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Atomic Scale Observations of Dislocation Core Structures in Bismuth Telluride

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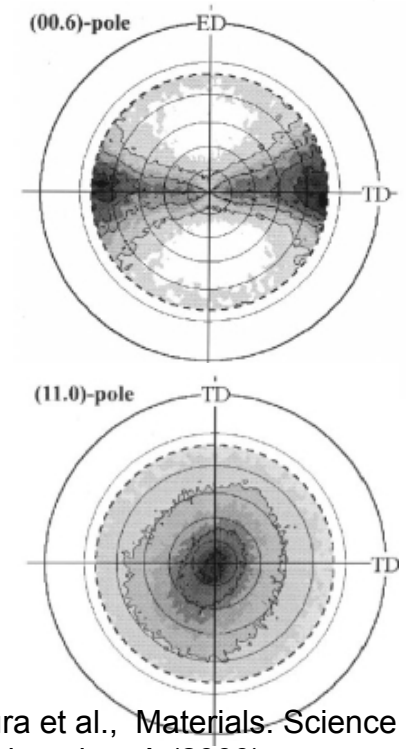
Why care about dislocations in Bi_2Te_3?

- **Impact on transport properties**
- **Processing:**
  - Deformation processing is common:
    - 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 interesting defect structures.

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 theory to understand structure of dislocations in Bi_2Te_3

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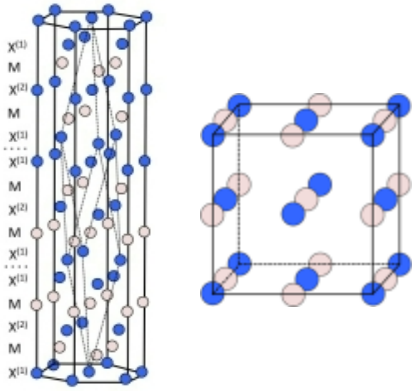
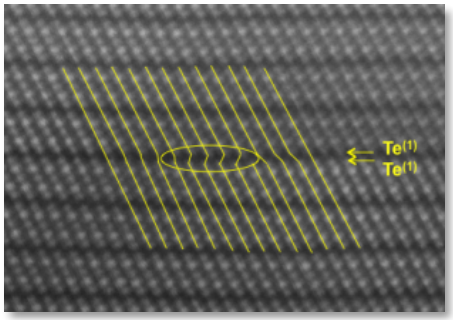
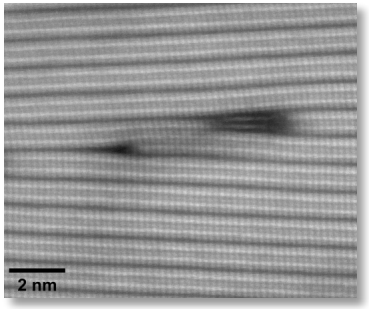
Outline

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

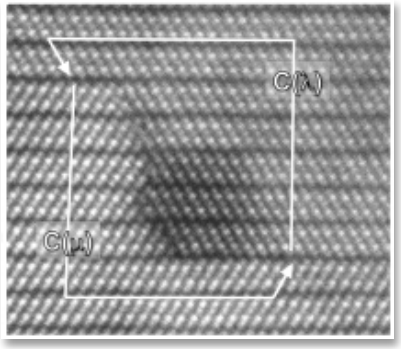


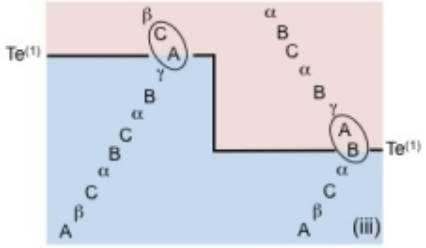
- *Dislocation Structure in Bi_2Te_3*
  - Basal dislocations
  - Non-basal dislocations
  - Low angle grain boundaries





- *Interfacial Dislocations*
  - High angle grain boundaries
  - Example: step defect at twin boundary





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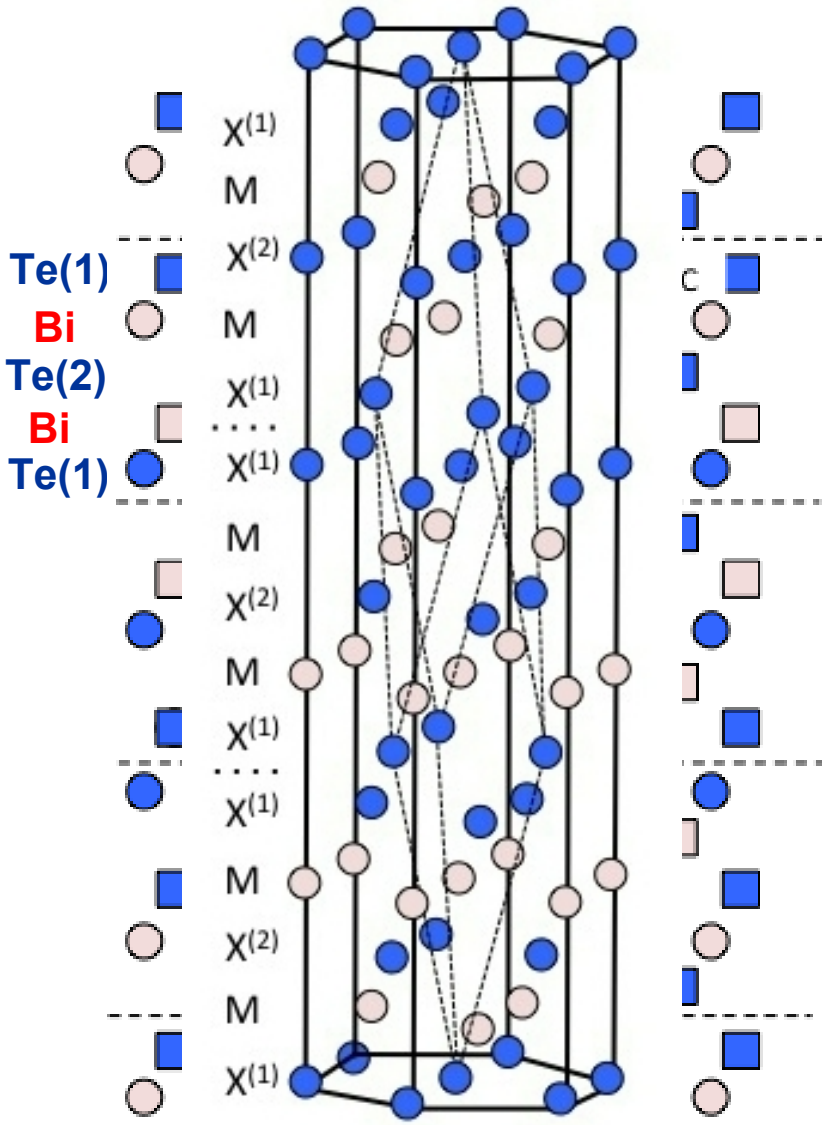
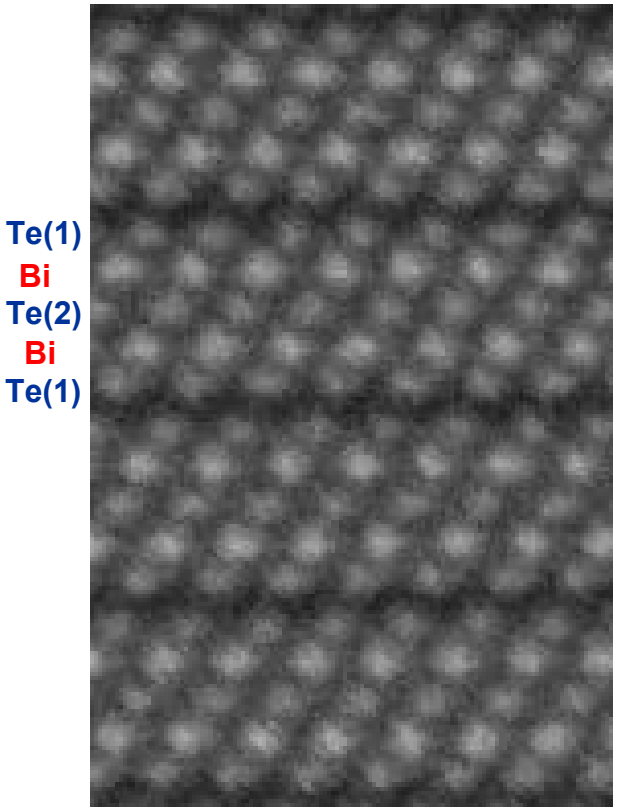
Bismuth Telluride (Bi_2Te_3): Crystal Structure



- 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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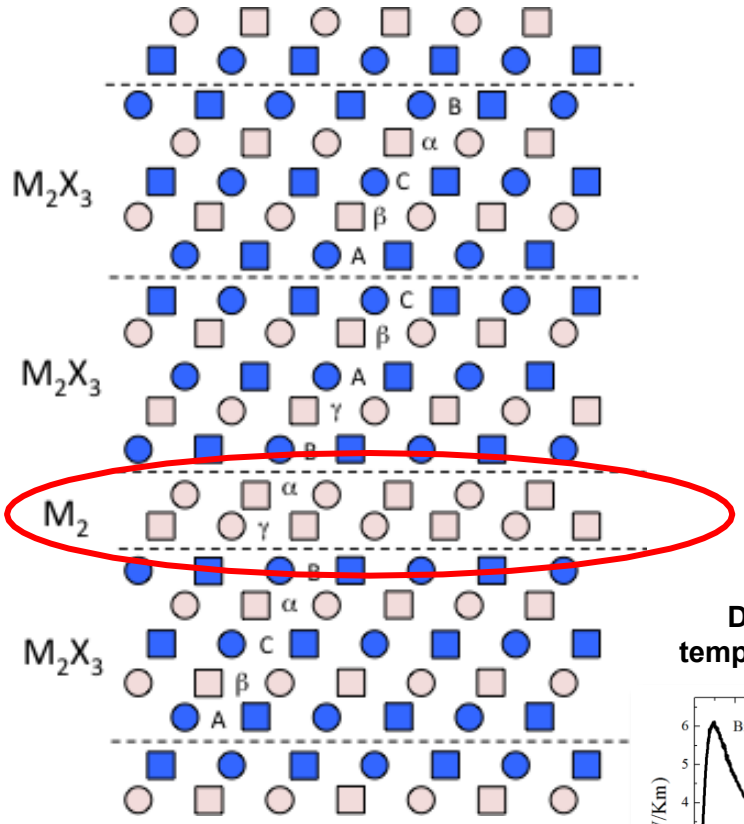
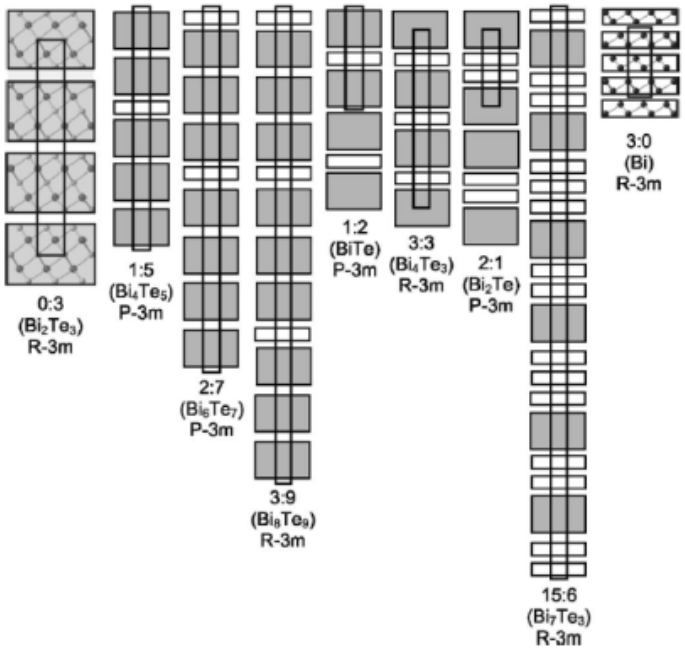
Layered structure allows flexibility in accommodating variations in composition

Insertion of metal bi-layers



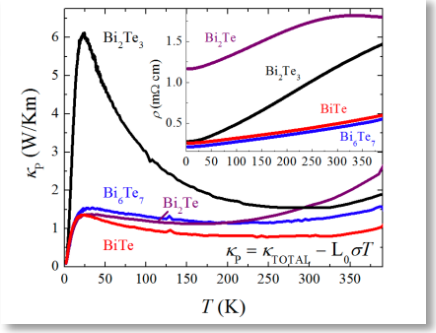
Example: $(Bi_2)_m(Bi_2Te_3)_n$ homologous series

