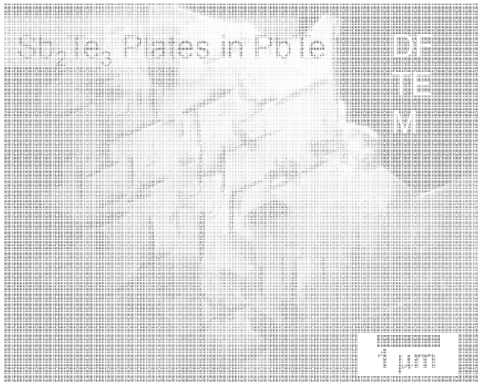
•Rocksalt/Tetradymite Telluride Interfaces

-$AgSbTe_2/Sb_2Te_3$
-$PbTe/Sb_2Te_3$

-Tetradymite plate formation.
- Interfacial strain accommodation.



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  -What is the compositional termination?
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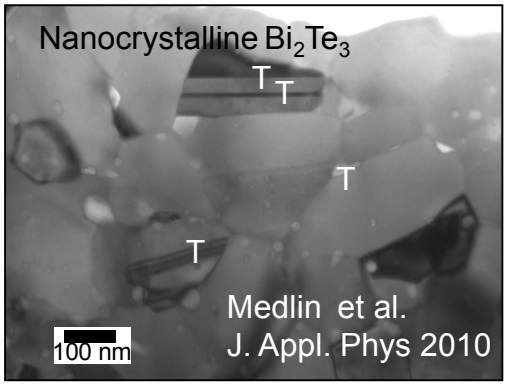

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Bismuth Telluride

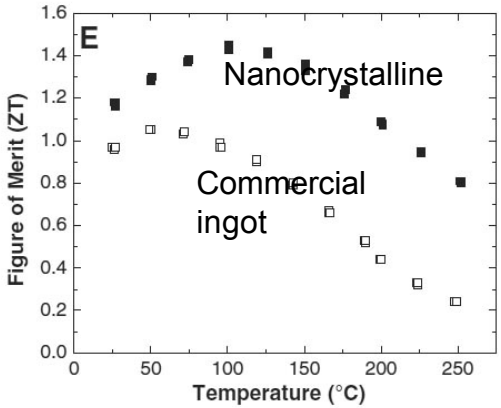
Motivation:
Large Enhancements in zT for nanostructured bulk Bi_2Te_3 (zT=1.4-1.6)

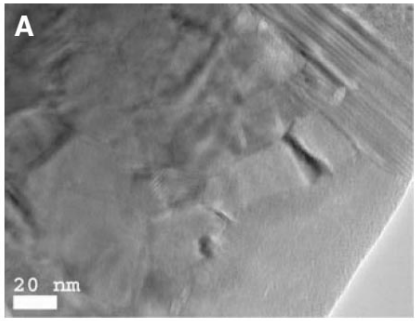
Poudel et al Science 2008 zT=1.4 @ 100°C
Xie et al, J. Appl. Phys 2009

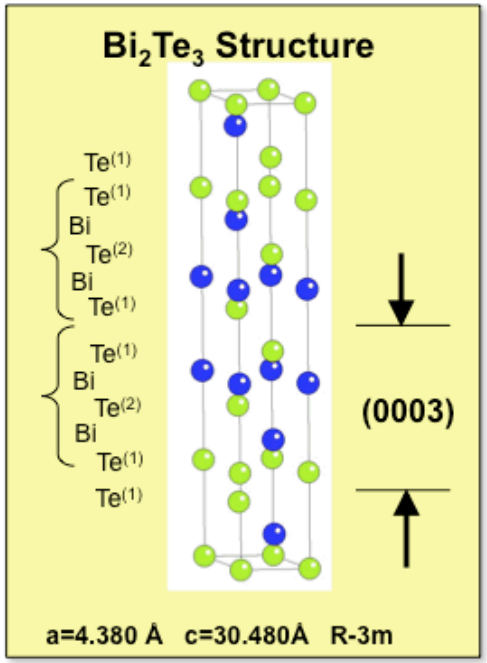
-Reduced κ_l, boundary phonon scattering

Enhanced zT in nanocrystalline $(Bi,Sb)_2Te_3$

Poudel et al. Science 2008







Little is known about GBs in Bi_2Te_3

-Twins make good starting point.

Twins have potential for favorable TE electronic transport properties

-Coherent structure, near bulk-like coordination.

]

