SAND2011-5173C

Interfacial Defect Structure at a twin boundary in Bi_2Te_3

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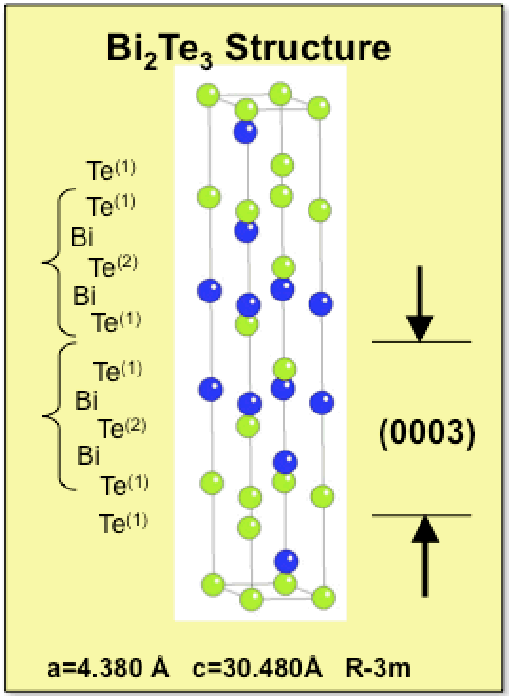
Control of Grain Structure important to Bi_2Te_3-Based Thermoelectrics



•Layered Crystal Structure

-anisotropic TE properties

-optimal zT parallel with basal planes

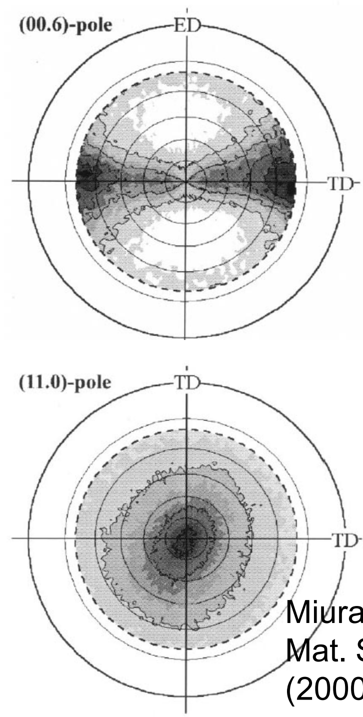
- anisotropic mass diffusivities

- easy fracture on basal planes

Microstructural Strategies applied to Bi_2Te_3-based materials

Control of crystal texture

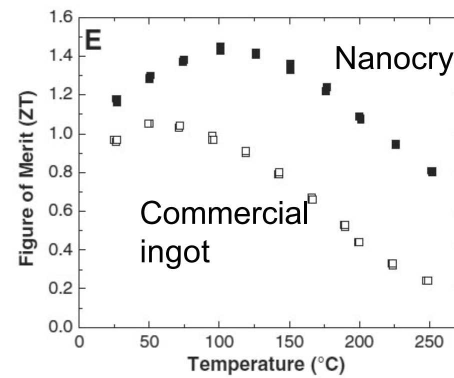
Example: Texture in Hot Extruded Bi_2Te_3

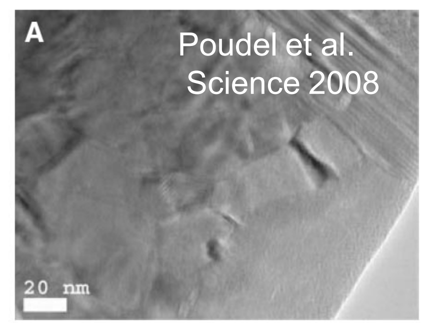


Miura et al., Mat. Sci. Eng. A (2000)

Reduction of Grain Size

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





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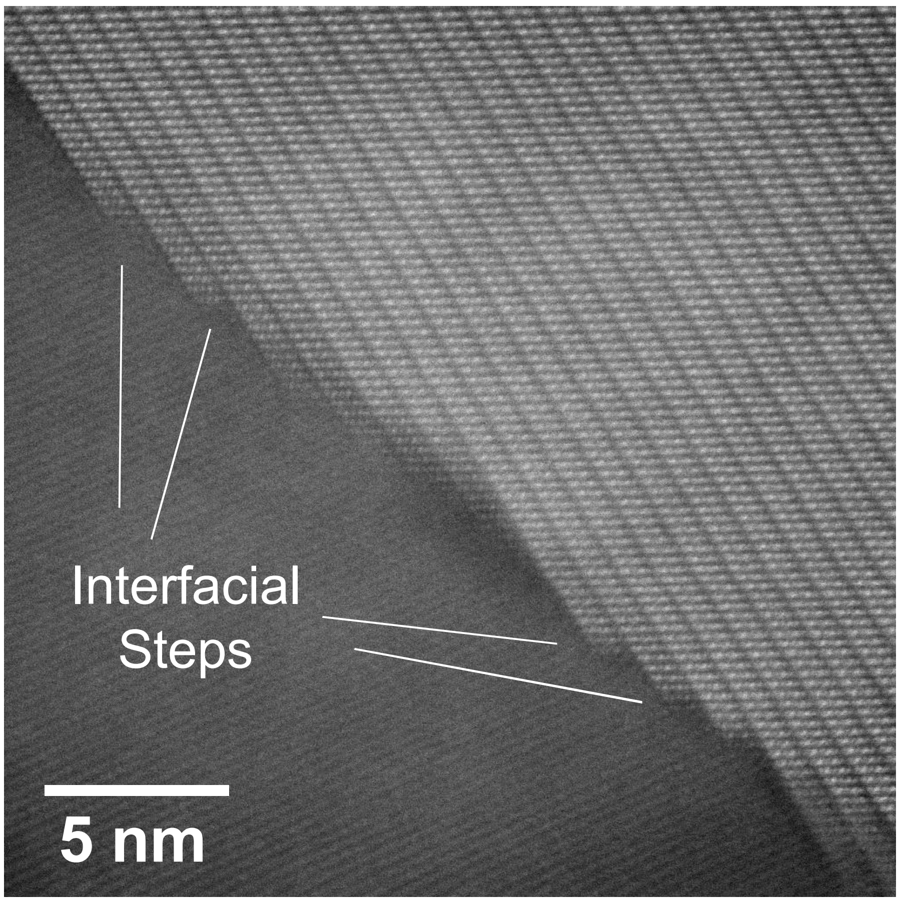
Our goal:
Connect interfacial structure to mechanisms governing interfacial behavior

Example:

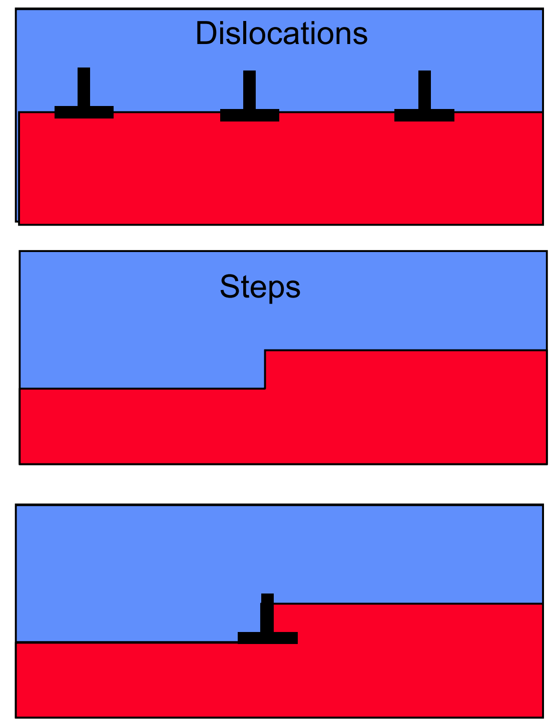
HAADF-STEM image, Grain Boundary in Bi_2Te_3



NBT20/21mar11/18.15.52

Interfacial Defects:

Building blocks to general understanding of interface structure and behavior



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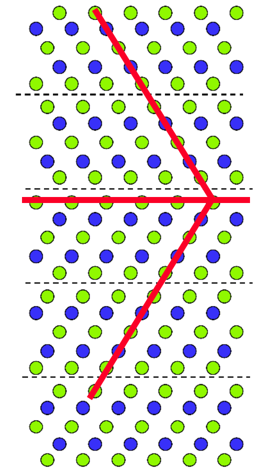
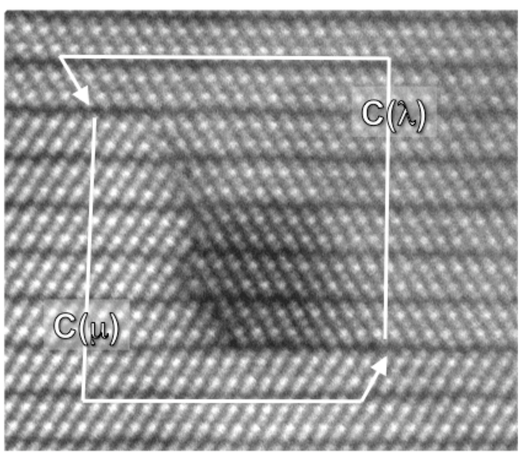
Focus for this talk: (0001) Twins in Bi_2Te_3

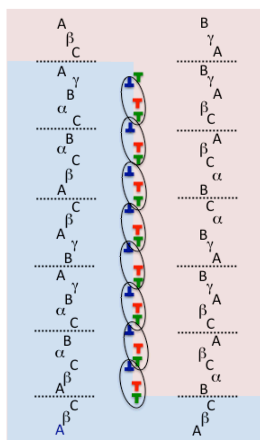
Good starting point for more complex grain boundaries

Twins have potential for favorable TE electronic transport properties

-Coherent structure, near bulk-like coordination.