Increasing Bismuth →

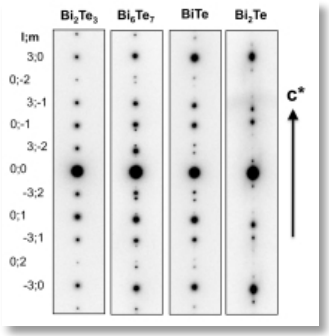


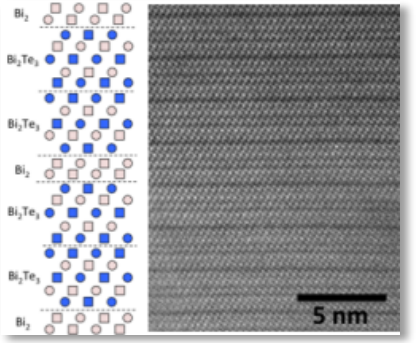
J.W.G. Bos, H.W. Zanderbergen, M.-H. Lee, N.P. Ong, R.J. Cava, Phys. Rev B 2007

Dramatic reduction in low-temperature thermal conductivity



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



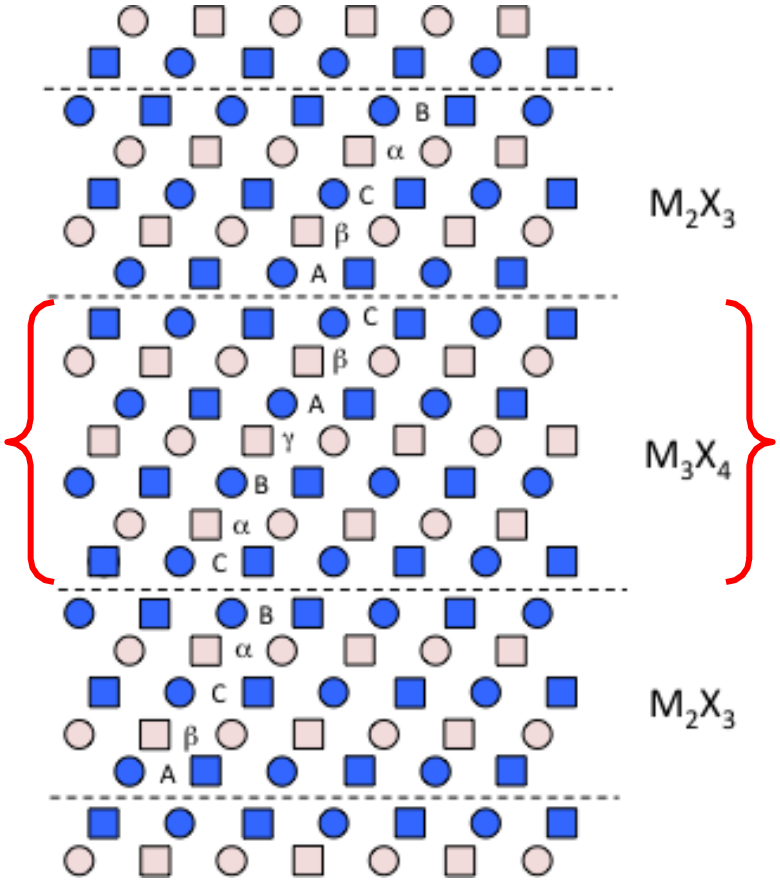


P. Sharma, D.Medlin, et al. PRB 83 (2011) 235209.

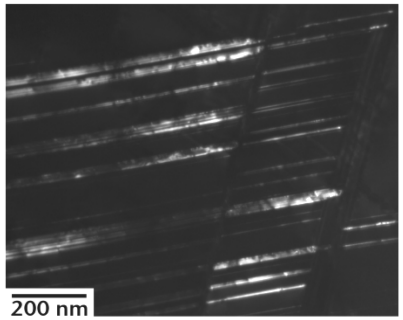
Medlin & Snyder, JOM 2013

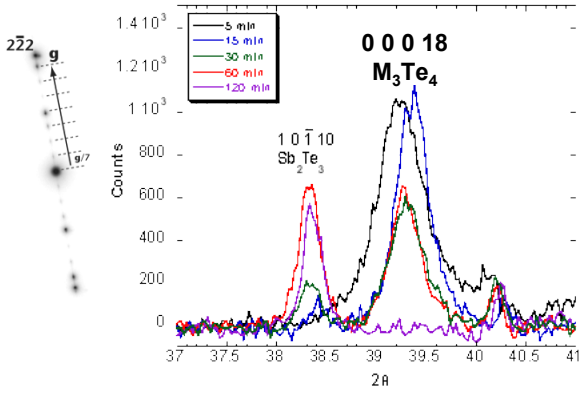
Layered structure allows flexibility in accommodating variations in composition

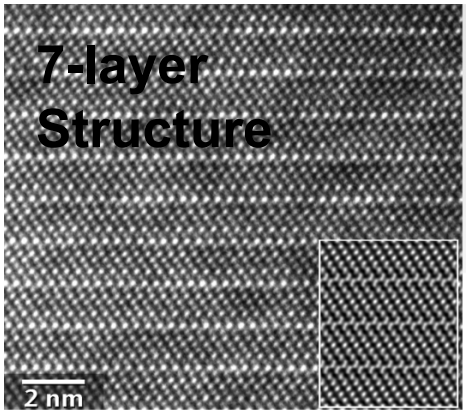
Metal rich, 7-Layer M_3X_4 fault

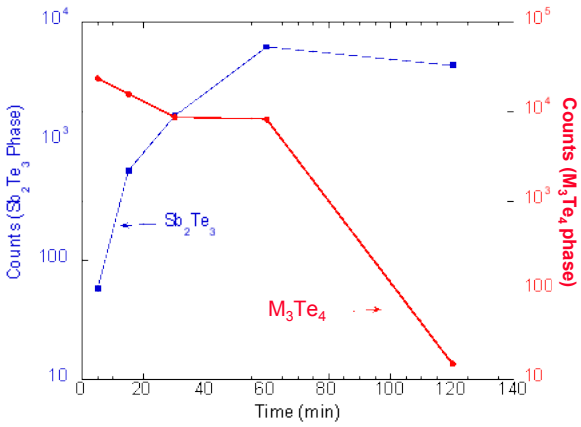


Example: $(Ag,Sb)_3Te_4$ transition phase during nucleation of Sb_2Te_3 precipitates in $AgSbTe_2$









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

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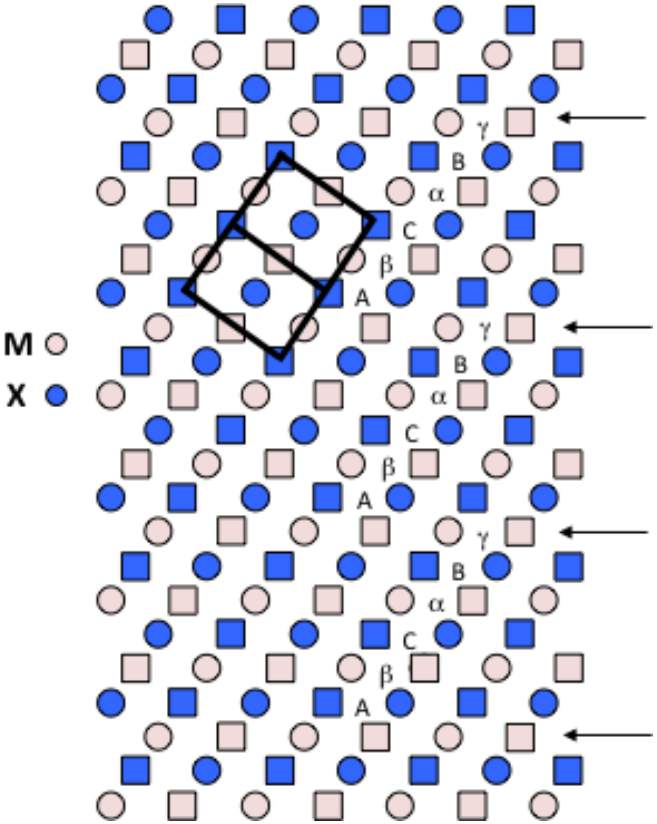
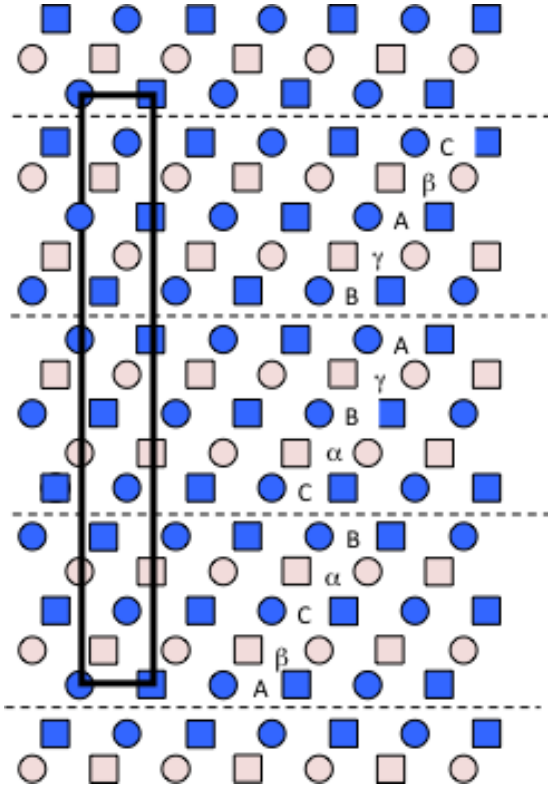
Tetradymite and Rocksalt structures are closely related

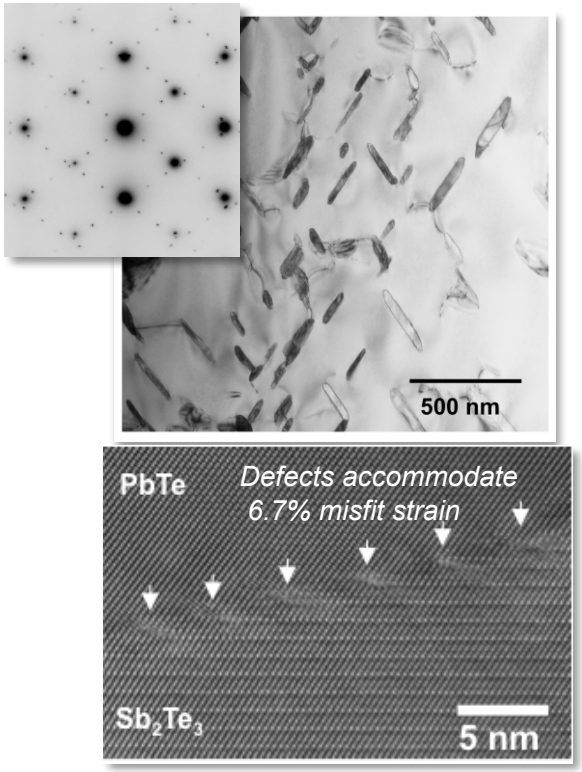
Rocksalt (MX) Structure



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

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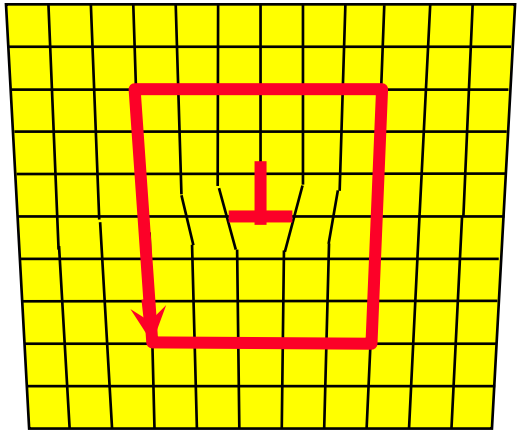
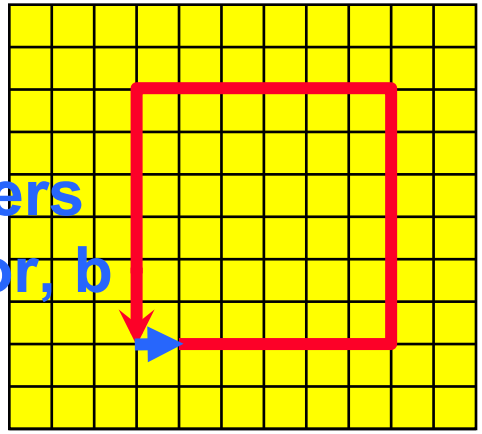
How do these structural considerations impact Dislocations and Interfaces?