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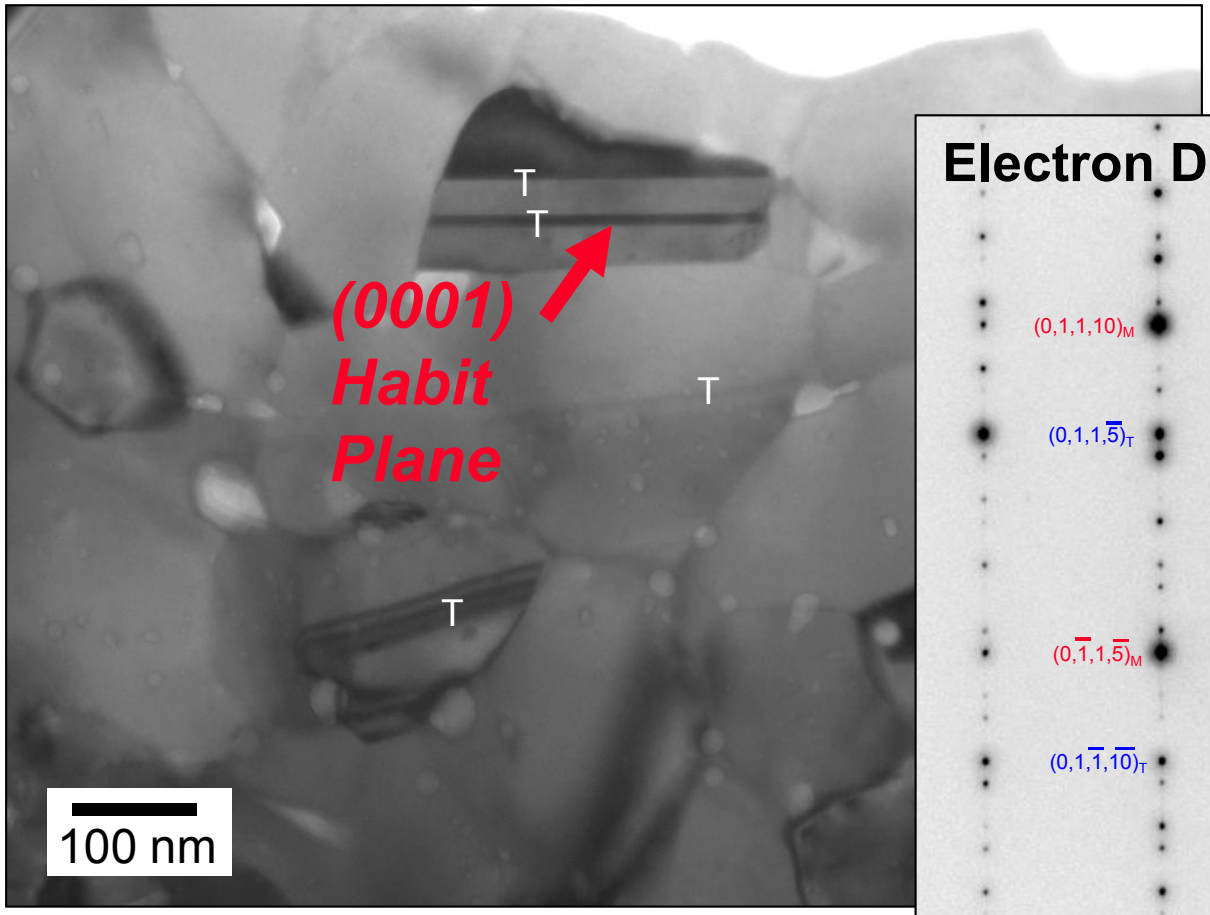
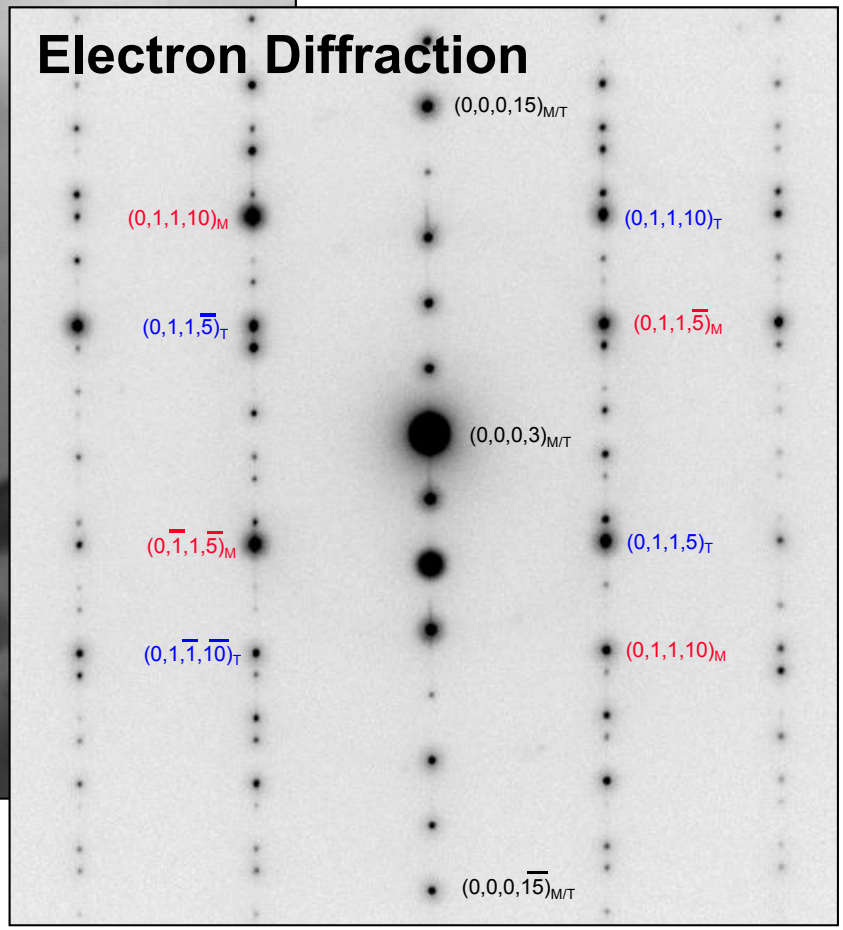
Twin microstructure and crystallography





Bi_2Te_3: Powder consolidated by spark plasma sintering

Orientation Relationship:
(0001)//(0001)
[2-1-10]//[-2110]

60° rotation about c-axis

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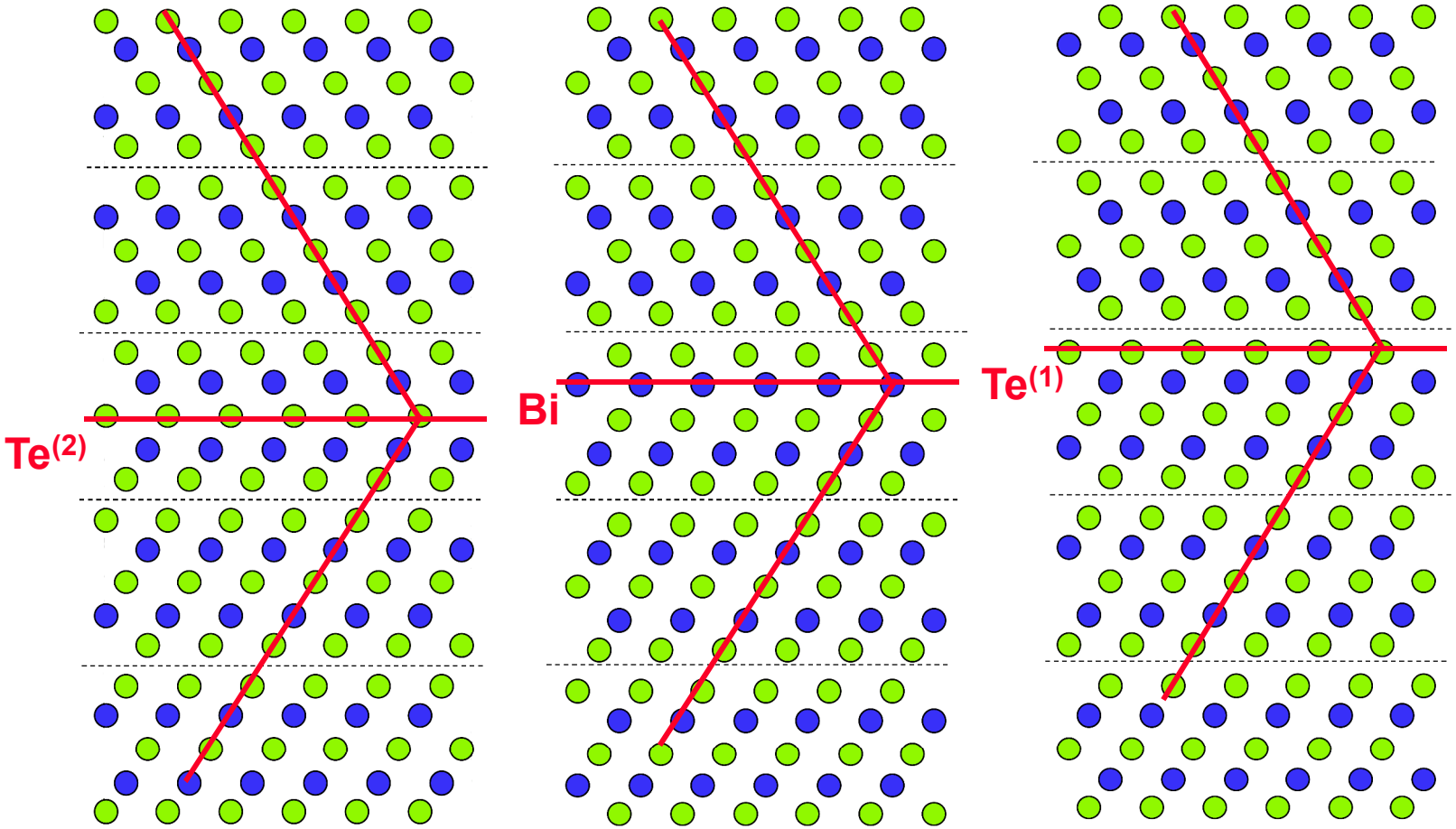
Question: How is twin terminated?