- **Structure of the (0001) Basal Twin**
  -comparison with *ab initio* calculations
- **Analysis of a twin boundary defect:**
  interfacial step
- **Analogies to twins in FCC materials**

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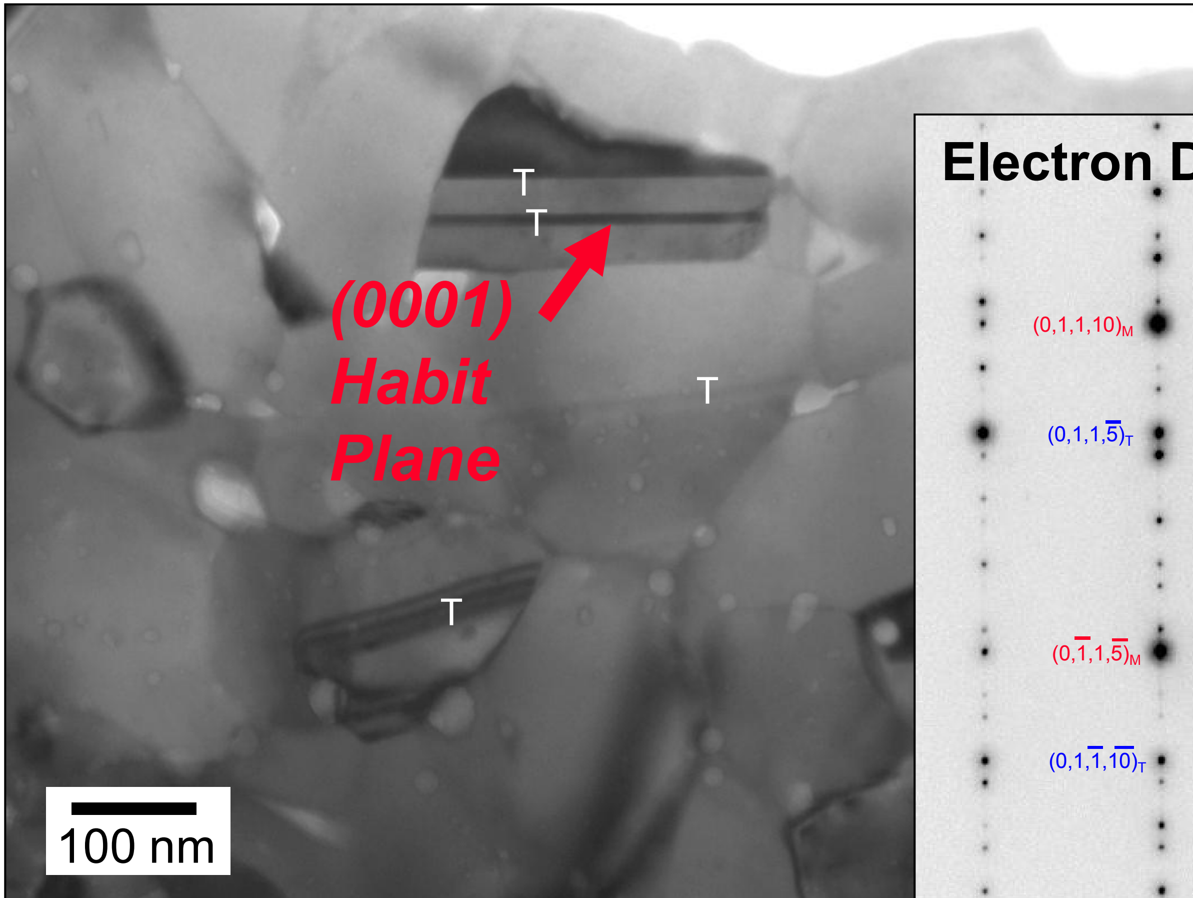
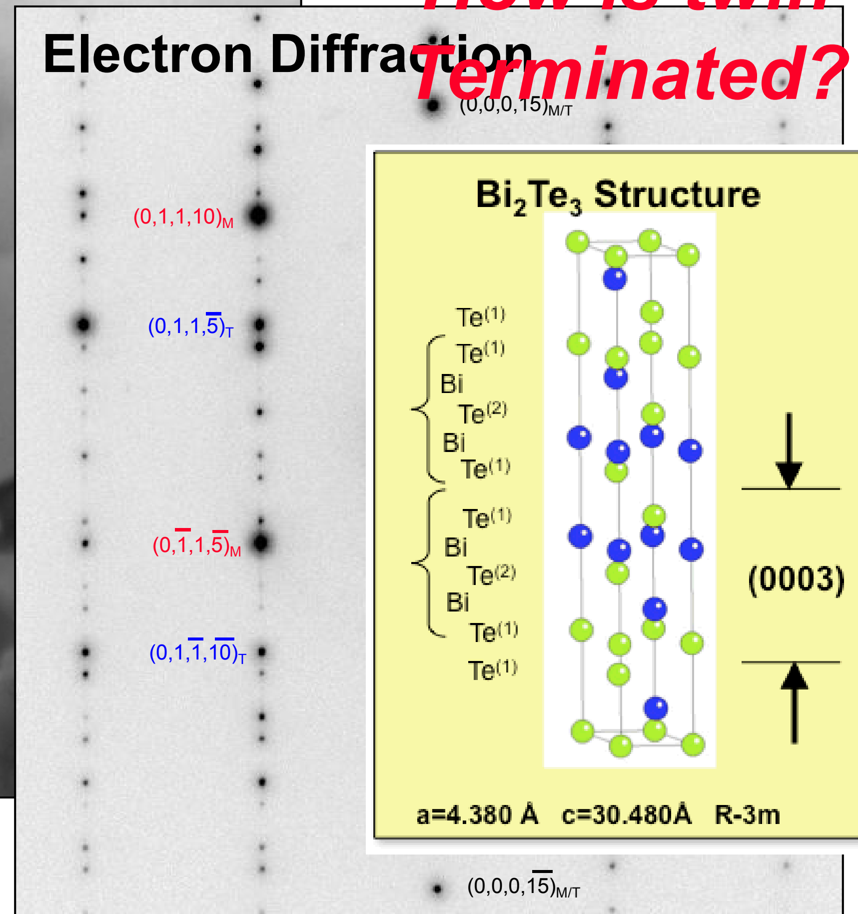
Twin microstructure and crystallography



How is twin Terminated?