Edge Dislocation

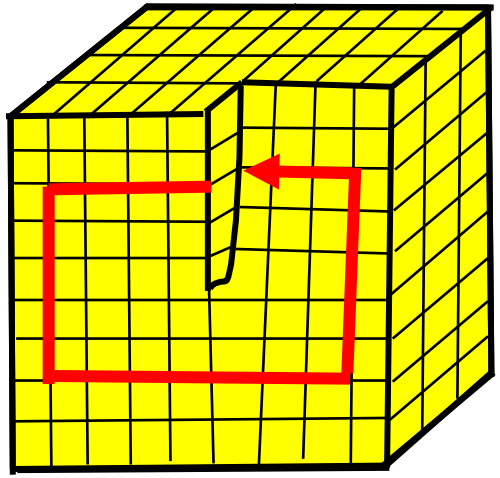


Reference Frame:
Perfect Crystal

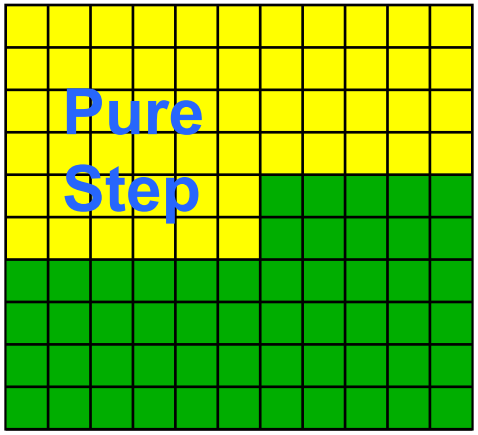


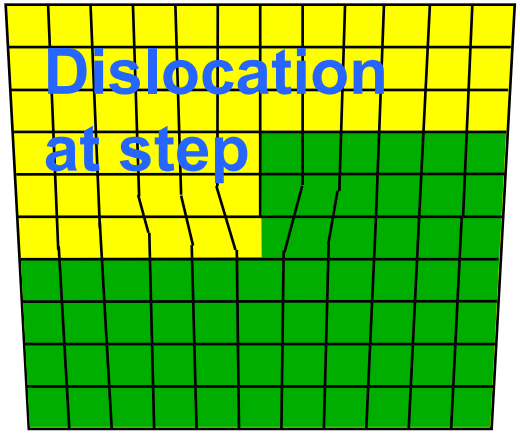
Burgers Vector, b

Screw Dislocation



Interfacial Disconnection





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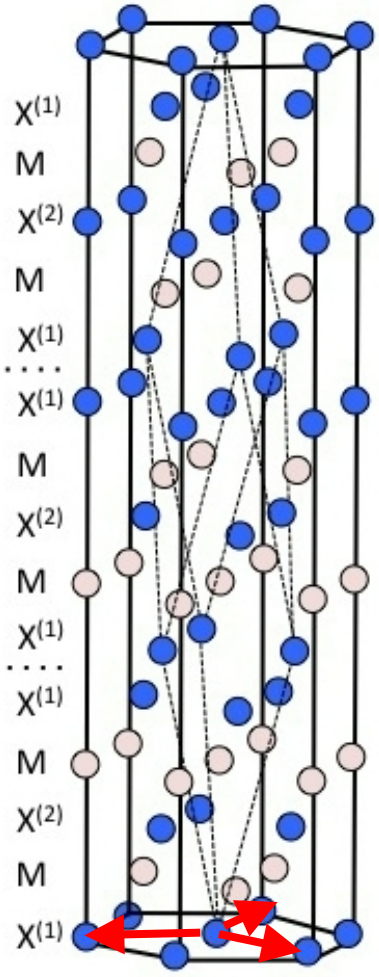
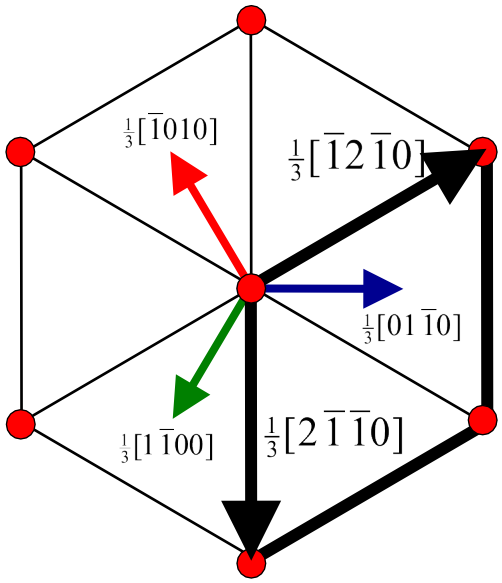
Dislocations in Bismuth Telluride

Basal dislocations: (1/3) <2-1-10>

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

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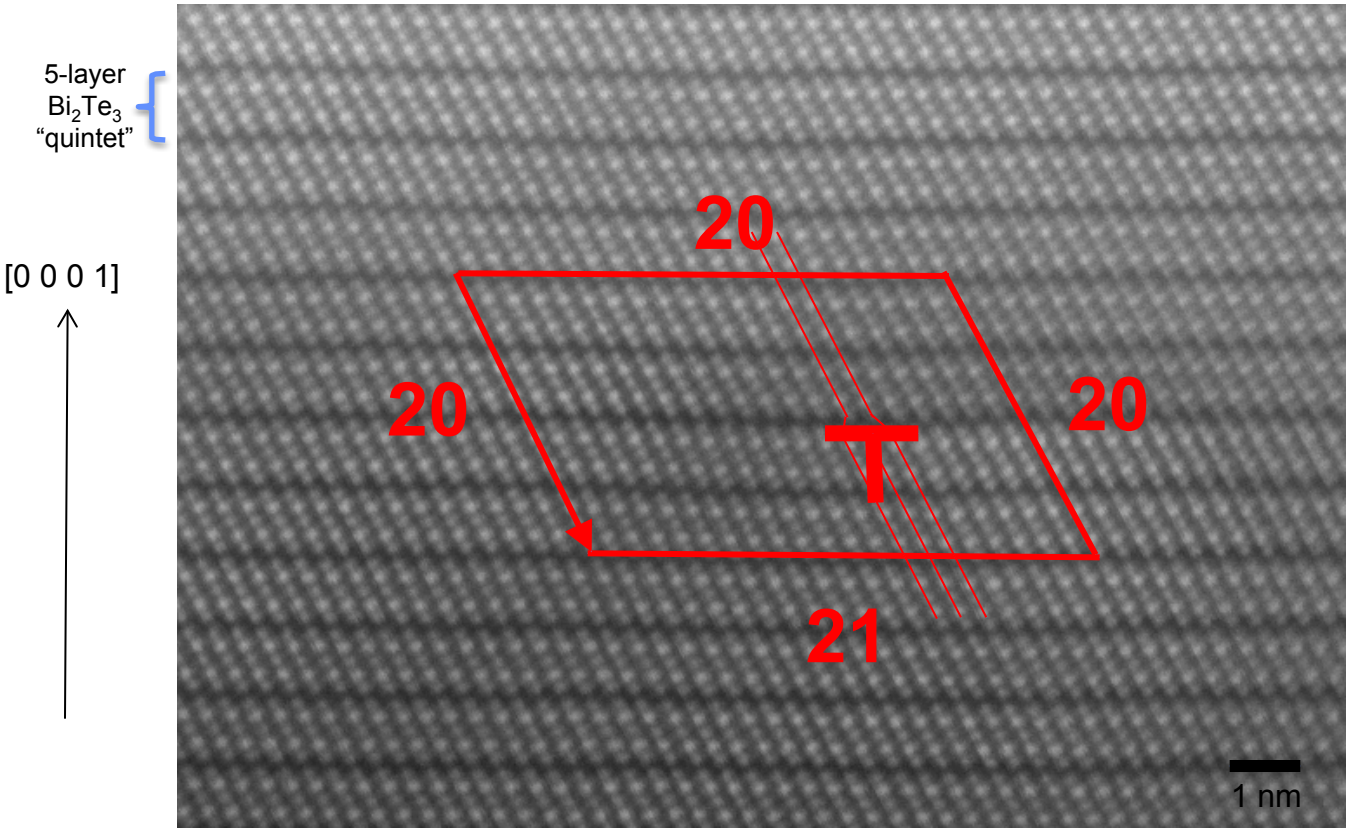
Dislocation Core structure: termination at $Te^{(1)}$-$Te^{(1)}$ layer, dissociation



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

T 60° mixed dislocation

HAADF-STEM
300 keV

<2 -1 -1 0 > projection

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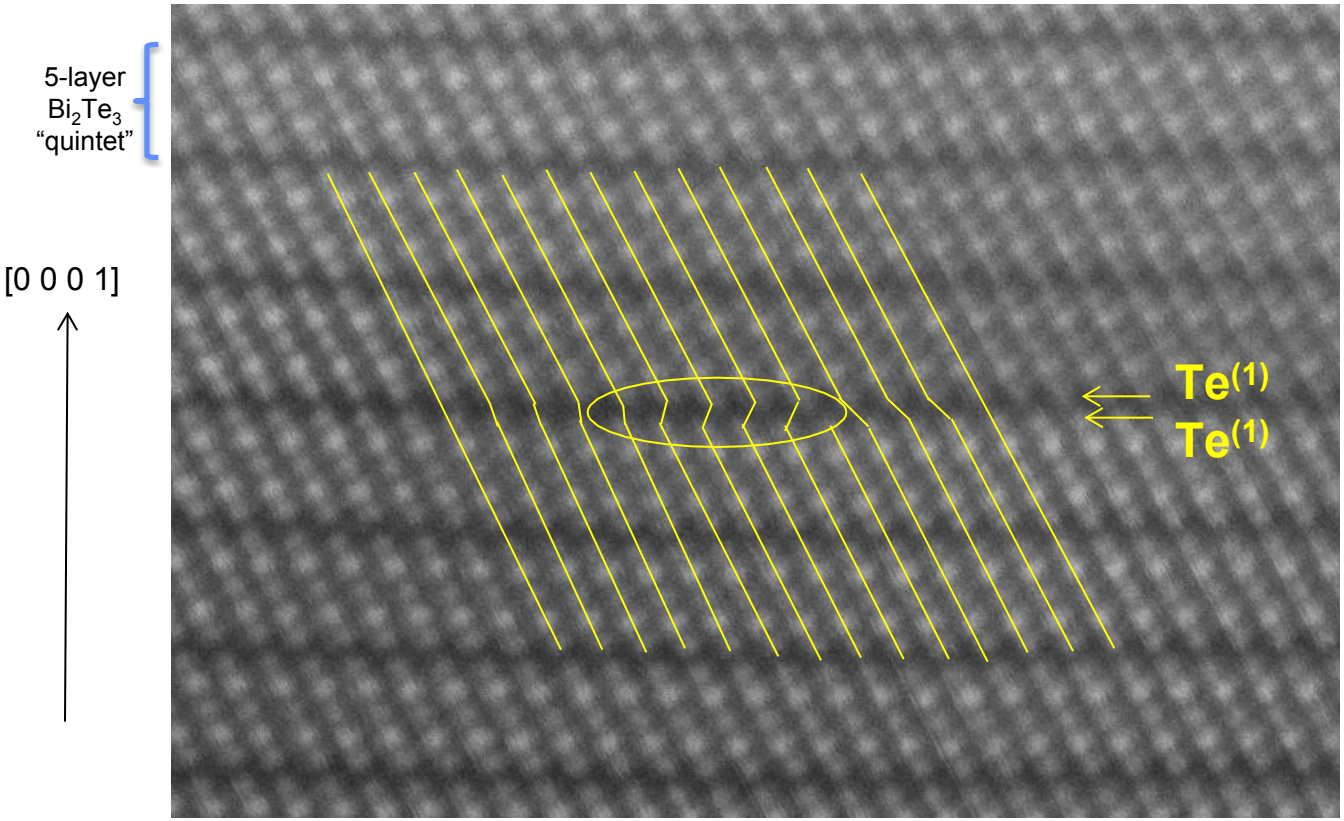
Dislocation Core structure: termination at $Te^{(1)}$-$Te^{(1)}$ layer, dissociation



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

60° mixed dislocation

30° mixed partial — Stacking Fault — **90° edge partial**

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

HAADF-STEM
300 keV

Weak, van der Waals bonding likely favors dissociated dislocation core at $Te^{(1)}$-$Te^{(1)}$ layer