DFT-LDA: 60.1 mJ/m^2 303.0 mJ/m^2 **40.7 mJ/m^2**

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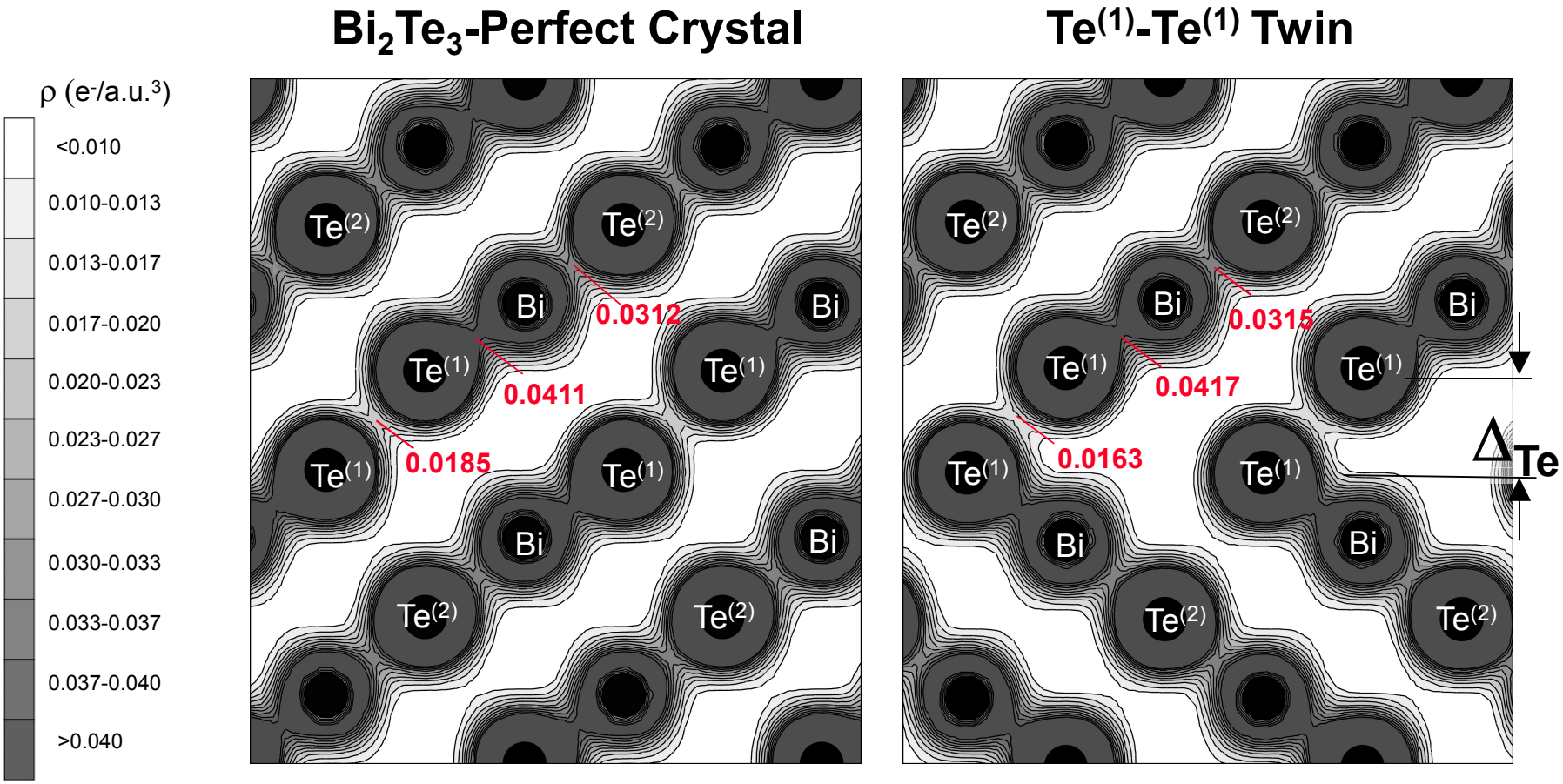
Calculations predict expansion at interface