Bi_2Te_3: Powder consolidated by spark plasma sintering

TEM Specimen Preparation:
Low voltage ion milling (1kV)
Cryo-cooling: <-100°C

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

180° rotation about c-axis

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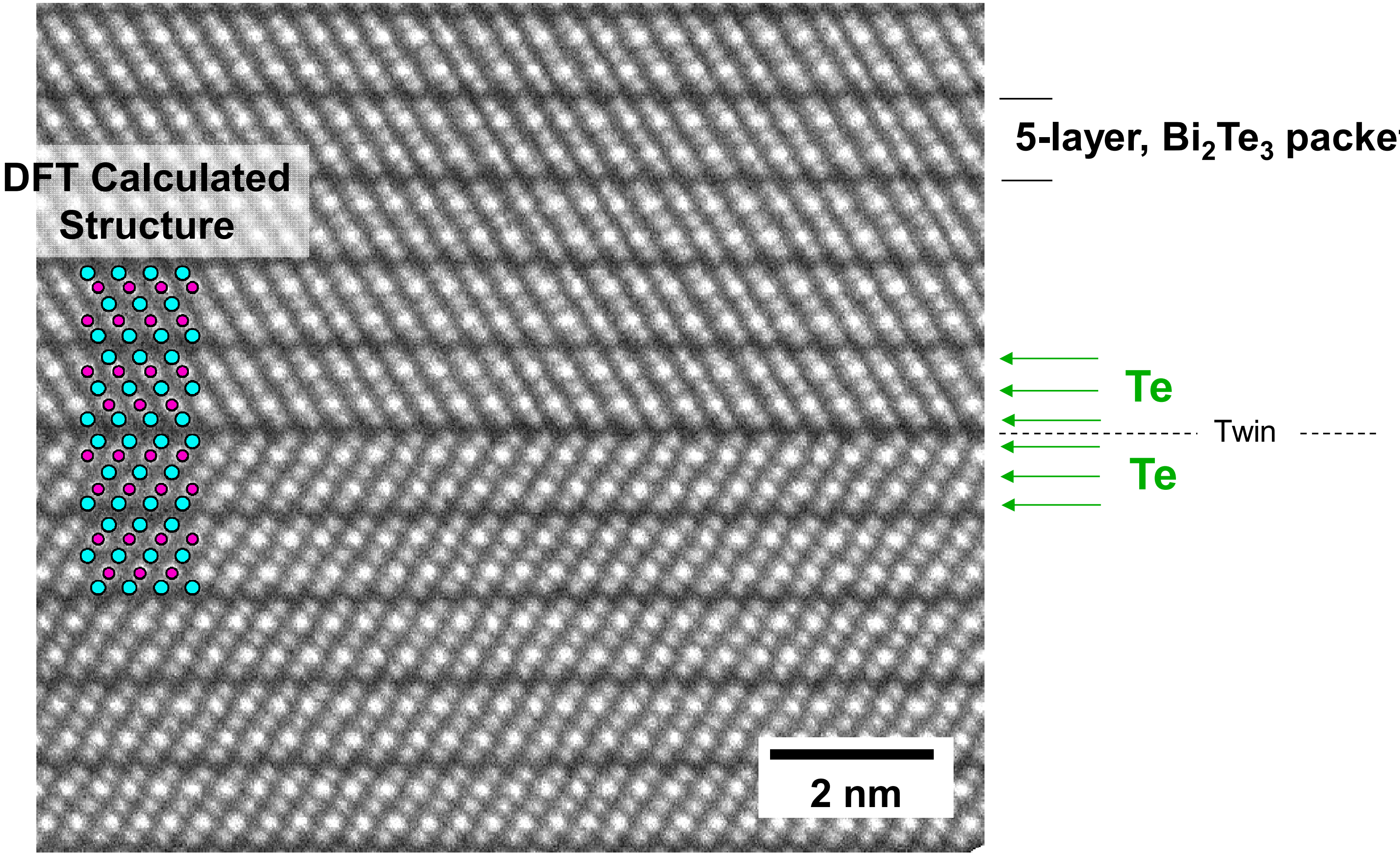
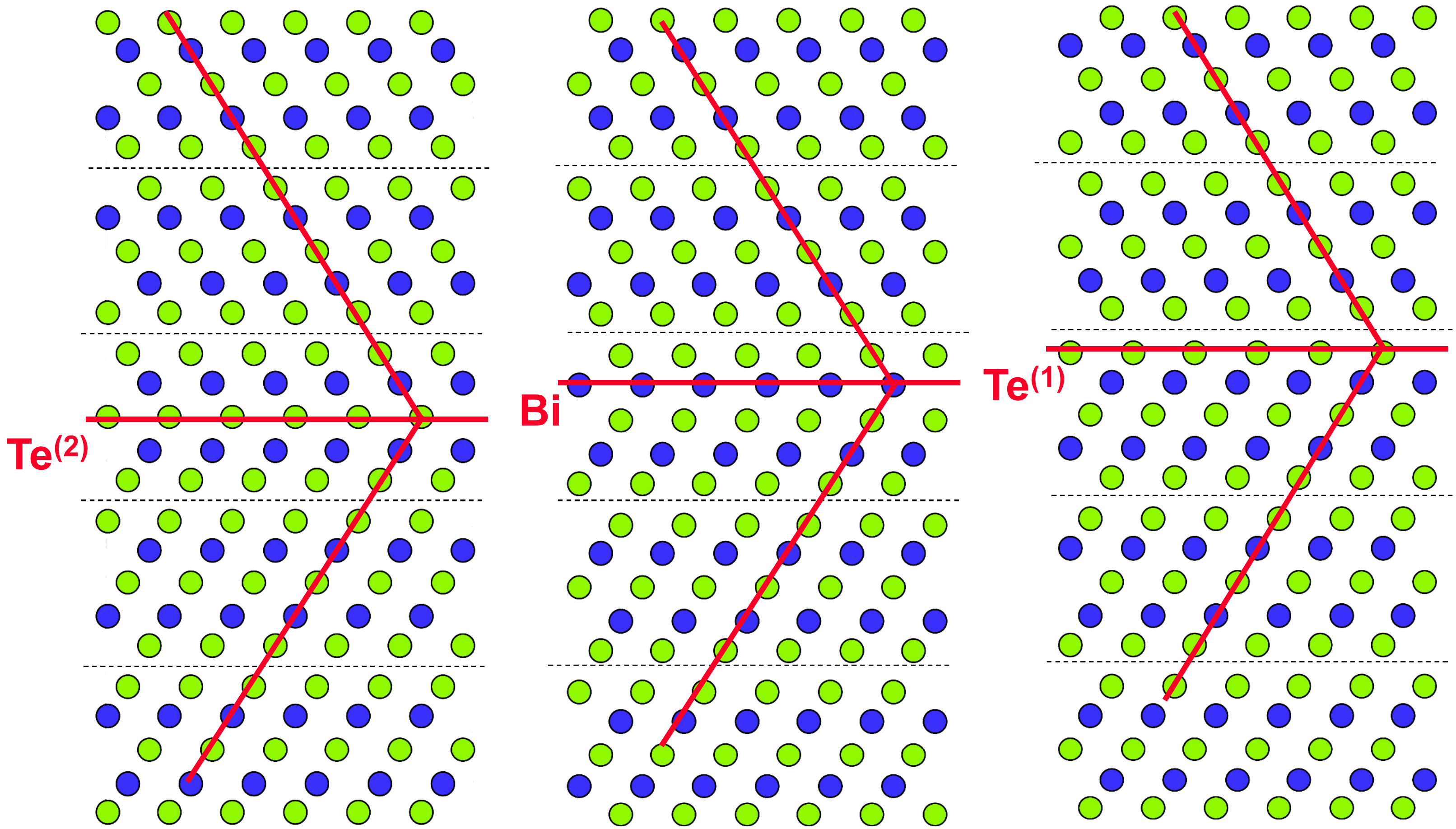
HAADF-STEM Observations: Twin terminated at $Te^{(1)}$-$Te^{(1)}$ layer



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

Twin boundary Energy depends on Interface Termination



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

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

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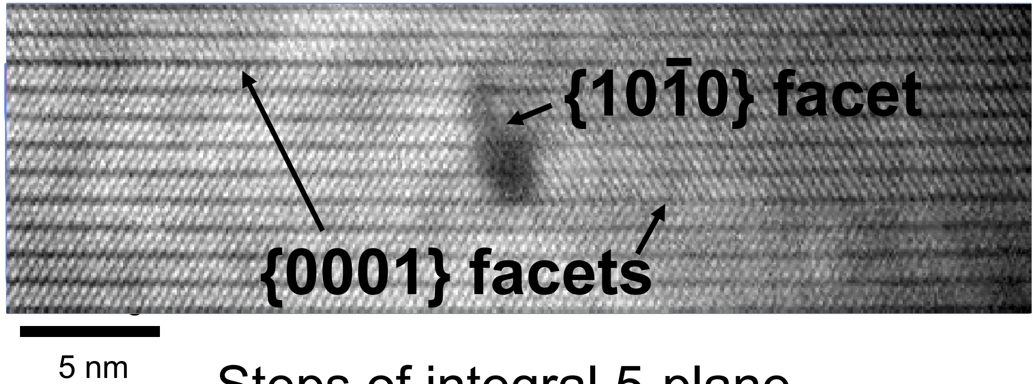
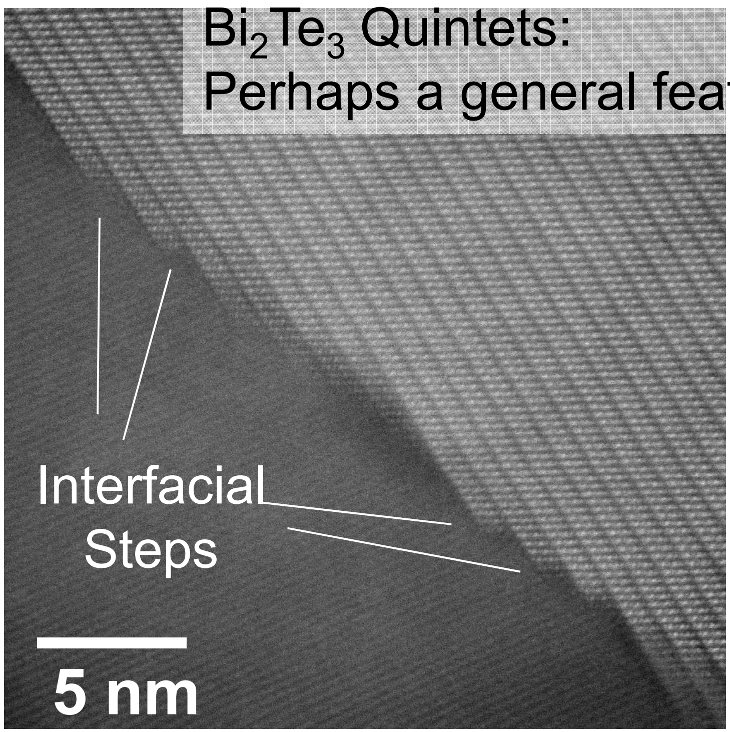
Steps in the Bi_2Te_3 Twin Boundary



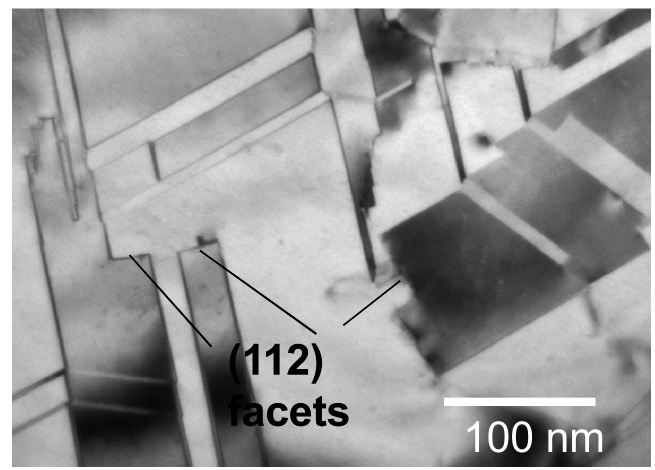
Morphology analogous to annealing and growth twins in FCC materials.