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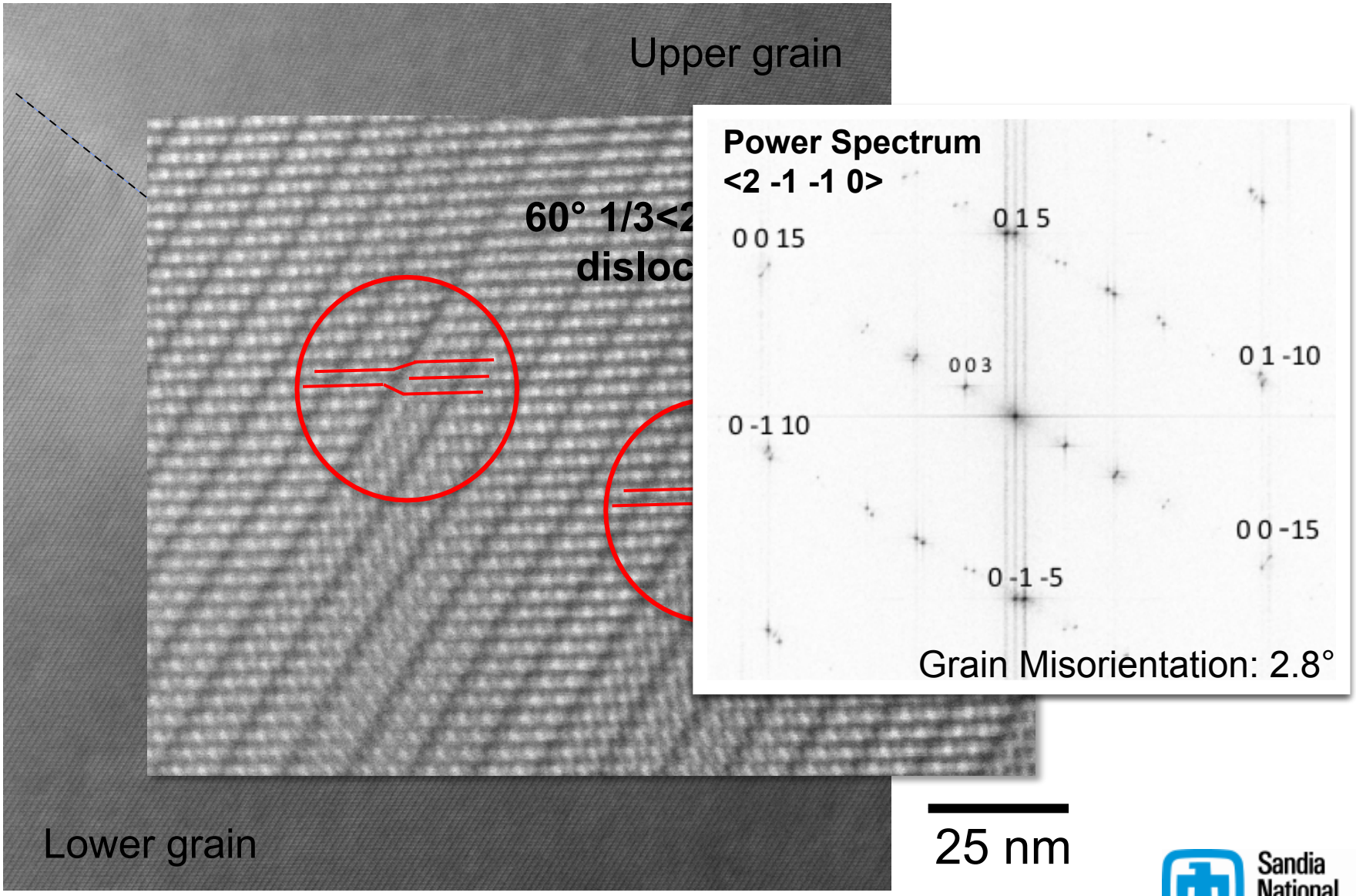
A Low Angle Tilt Boundary



STEM-HAADF

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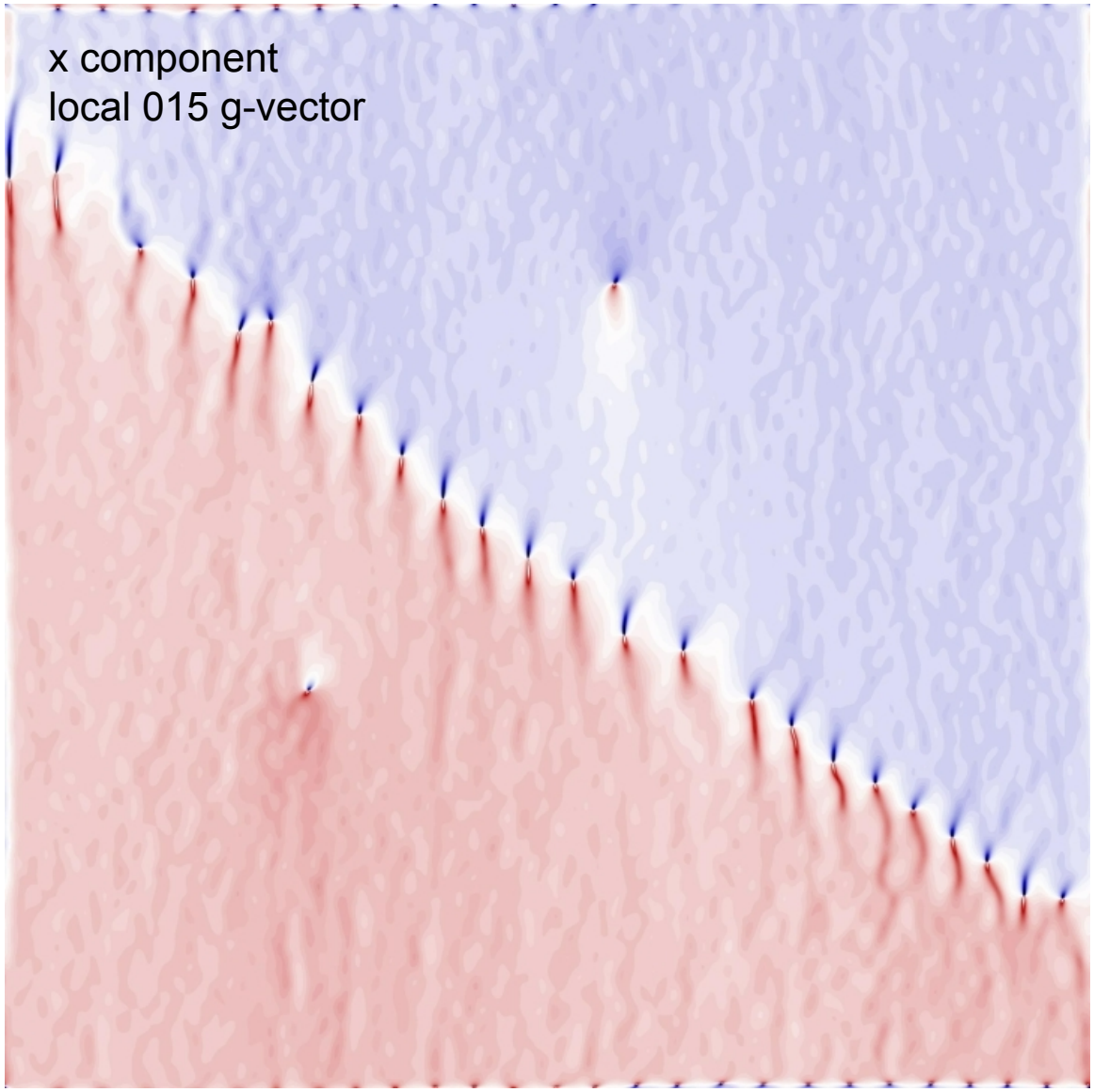
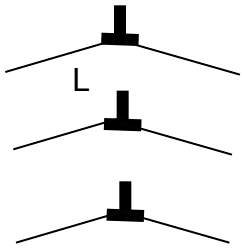
A Low Angle Tilt Boundary



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)

25 nm

MacTempas Software. Geometric phase object routines: Hÿtch, Snoek, Kilaas, Ultramicroscopy 1998

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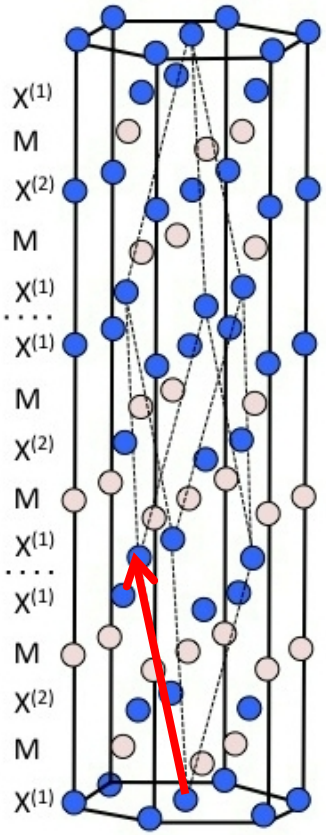
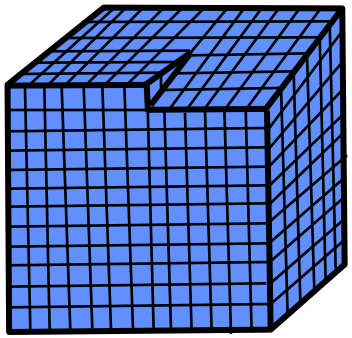
Non-basal dislocations:

Screw dislocations important to crystal growth

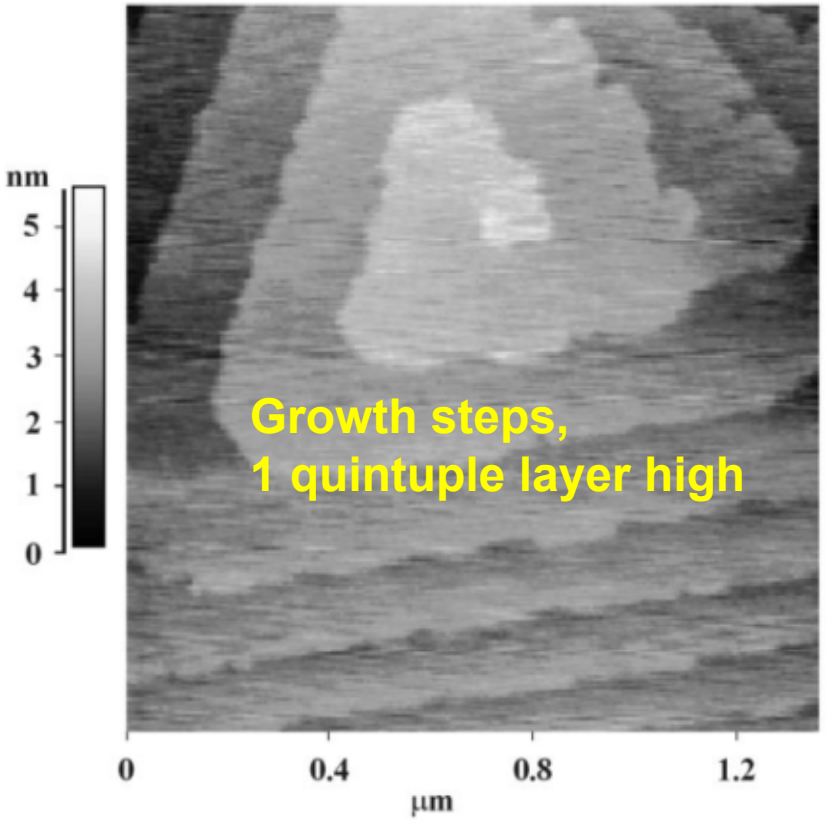


Screw Dislocation



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

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?