Charge density between $Te^{(1)}$-$Te^{(1)}$ atoms is lower at twin.
Calculations predict expansion normal to interface:

$$\Delta_{Te,interface} - \Delta_{Te,bulk} = +0.12Å$$

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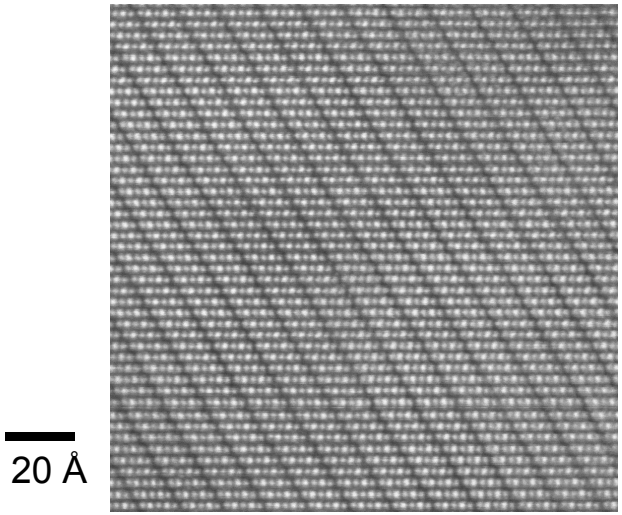
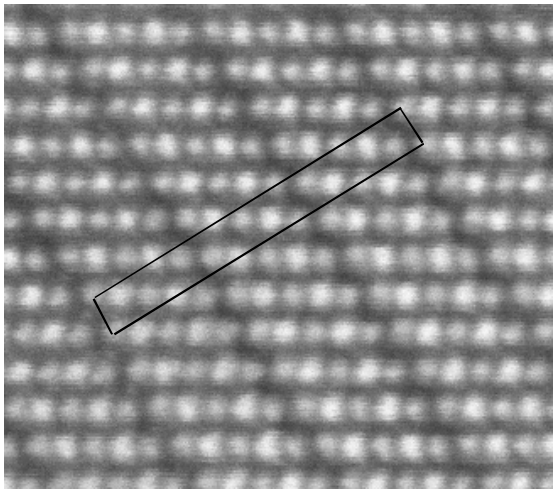
Bi_2Te_3 : High Angle Annular Dark Field STEM

Bi_2Te_3: $\langle 2\bar{1}\bar{1}0 \rangle$ Projection

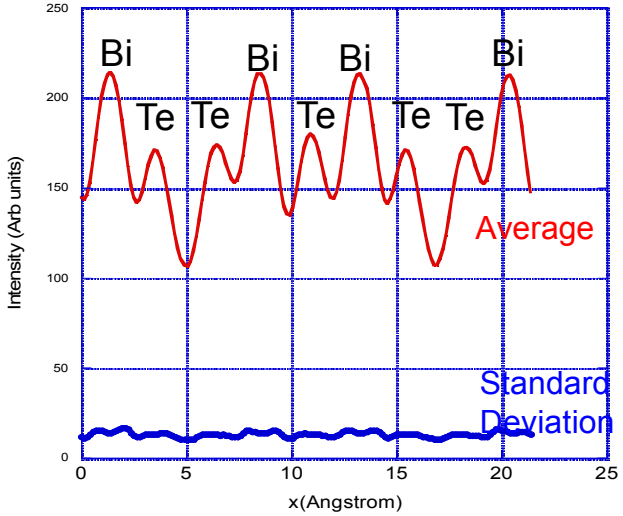


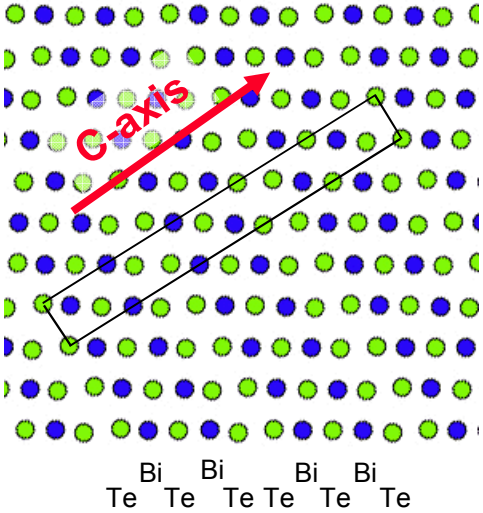


Bi and Te are well Discriminated by HAADF-STEM

Bi: Z=83

Te: Z=52





Aberration Corrected TEAM 0.5 Instrument National Center for Electron Microscopy

With Quentin Ramasse

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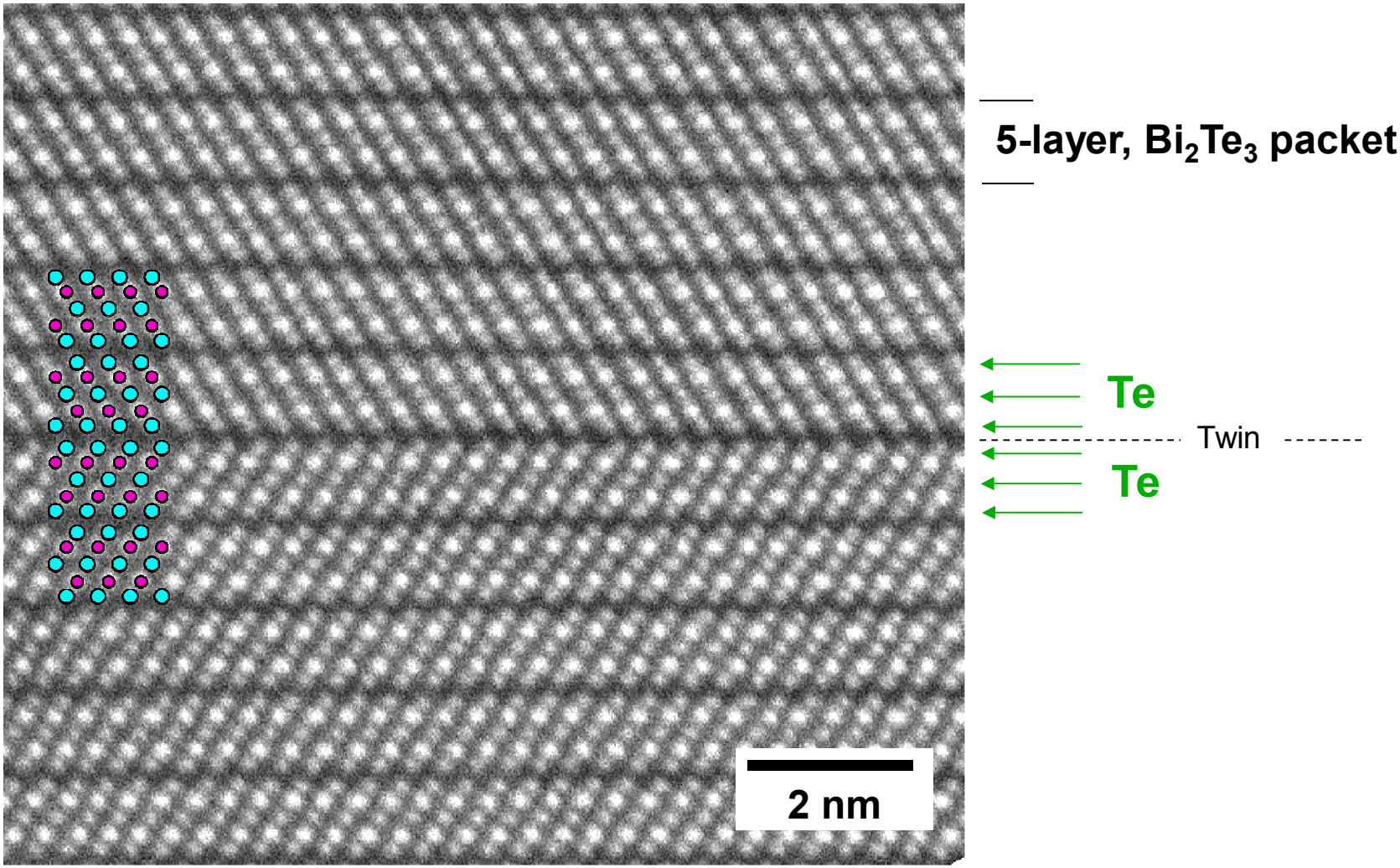
Observations:
Twin terminated at $Te^{(1)}$-$Te^{(1)}$ layer