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



NBT20/21mar11/18.15.52

Example: Twins in Electrodeposited Ni



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

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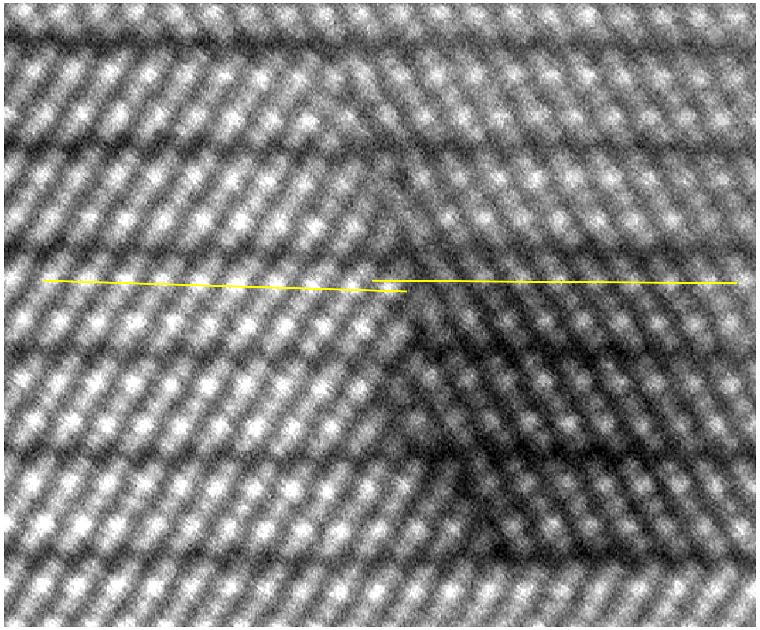
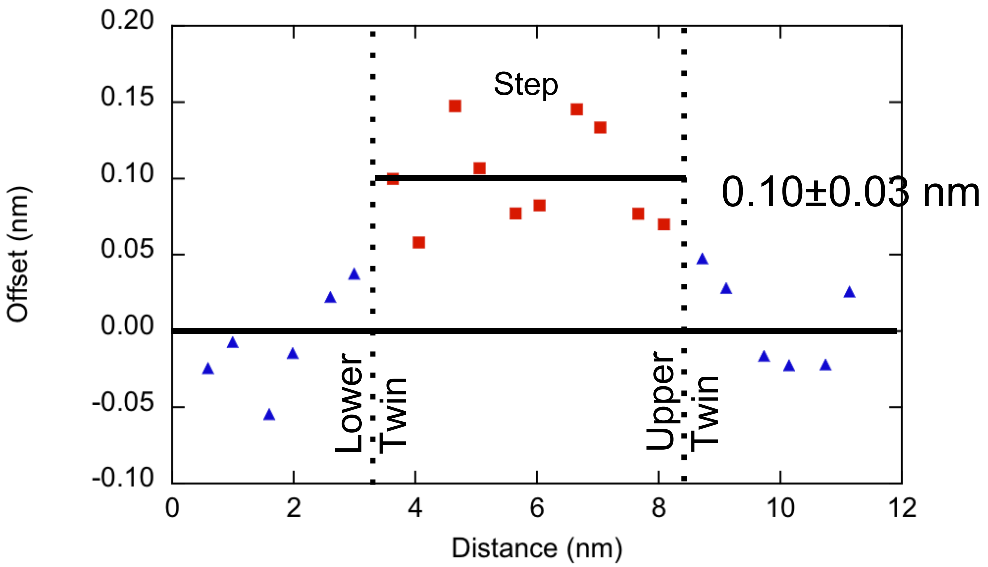
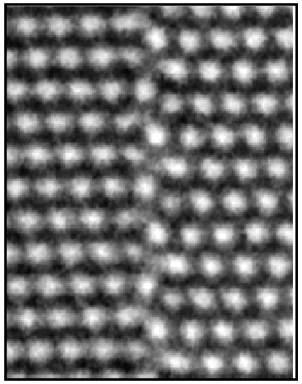
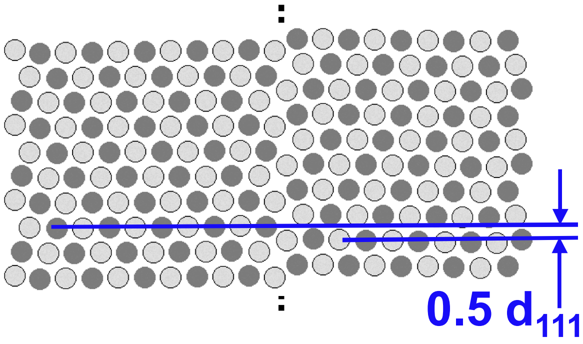
(0001) Planes are offset at step:





Offset similar to FCC {112} Twins
Example: Gold





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

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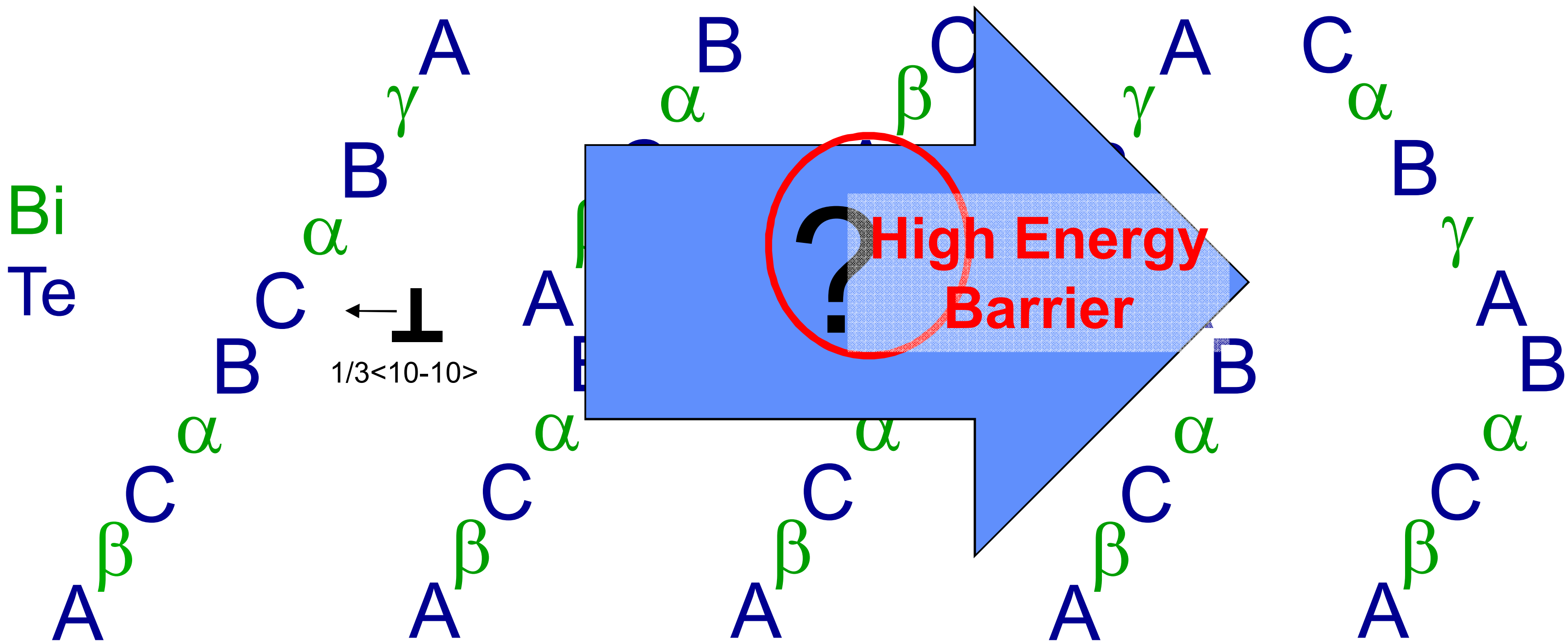
How do twins form in Bi_2Te_3?