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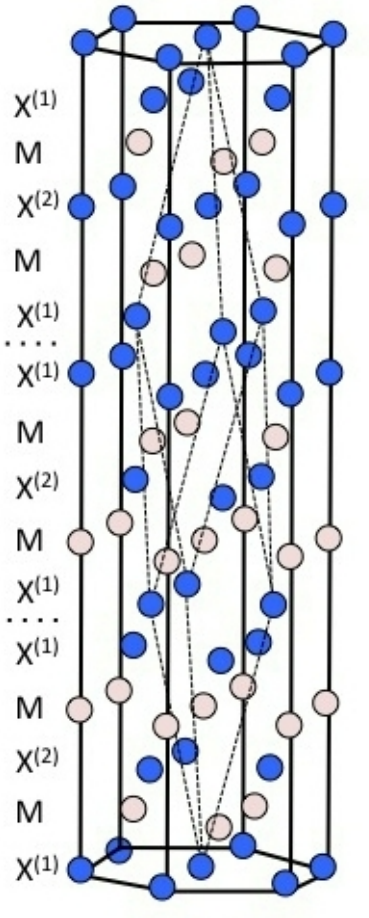
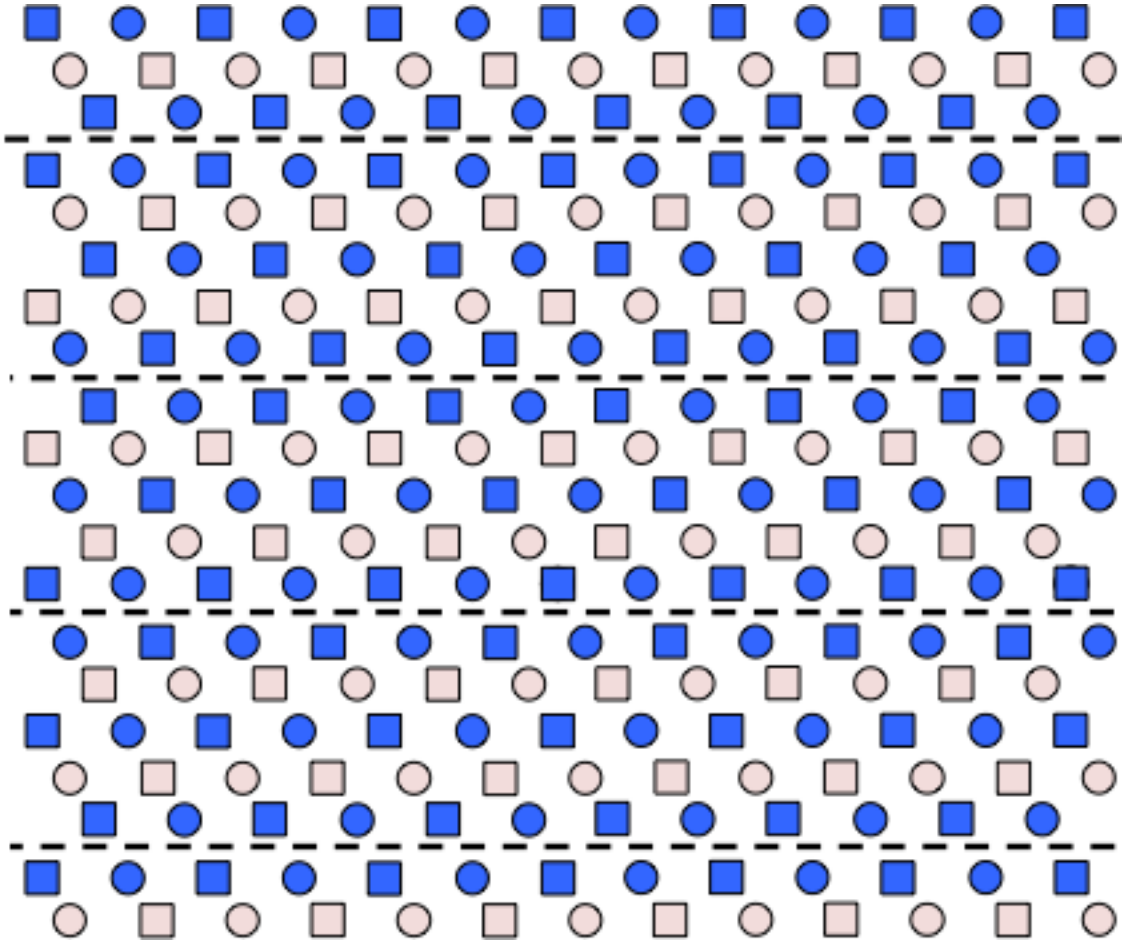
Non-basal edge dislocations: What happens if we pull out a quintuple unit?





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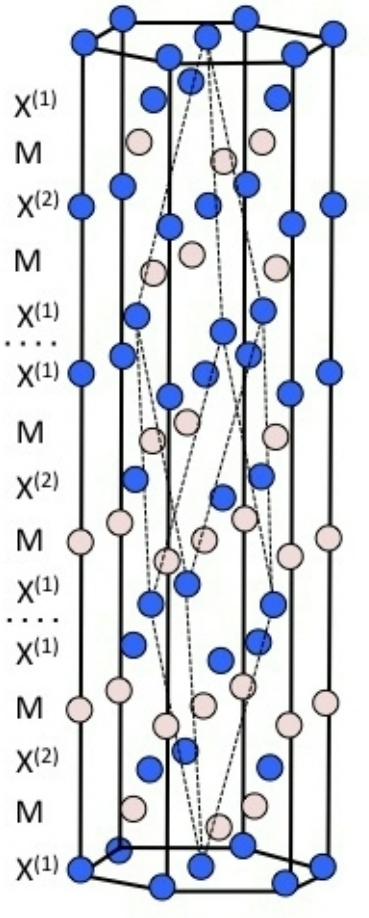
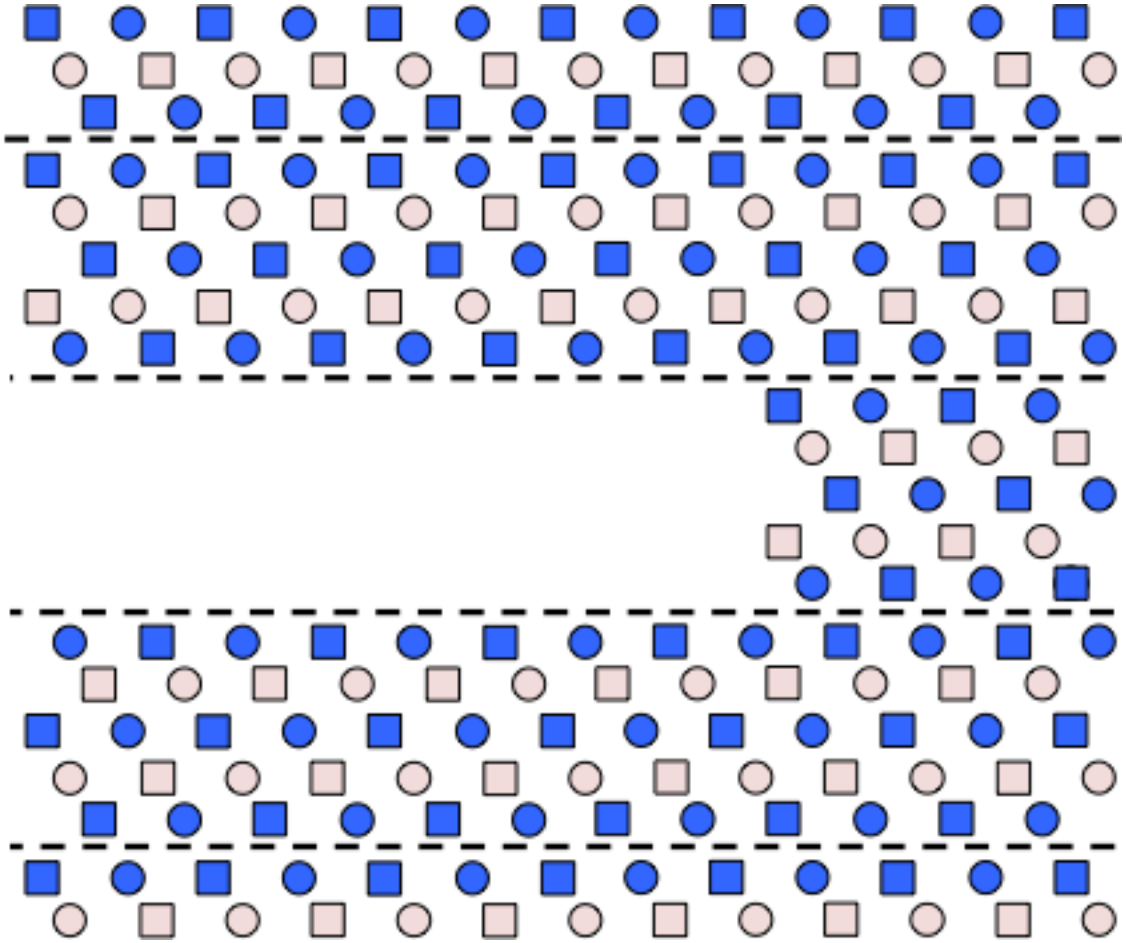
Non-basal edge dislocations: What happens if we pull out a quintuple unit?





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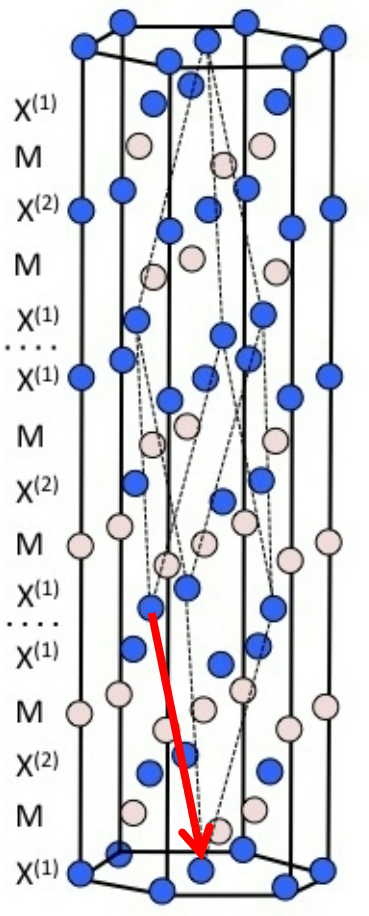
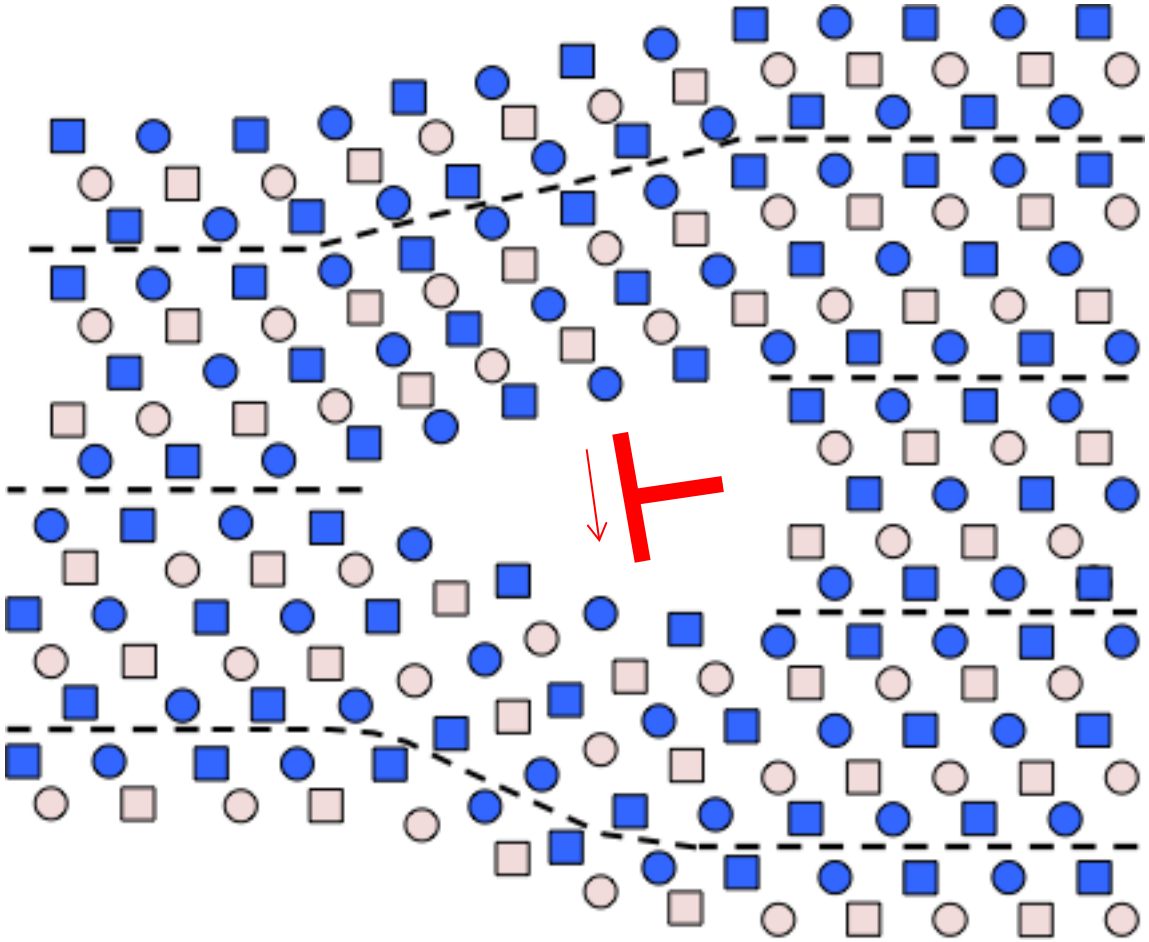
Non-basal edge dislocations: What happens if we pull out a quintuple unit?