Medlin, Ramasse, Spataru, Yang, J. Appl. Phys (2010)

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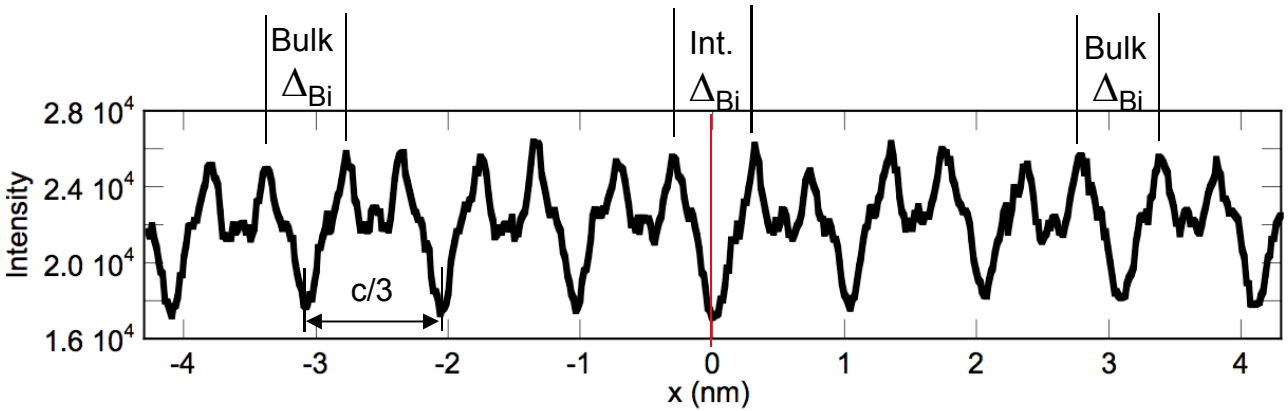
Experimental measurements confirm expansion

Peak positions measured from intensity line profiles



60 line profiles, integrated over 8Å width
4 independent images

Peak positions refined by fitting to sum of Gaussians:

$$I(x) = A_0 + \sum_{i=1}^{5} A_i e^{\left[\frac{-(x-x_{0,i})^2}{2\sigma_i^2}\right]}$$

	$\Delta_{int}-\Delta_{bulk}$	
	Theory	Exp
Te(1)	+0.120 Å	+0.12±0.04Å
Bi	+0.116 Å	+0.13±0.03Å

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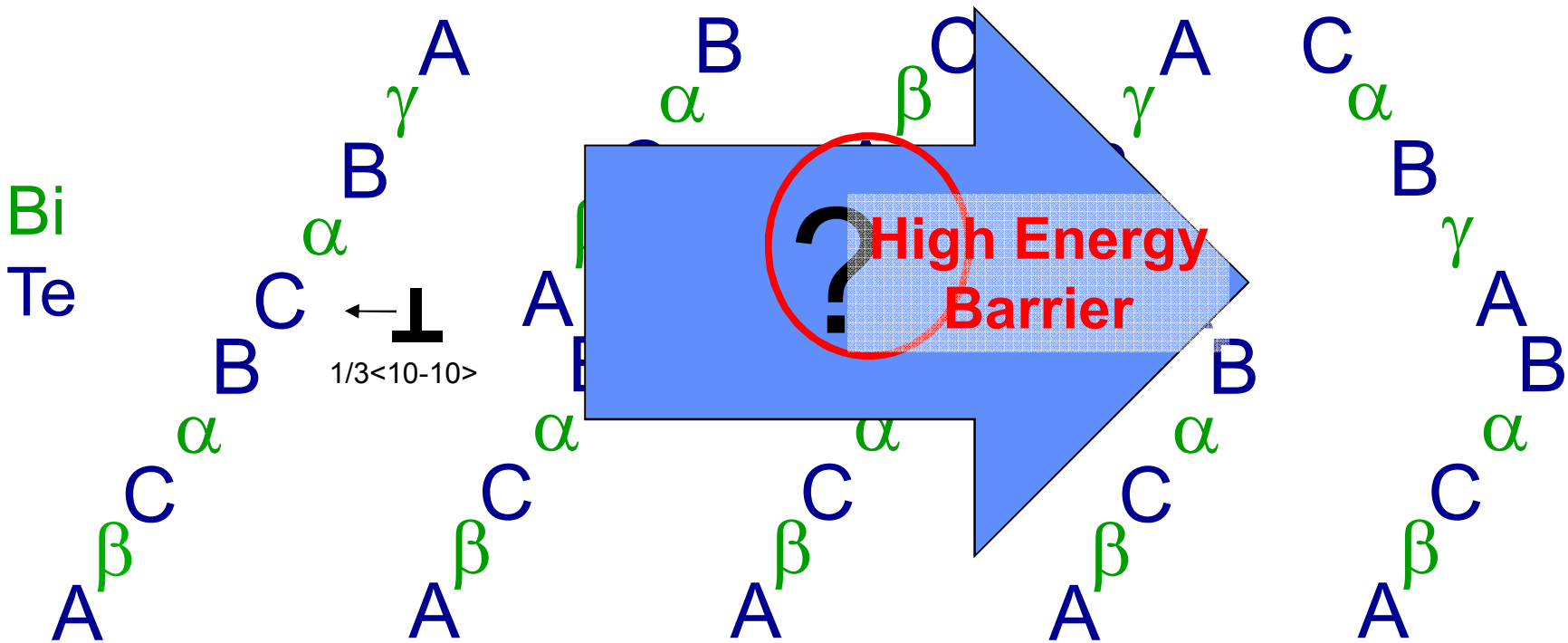
How do twins form in Bi_2Te_3?