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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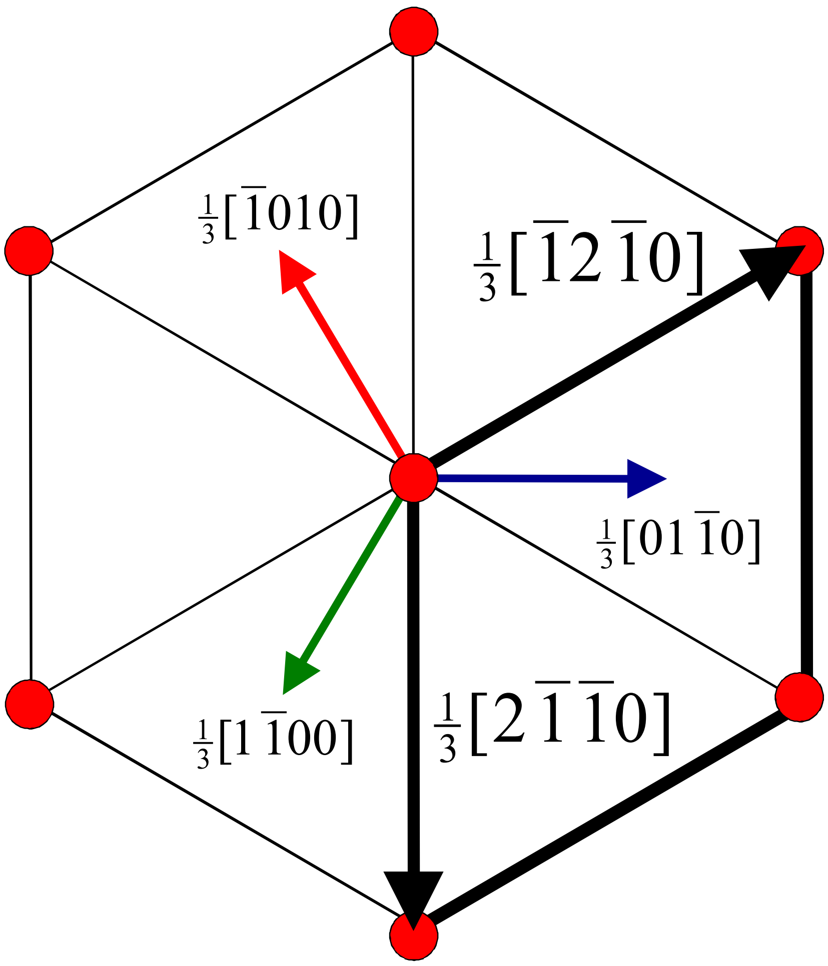
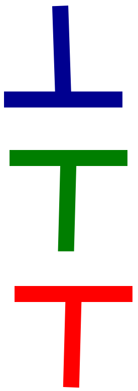
Groupings of 3 allowed twinning dislocations in Bi_2Te_3 structue



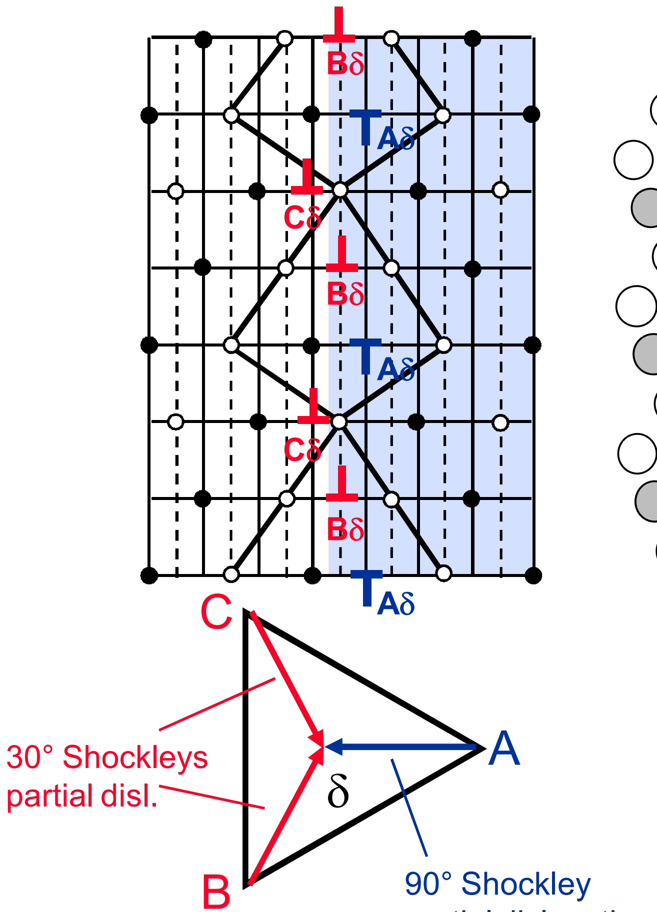


Zero Net Burgers Vector

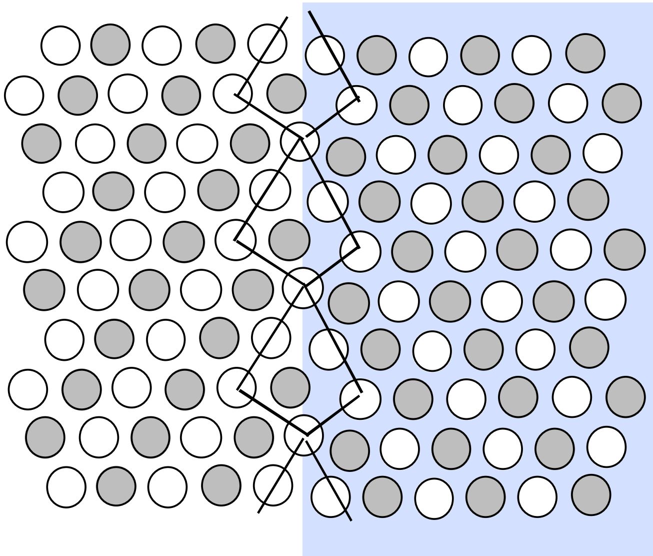
Grouping of 3 twinning dislocations is analogous to FCC {112} twin facets

Example: Aluminum {112} Twin Structure:

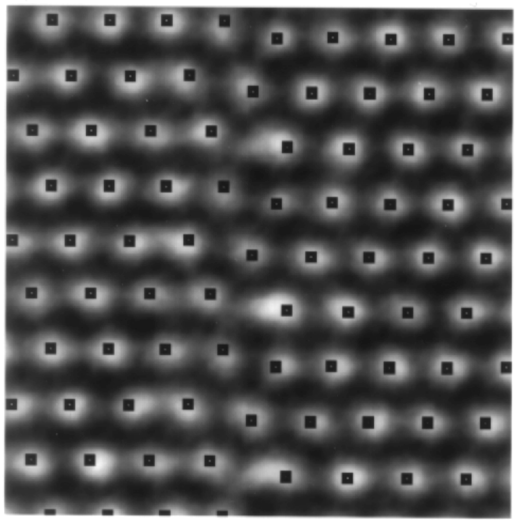
Boundary dislocation arrangement



Relaxed Structure
(Aluminum-Voter & Chen EAM)



HRTEM



-D.L. Medlin, M.J. Mills, W.M. Stobbs, M.S. Daw, F. Cosandey MRS 295 (1993).
-D.L. Medlin, S.M. Foiles, G.H. Campbell, C.B.Carter,Materials Science Forum (1999).

Facile migration of {112} facets by coordinated motion of 3-layer groupings of 90° and 30° 1/6<112> dislocations