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

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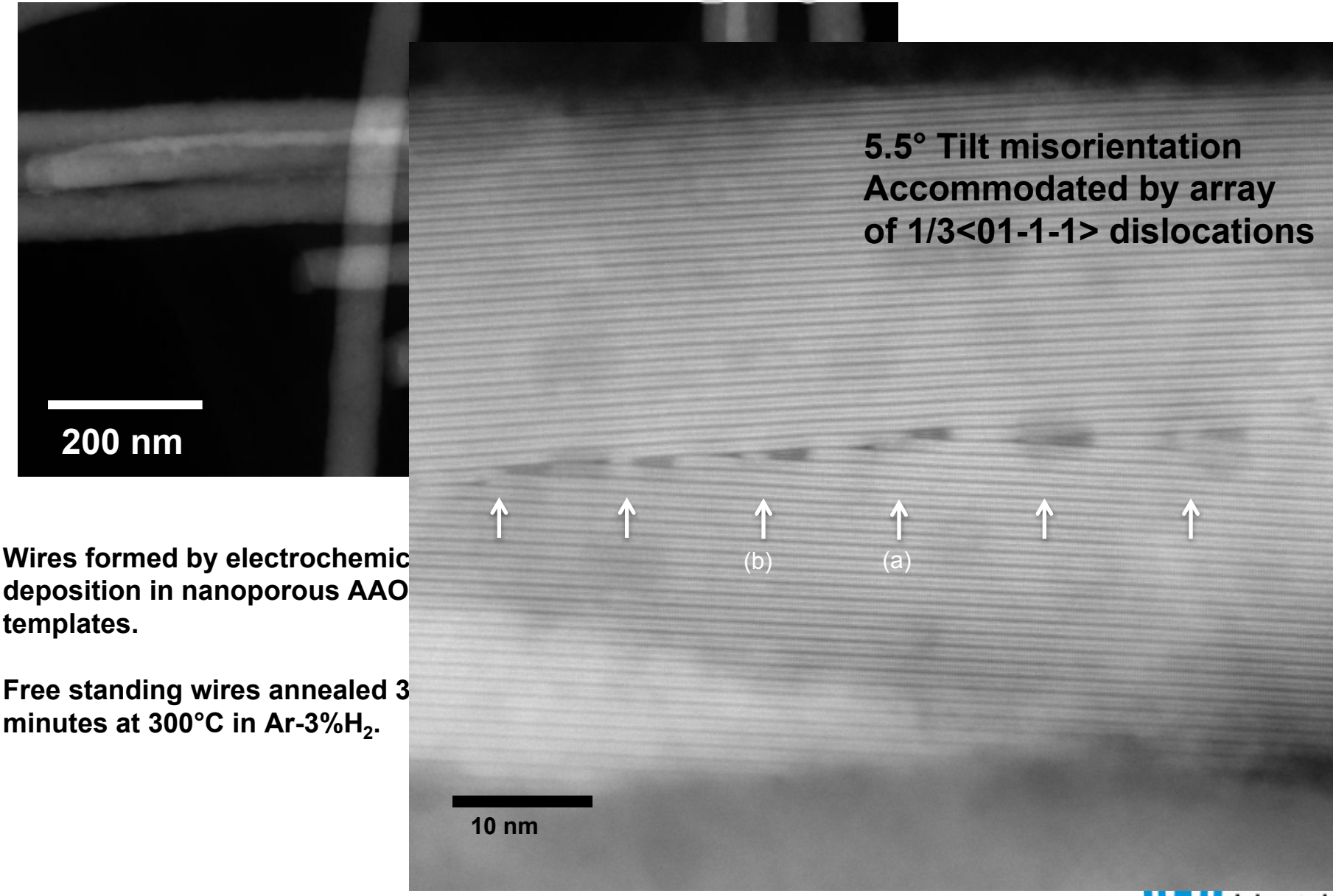
Dislocations in Bi_2Te_3 Nanowires



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

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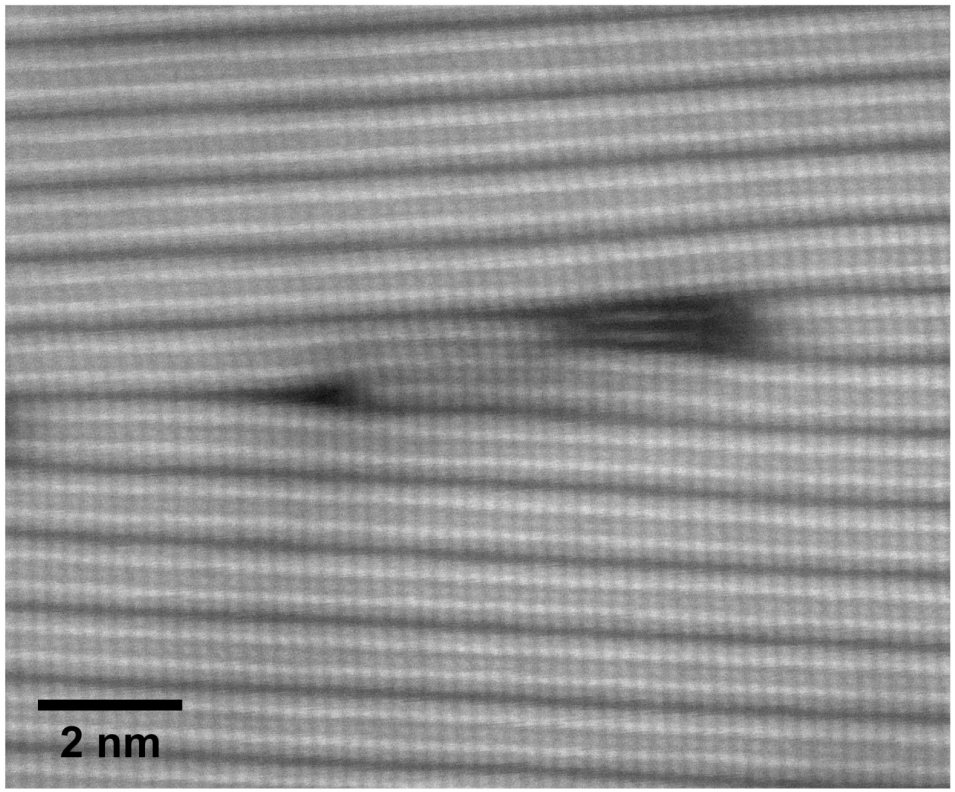
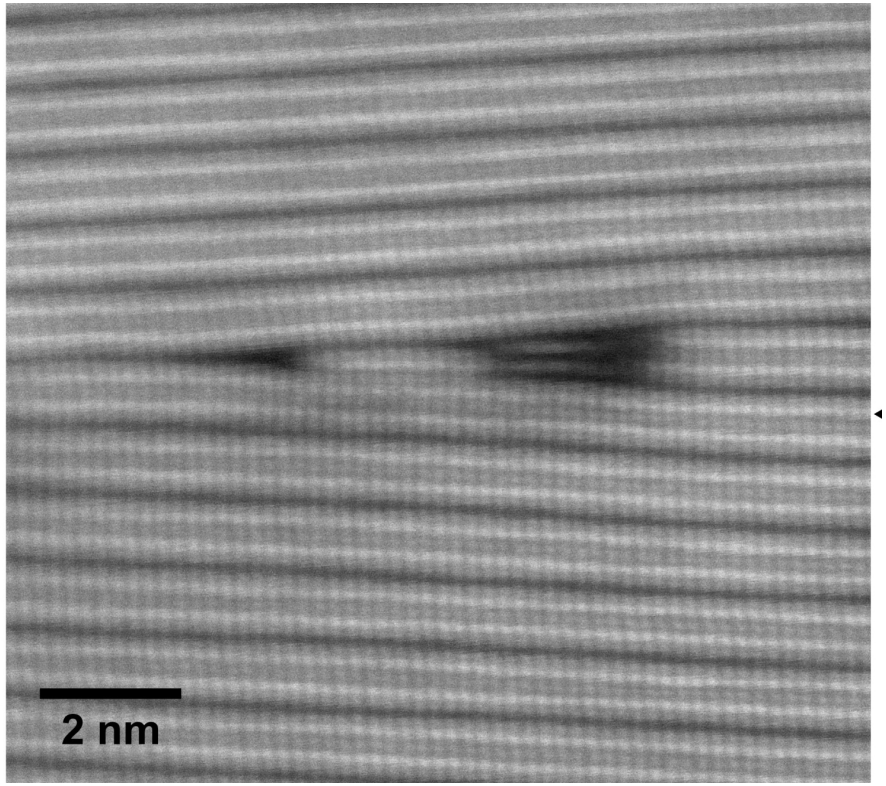
Dislocations have dissociated core: two configurations





<1 0 -1 0> Projection

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

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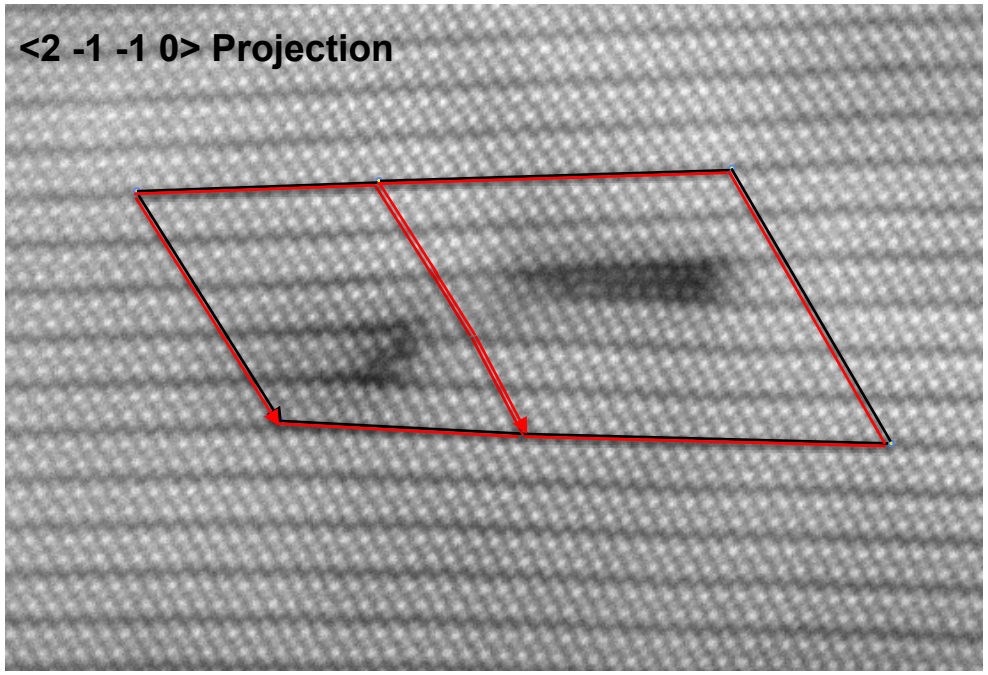
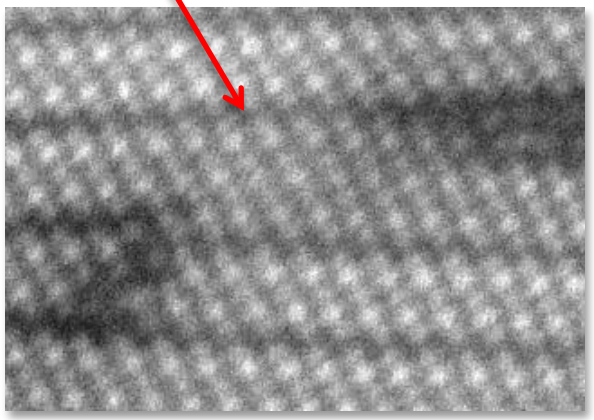
(1/3)[0 1 -1 -1] Dislocation in Bi_2Te_3:



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 Å² > 22.9 Å² + 37.2 Å² =60.2 Å²

Reduced strain energy with dissociation

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

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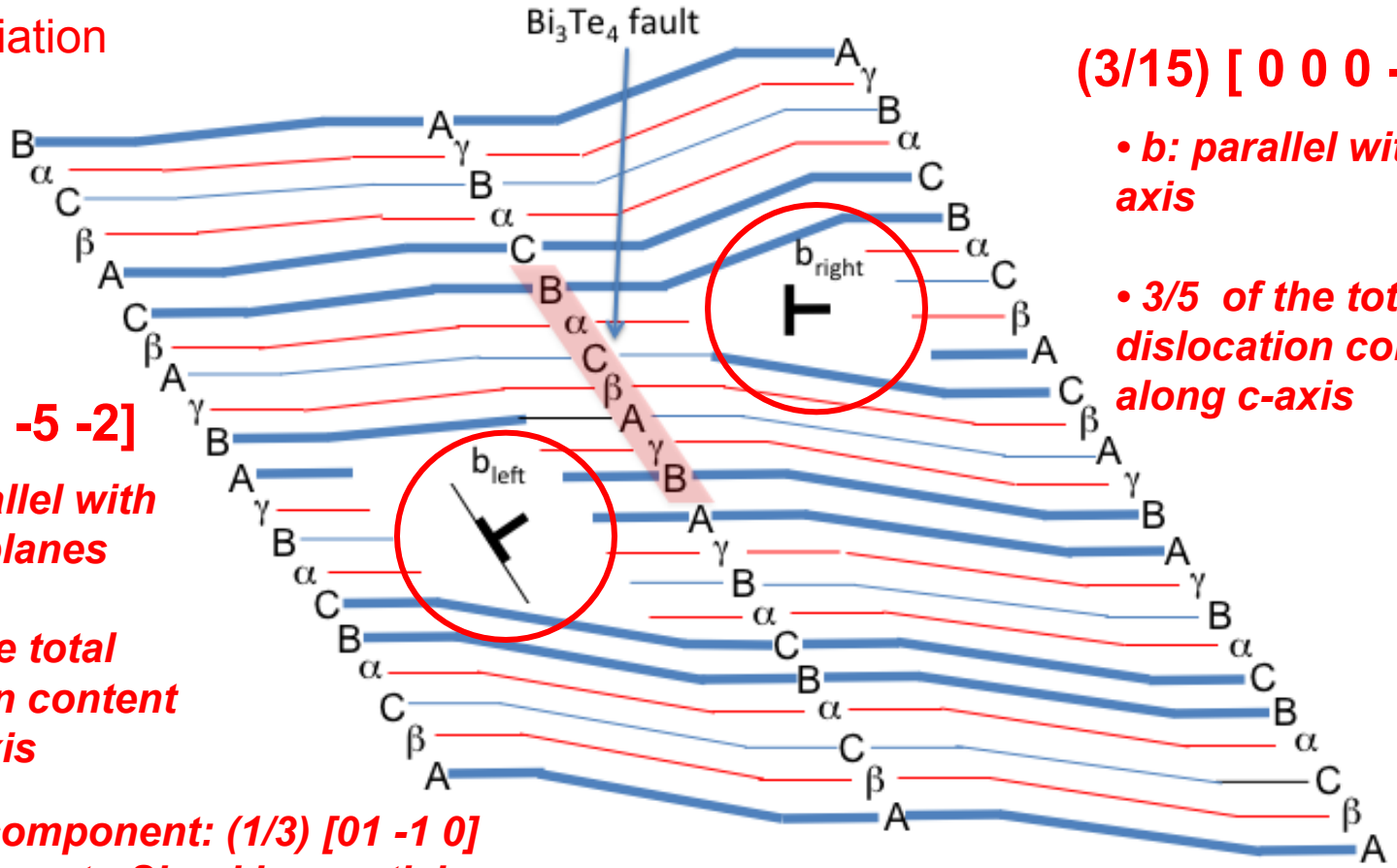
7-Layer Bi_3Te_4 faults: Mechanism to accommodate Te loss during annealing