Sequential motion of twinning dislocations?



-High energy barrier for Bi-terminated interface

➔ independent motion of twinning dislocations unlikely.

-Alternative: Coordinated defect motion.

Groupings of *unlike* twinning dislocations

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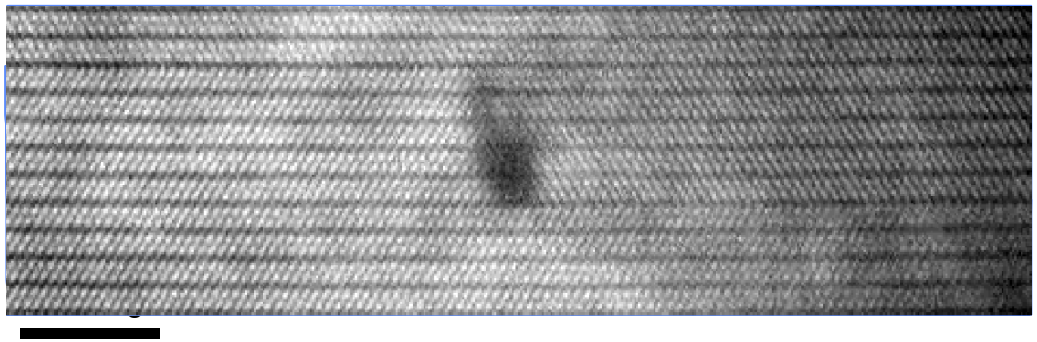
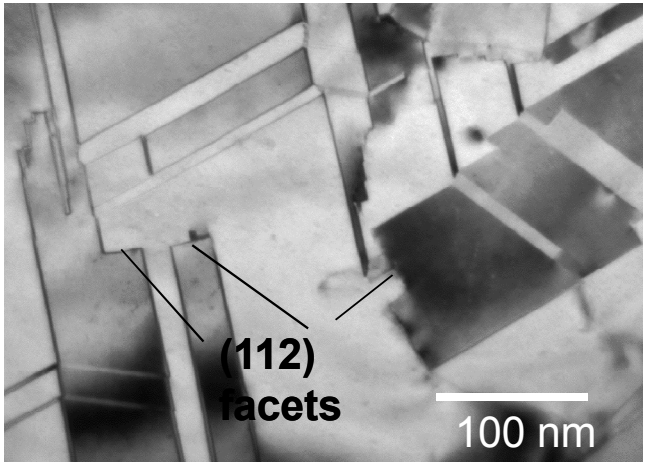
Steps in the Bi_2Te_3 Twin Boundary

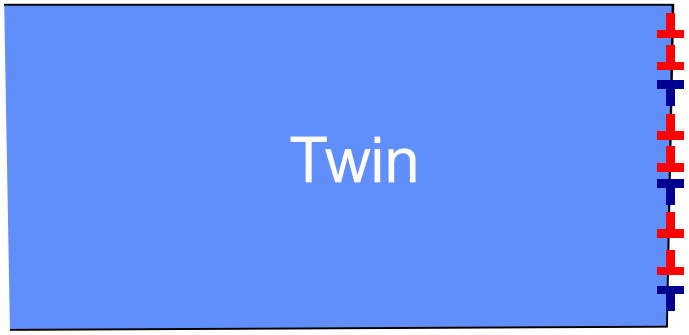


Analogies to {112} twins in FCC materials.

Example: Twins in Electrodeposited Ni



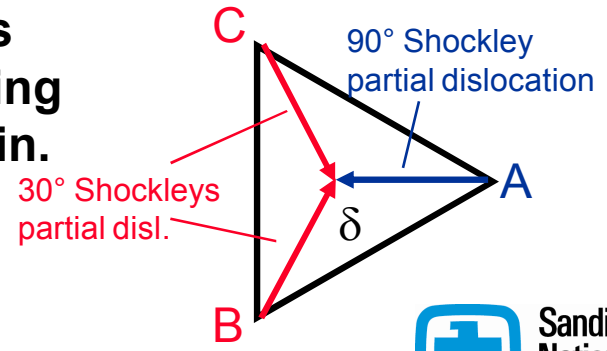
Lucadamo, Medlin, Talin, Yang, Kelly, Phil Mag 2005



1/6<112> Dislocations

Groupings of 3 unlike dislocations

Burgers vectors cancel eliminating long-range strain.