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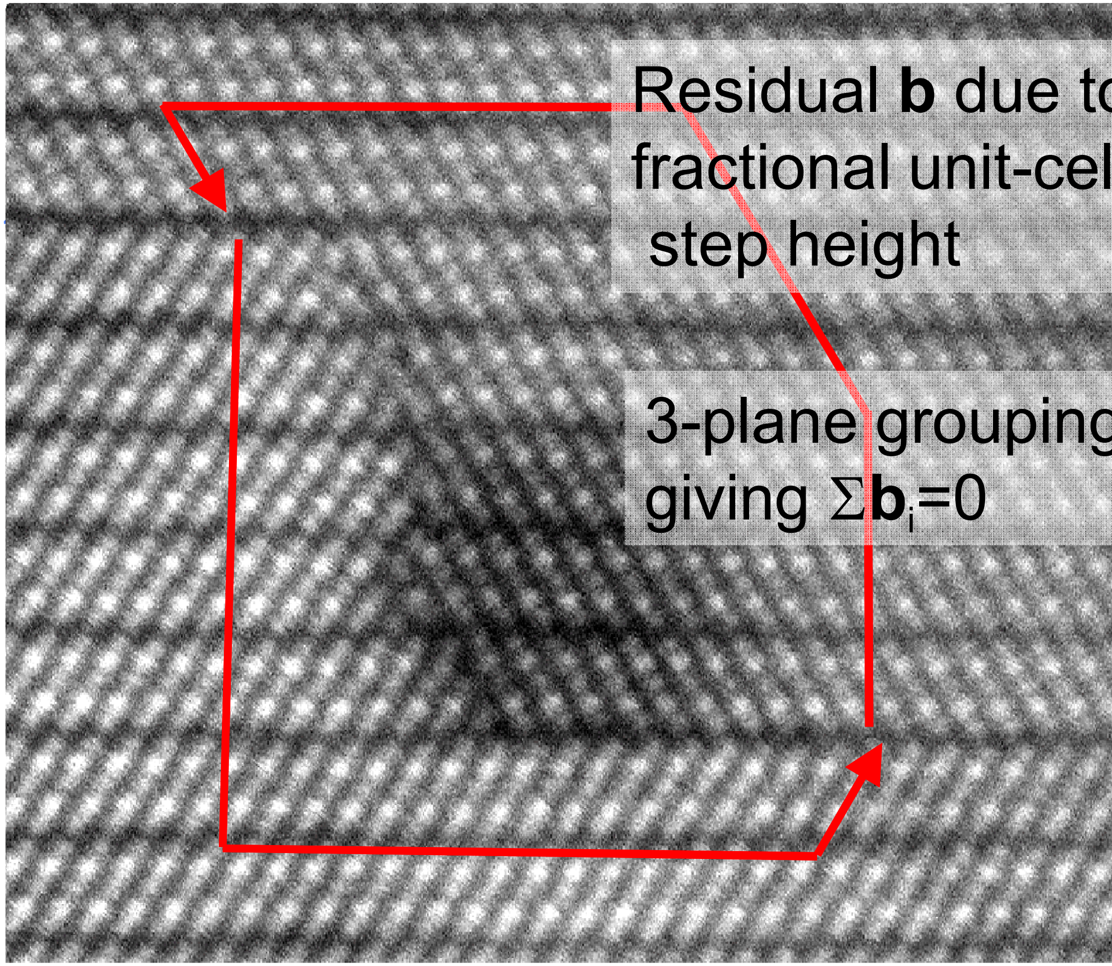
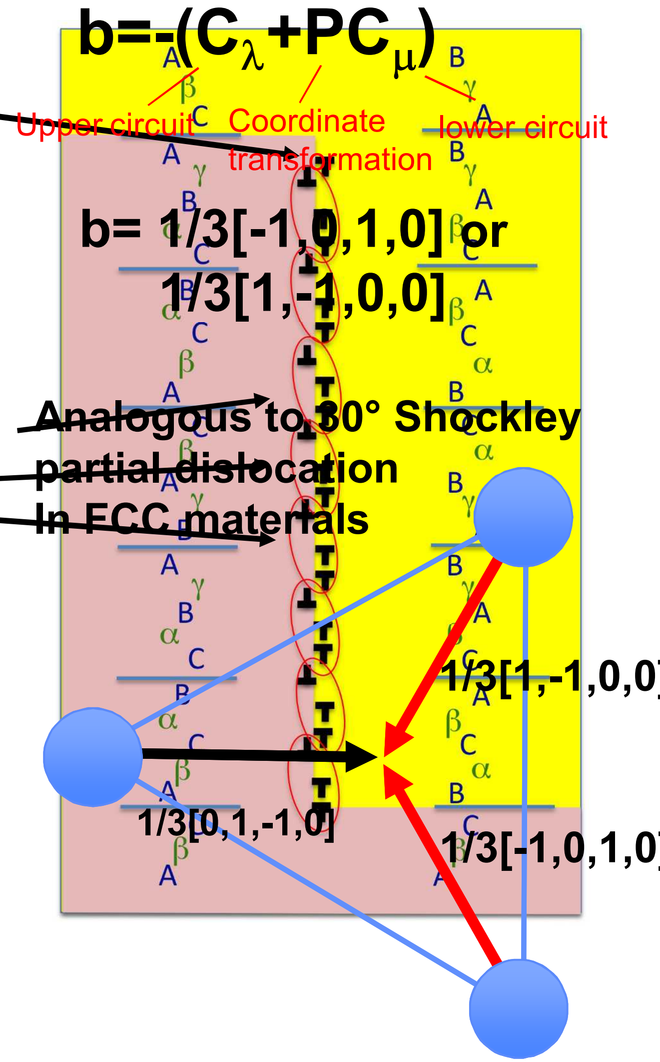
What is the dislocation content of the step?





LLNL-Titan
HAADF-STEM
300 keV

Medlin and Yang, Journal of Electronic Materials (submitted) 2011

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Conclusions

- **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

- **Twin boundary defect structure:**

  -Analogies to FCC twins and defects.

  -chemical constraint due to energetics of interface termination.

- **Foundation for more general understanding of grain boundary structure in bismuth telluride.**

Special thanks to:

-LBNL: User program, National Center for Electron Microscopy

-LLNL: John Bradley, for use for LLNL's Titan 80/300 instrument

-UCD: Z. Zhang and E. Lavernia, for assistance with SPS processing

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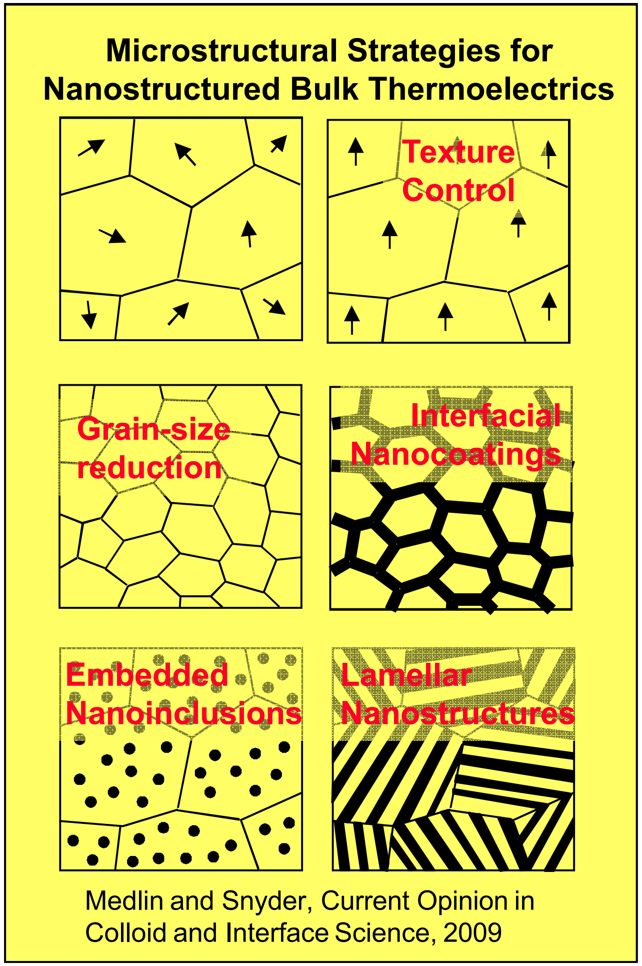
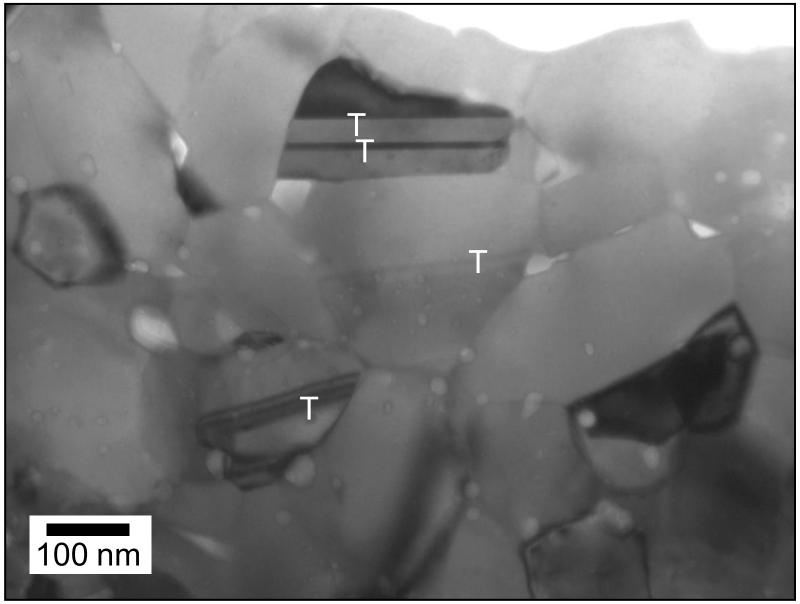
Extra

We are investigating interface structure in nanostructured bulk thermoelectrics



Example: Twins in nanocrystalline Bi_2Te_3



Focus of this talk: **(0001) Twins in Bi_2Te_3**

- **-Several possible compositional terminations**
- **-HAADF-STEM to determine structure**
- **-Compare with *ab initio* calculations**
  - **-Local relaxations**
- **-Twin formation: dislocation mechanisms**

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Interest in Grain Boundaries in Bi_2Te_3

Motivation:

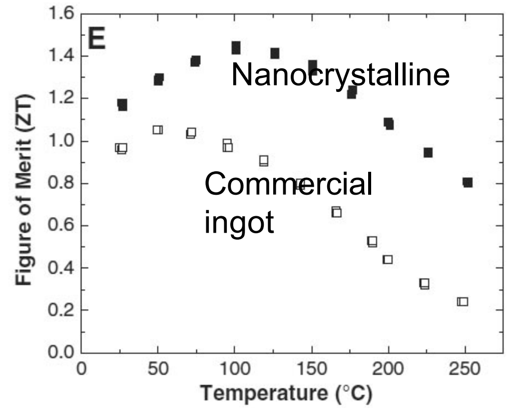
Large Enhancements in zT for nanostructured bulk Bi_2Te_3 (zT=1.4-1.6)

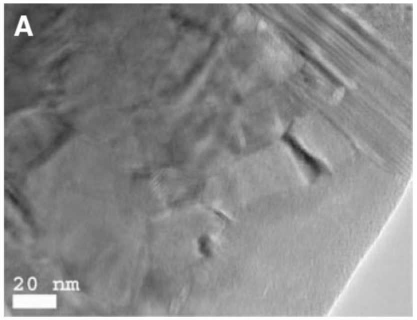
Poudel et al Science 2008 zT=1.4 @ 100°C
Xie et al, J. Appl. Phys 2009

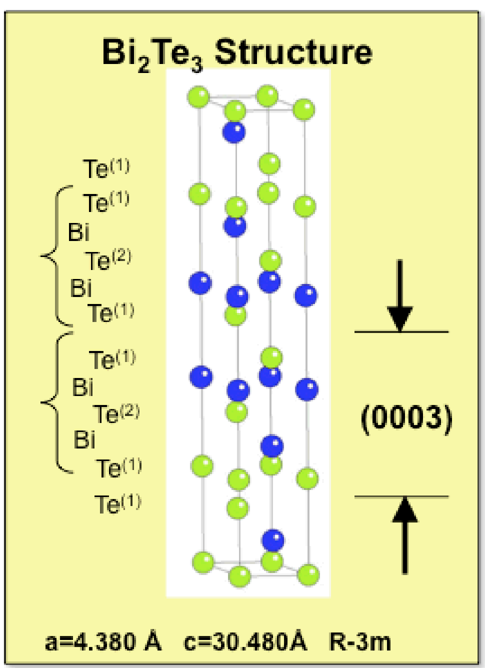
-Reduced κ_l, boundary phonon scattering

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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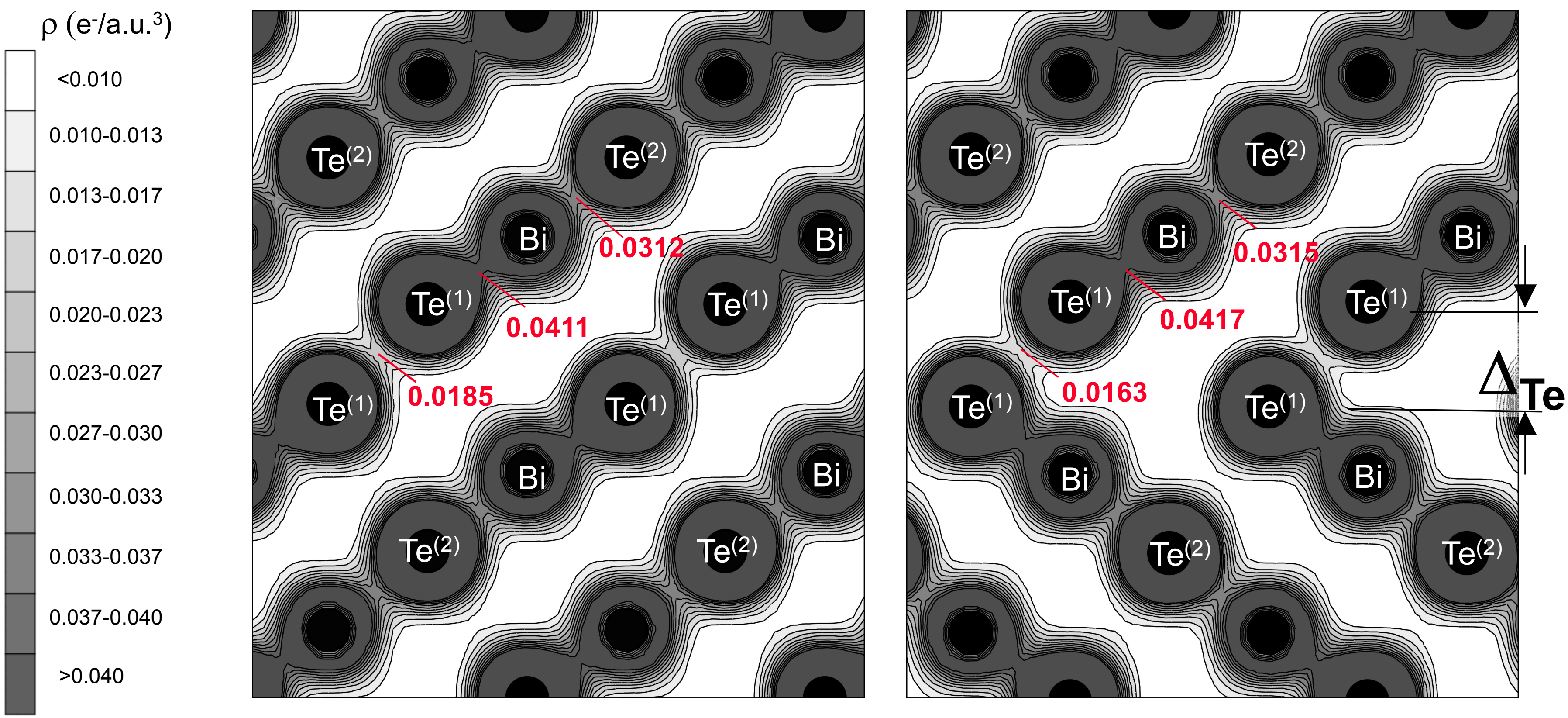
Calculations predict expansion at interface

Bi_2Te_3-Perfect Crystal | **$Te^{(1)}$-$Te^{(1)}$ Twin**



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

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

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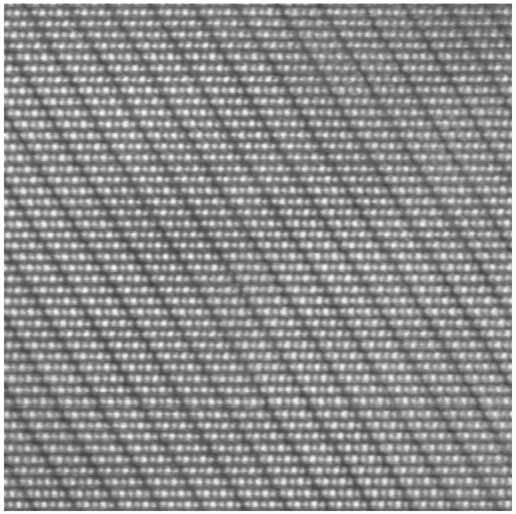
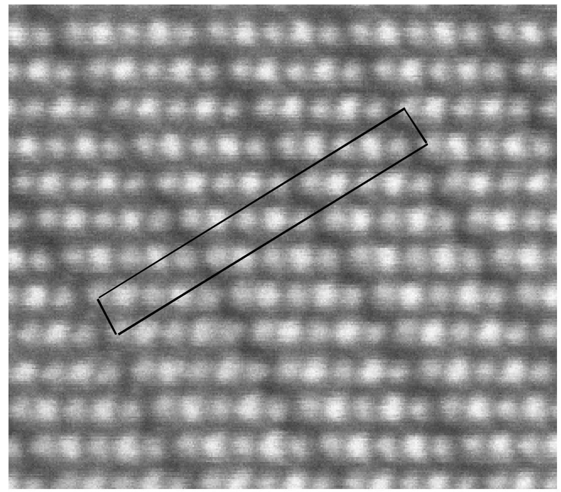
Bi_2Te_3 : High Angle Annular Dark Field STEM