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*

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

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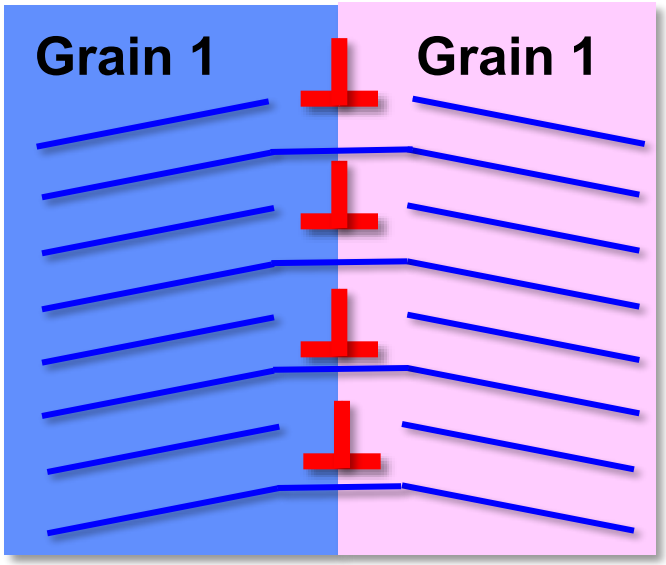
Dislocations at Grain Boundaries

Low Angle Grain Boundaries

-Arrays of discrete lattice dislocations

-Reference state: single crystal

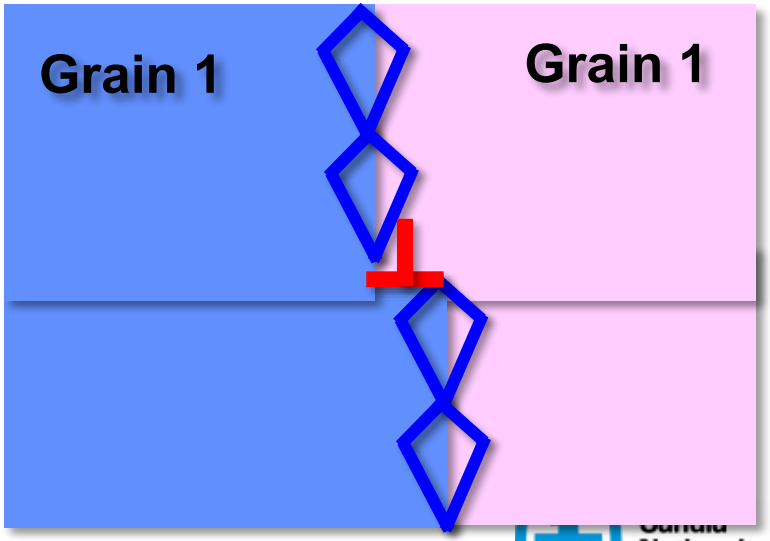


High Angle Grain Boundaries

-Lattice dislocation cores too close to be meaningful.

-Reference state: singular, low-energy reference orientations.

-Burgers vector and step content are important.



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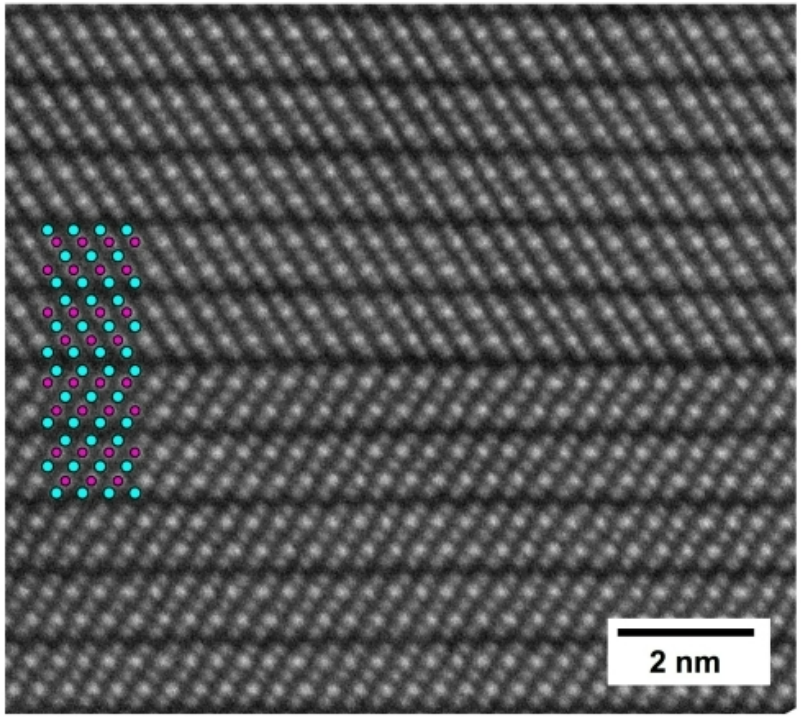
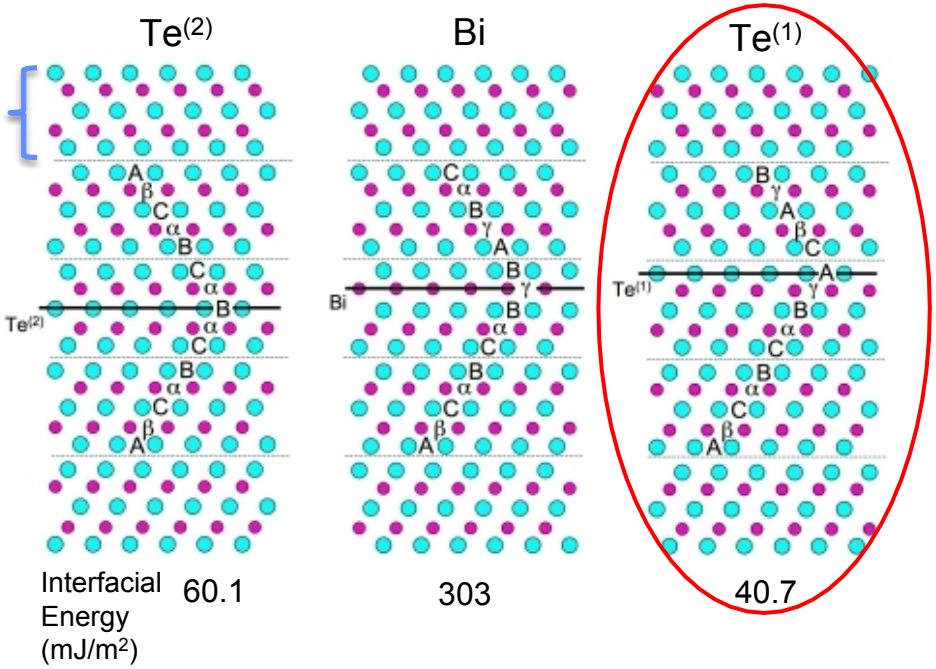
Bi_2Te_3 Basal Twin: A singular, low-energy interface structure

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



DFT Calculations:
Three Possible Compositional Terminations



Energetic preference for termination at $Te^{(1)}$ sites

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

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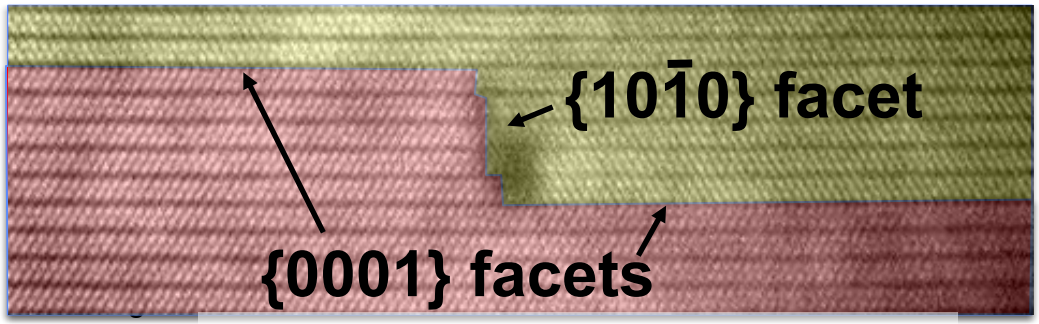
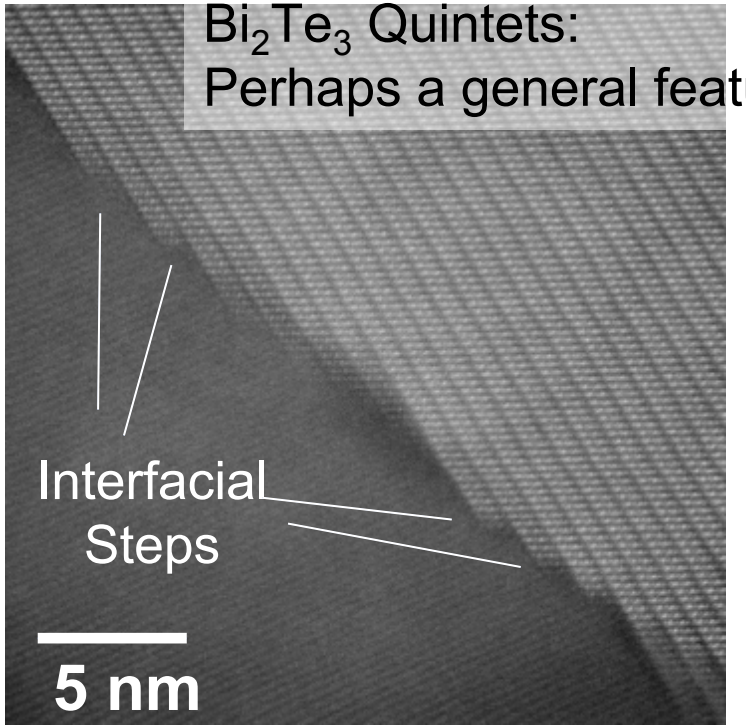
Steps in the Bi_2Te_3 Twin Boundary



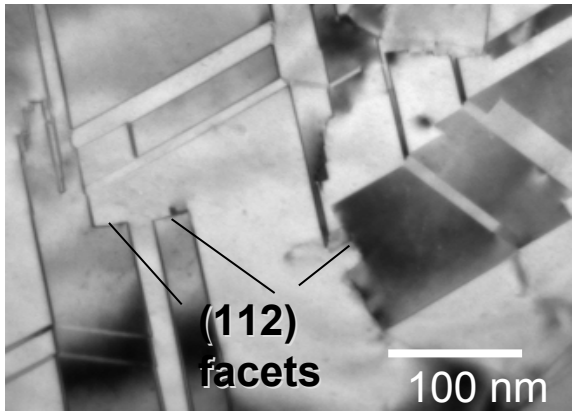
Steps of integral 5-plane Bi_2Te_3 Quintets:
Perhaps a general feature?