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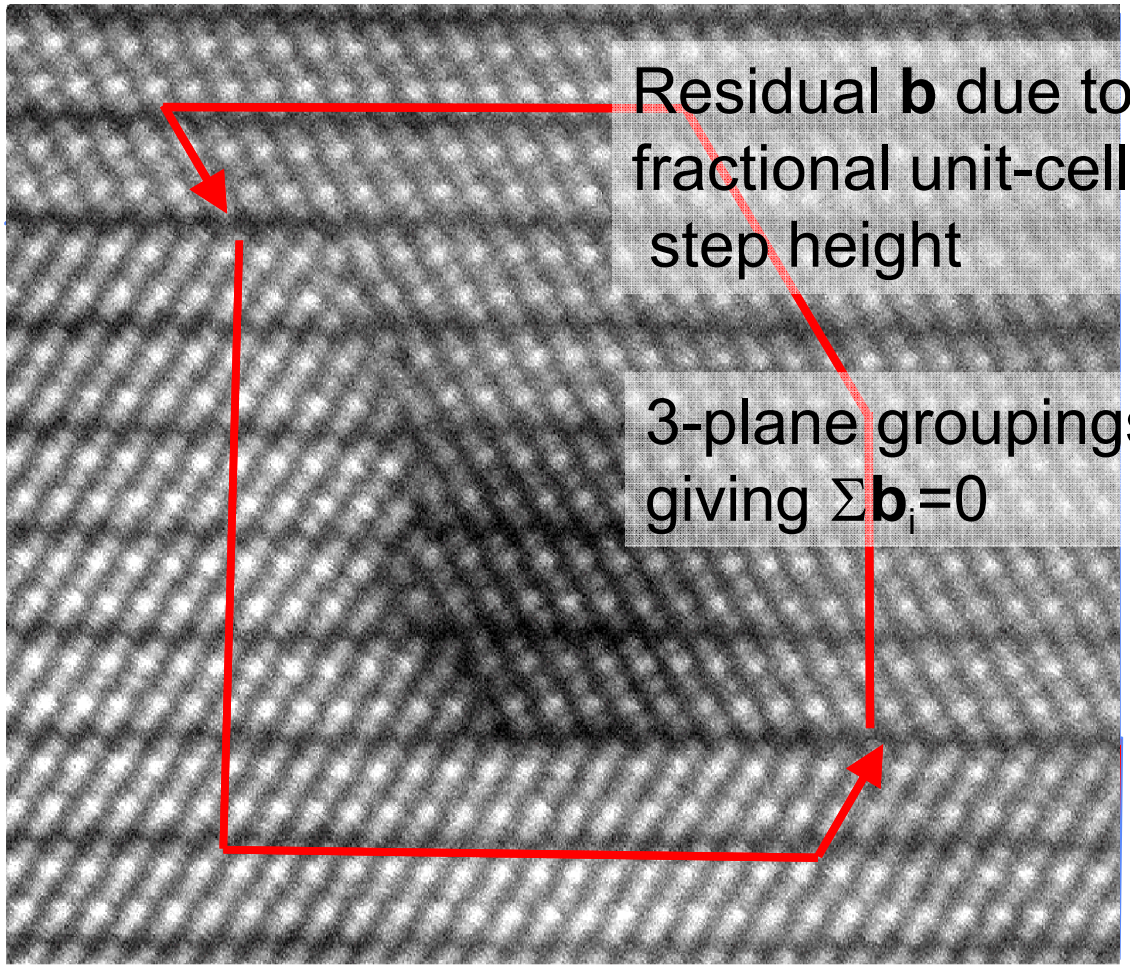
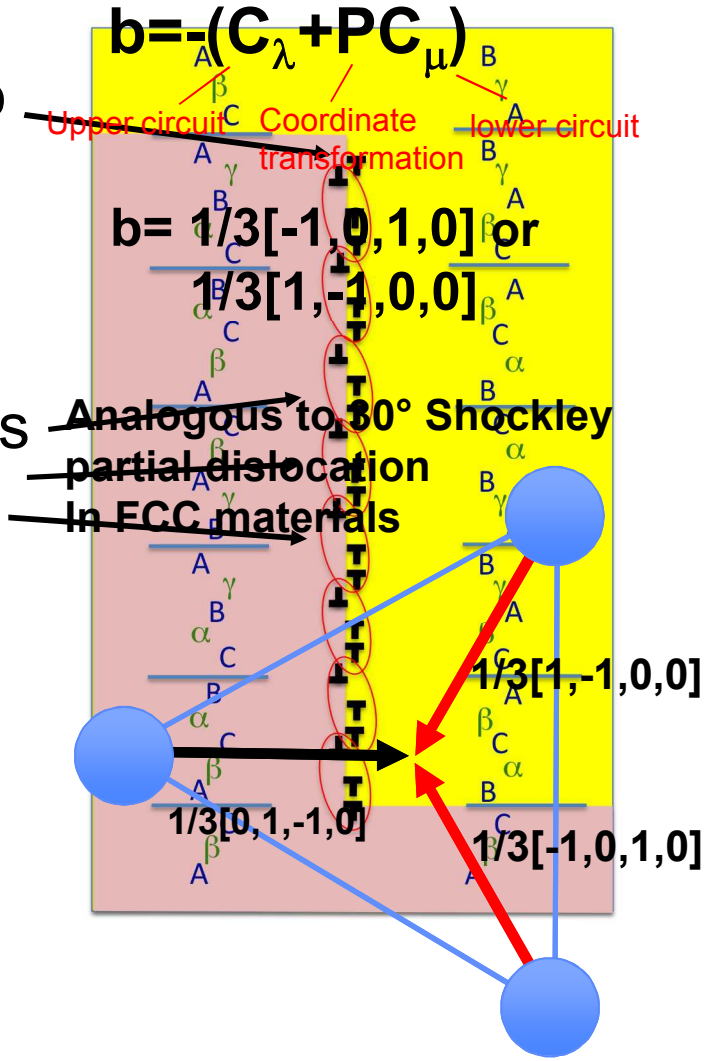
What is the dislocation content of the step?





LLNL-Titan
HAADF-STEM
300 keV

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Summary

- **Defect mechanism for tetradymite plate growth in rocksalt tellurides discovered.**
  - -Disconnection motion: removes metal layer and restores stacking.
  - -Interplay between misfit accommodation and interface morphology through dislocation/step character.

- **Bi_2Te_3 (0001) Twin boundary structure determined.**
  - •Termination at Te(1)-Te(1) layer
    - -Lowest energy structure from *ab initio* calculations
    - -Structure confirmed with HAADF-STEM
  - • Defect structure:
    - -Analogies to FCC twins and defects.
    - -chemical constraint due to energetics of interface termination.

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Sandia:

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Teruyuki Ikeda

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Quentin Ramasse

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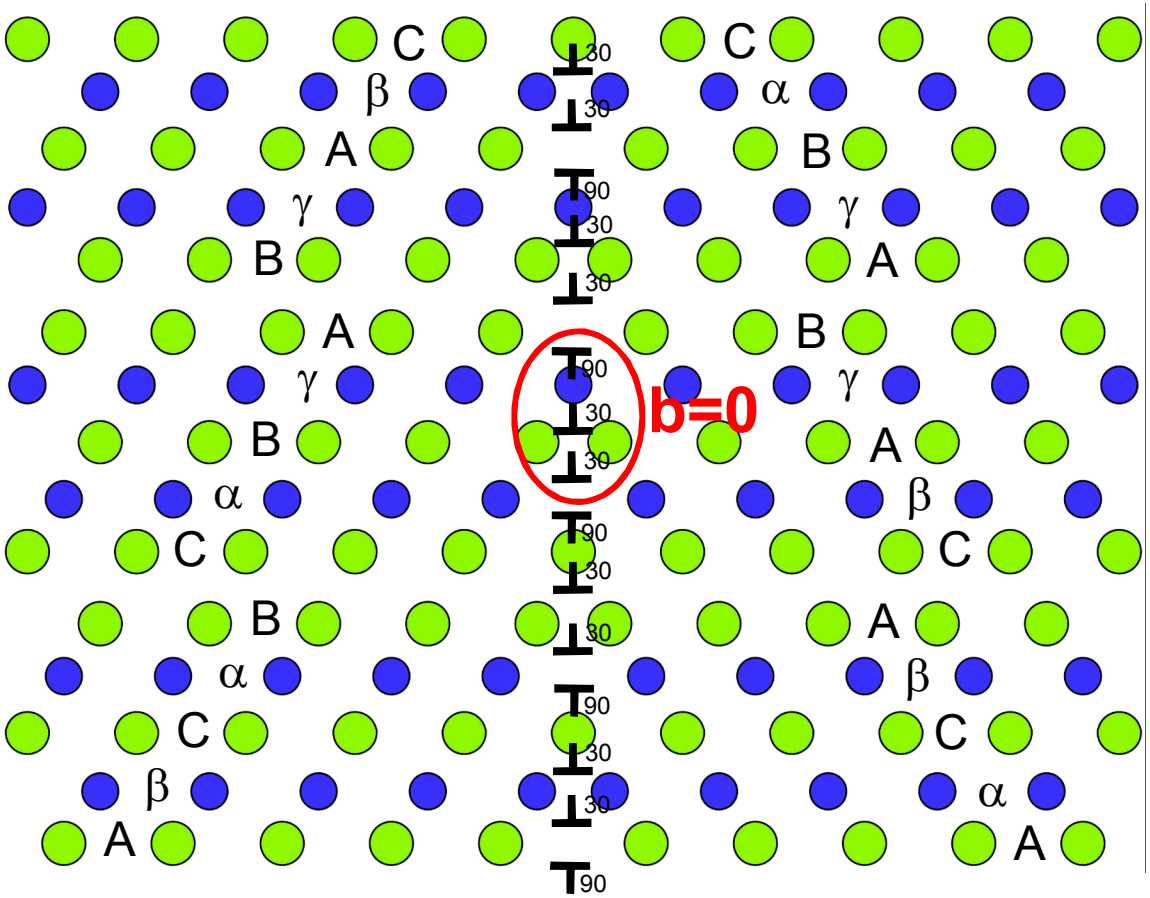
EXTRA

Schematic of Bi_2Te_3 {10-10} twin



Analogous dislocation structure to FCC {112} twin facets?

Migration by coordinated motion of 30° and 90° 1/3<10-10> twinning dislocations

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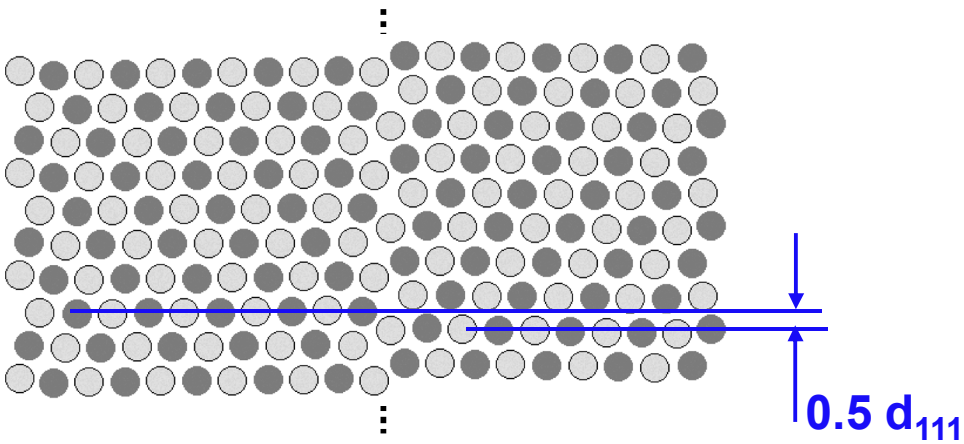
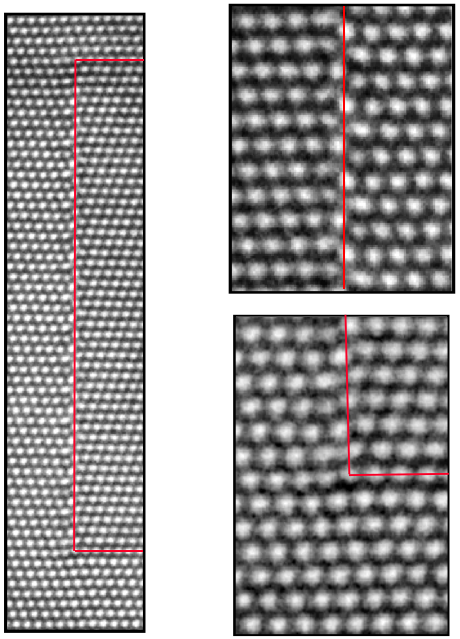
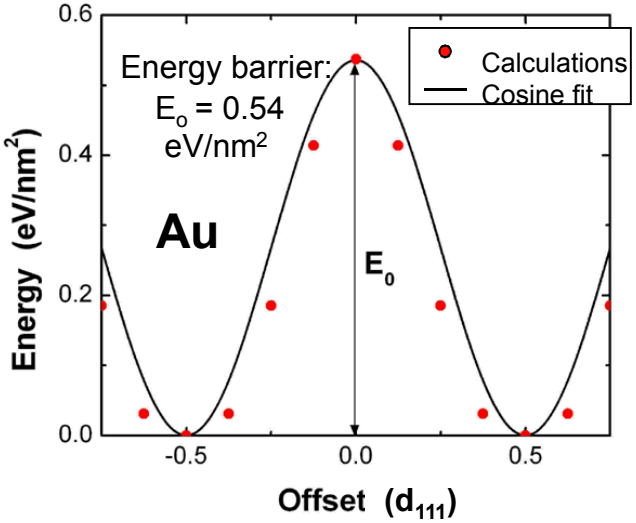
Translation of {111} planes at Σ=3 {112} Boundary

{111} Planes Offset in Unconstrained Boundary



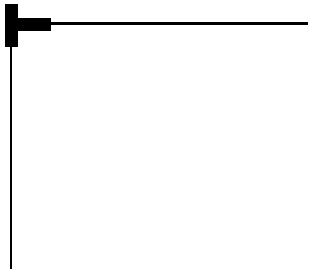


First-principles calculations of GB energy



Dislocation-like strain field at junction

b=1/6[111]
(=1/2 **D**δ)



Marquis, Hamilton, Medlin, Léonard, Phys. Rev. Lett. (2004)

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