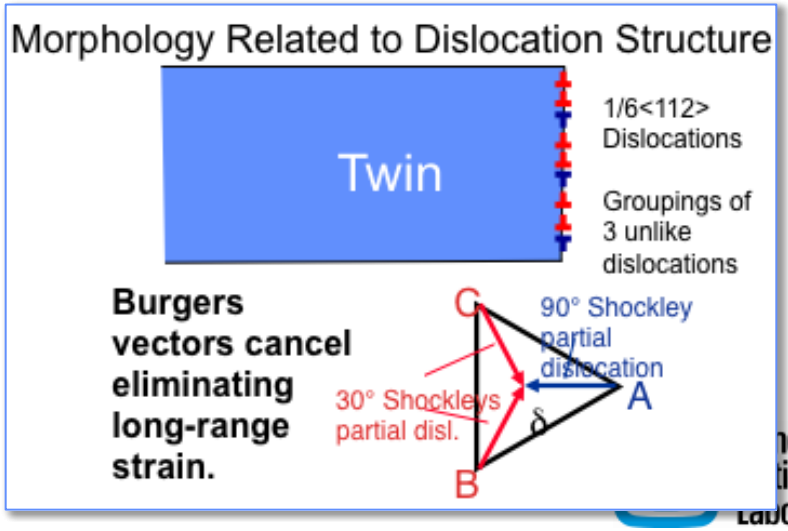
NBT20/21mar11/18.15.52

Morphology analogous to annealing and growth twins in FCC materials.

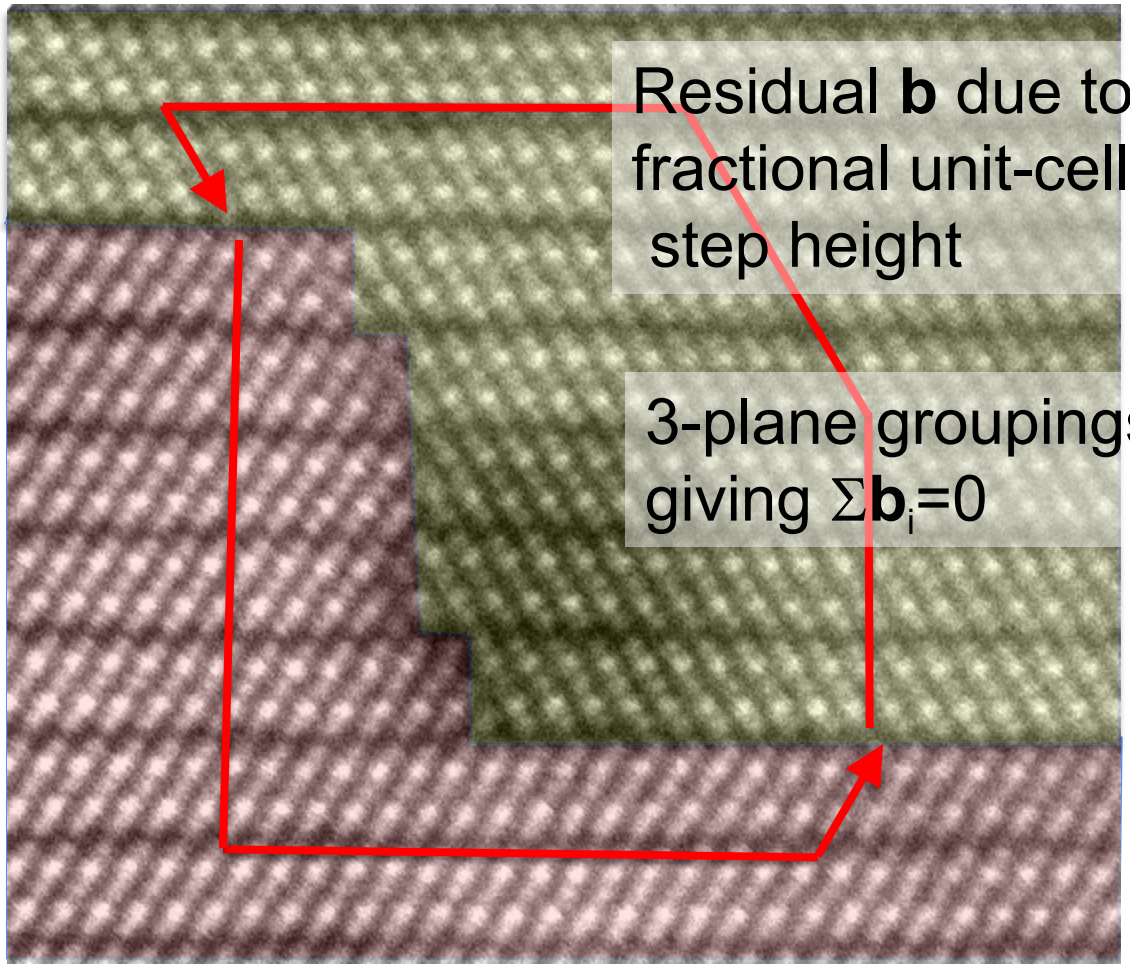
Example: Twins in Electrodeposited Ni



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



What is the dislocation content of the step?

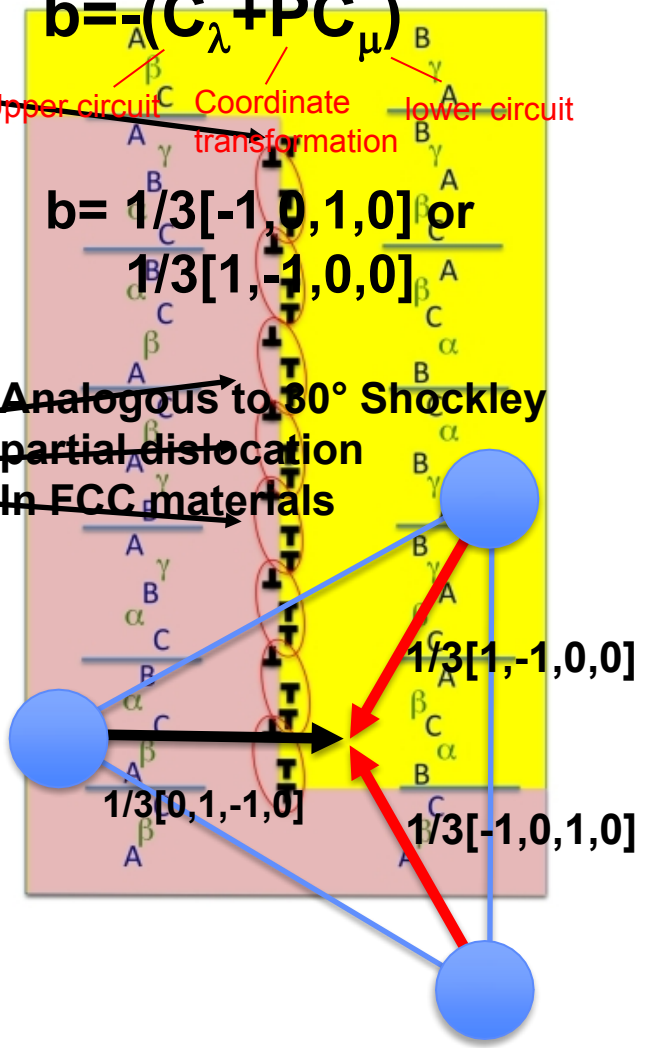


$\mathbf{b} = -(C_\lambda + PC_\mu)$

Upper circuit — Coordinate transformation — lower circuit

b= 1/3[-1,0,1,0] or 1/3[1,-1,0,0]

Analogous to 30° Shockley partial dislocation In FCC materials



Medlin and Yang, Journal of Electronic Materials (2012)

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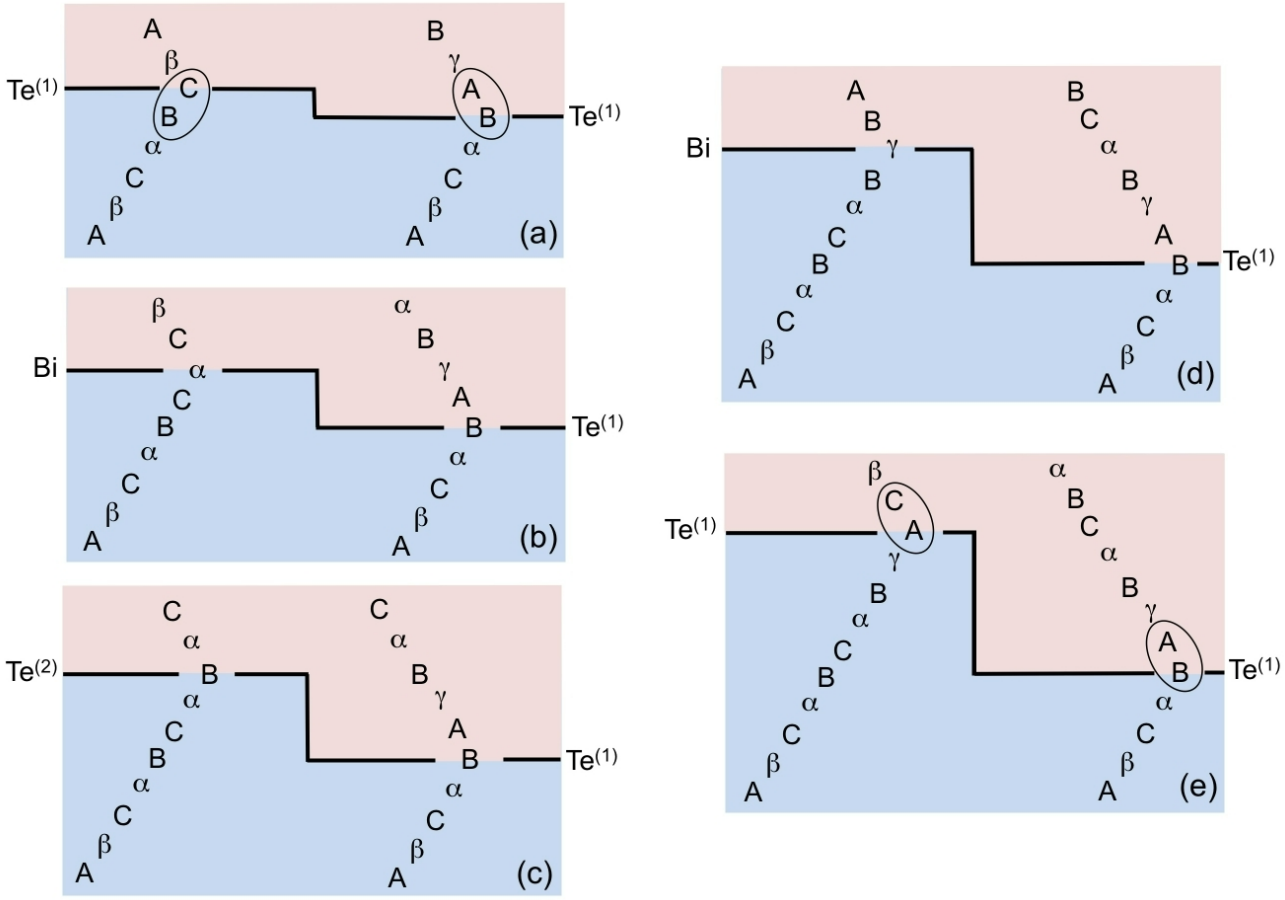
Consideration of other possible (0001) twin defects



Medlin and Yang, Journal of Electronic Materials (2012)

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Consideration of other possible (0001) twin defects

Step Height, h	Terminating Planes on Either Side of Step	Equivalency of Adjacent Twin Terraces	Burgers Vector, b
1	$Te^{(1)}/Te^{(1)}$	Equivalent (inverted)	$\frac{1}{3}\langle 10\bar{1}0\rangle$
	$Bi/Te^{(1)}$	Nonequivalent	
	$Te^{(2)}/Bi$	Nonequivalent	
2	$Te^{(1)}/Bi$	Nonequivalent	$\frac{1}{3}\langle 10\bar{1}0\rangle$
	$Te^{(2)}/Te^{(1)}$	Nonequivalent	
	Bi/Bi	Equivalent (inverted)	
3	$Te^{(1)}/Te^{(2)}$	Nonequivalent	0
	Bi/Bi	Equivalent (inverted)	
	$Bi/Te^{(1)}$	Nonequivalent	
4	$Te^{(1)}/Bi$	Nonequivalent	$\frac{1}{3}\langle 10\bar{1}0\rangle$
	$Bi/Te^{(2)}$	Nonequivalent	
	$Te^{(1)}/Te^{(1)}$	Equivalent (inverted)	
5	Same	Equivalent	$\frac{1}{3}\langle 10\bar{1}0\rangle$
10	Same	Equivalent	$\frac{1}{3}\langle 10\bar{1}0\rangle$
15	Same	Equivalent	0

Low Energy: $Te^{(1)}/Te^{(1)}$ termination.

Intermediate energy:

Termination at either Te site: $Te^{(1)}$ and $Te^{(2)}$

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Conclusions

Key structural aspects of Bi_2Te_3 and related 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 thermoelectrics.**
- **Set of elementary "building blocks" for a general picture of interfacial structure in chalcogenide thermoelectrics**

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