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



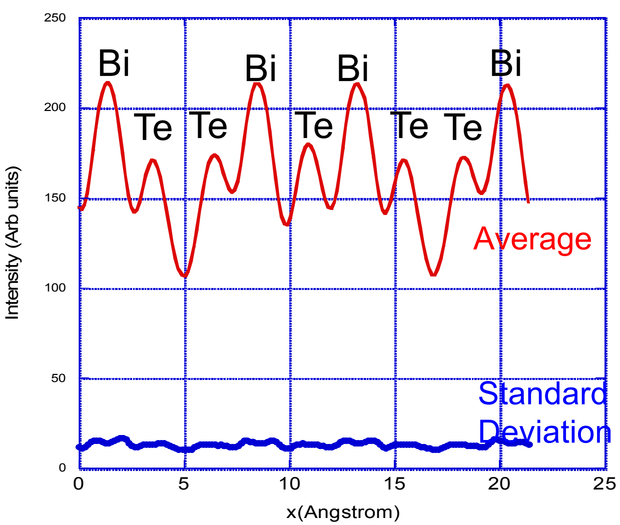
20 Å

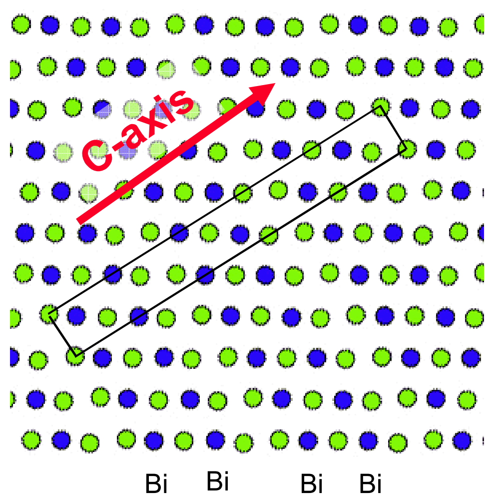


Bi and Te are well Discriminated by HAADF-STEM

Bi: Z=83

Te: Z=52





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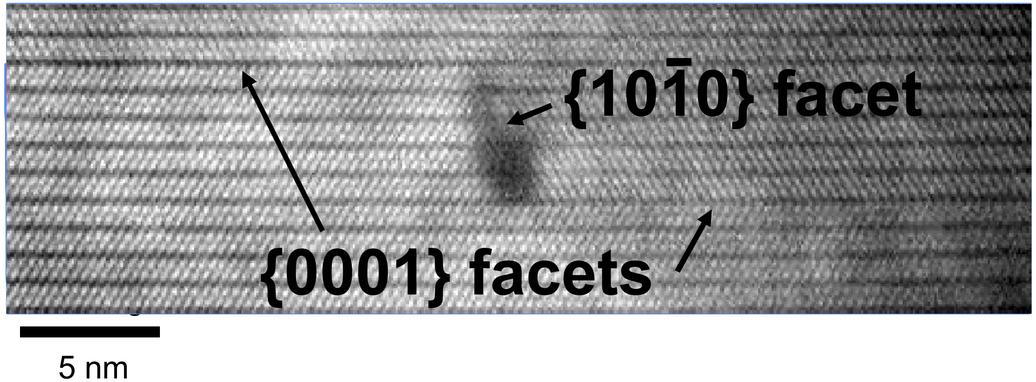
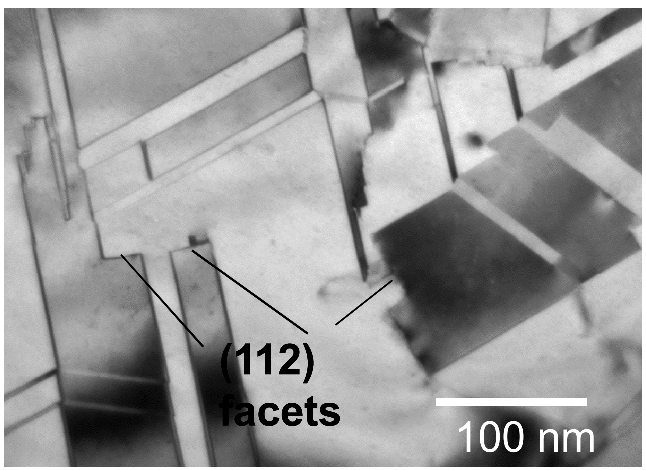
Steps in the Bi_2Te_3 Twin Boundary

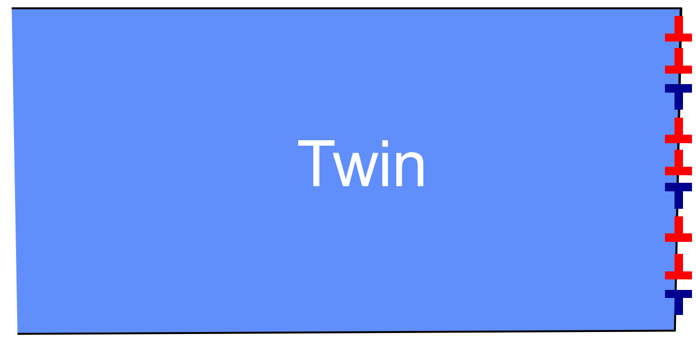


Morphology analogous to annealing and growth twins in FCC materials.

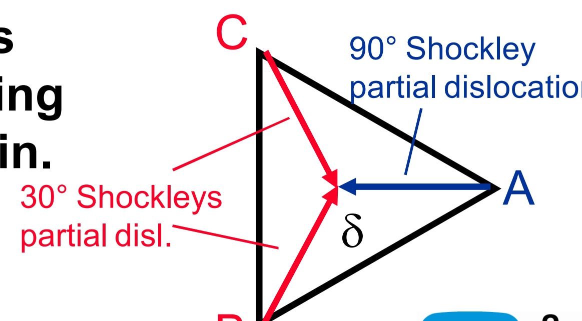
Example: Twins in Electrodeposited Ni



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

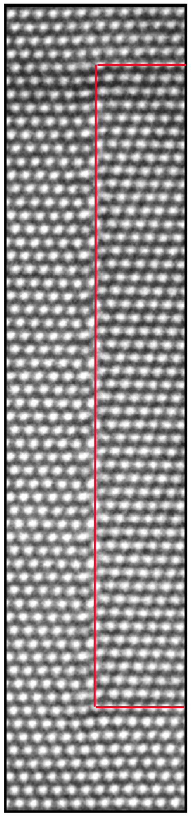


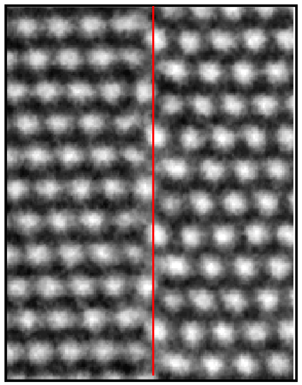
Burgers vectors cancel eliminating long-range strain.



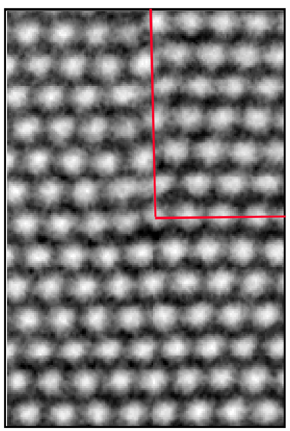
Translation of planes is similar to that observed at FCC Σ=3 {112} Twin Boundaries

Example: Au Σ=3 {112}





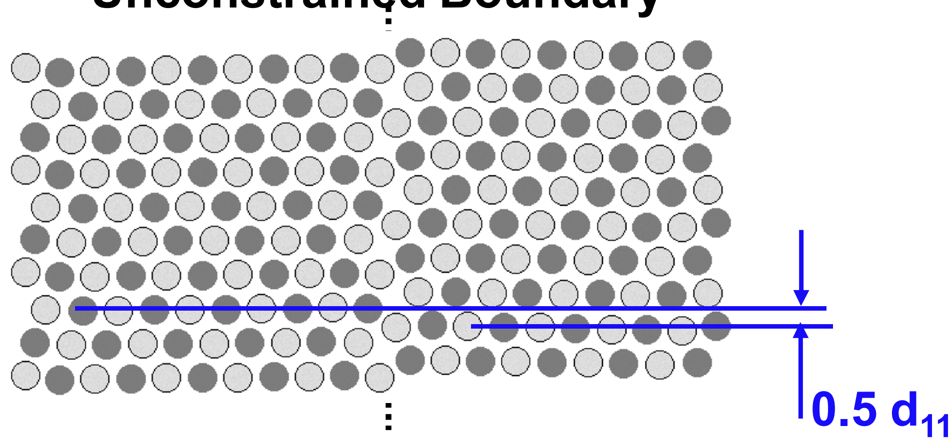
0.5 d_{111} away from junction (=1/6[111])



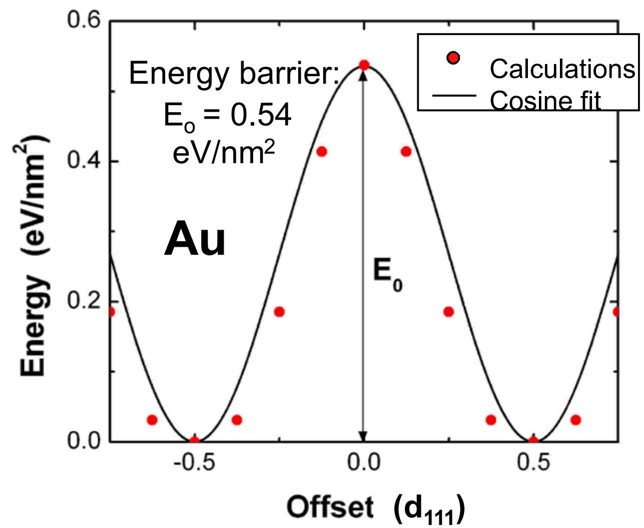
Translation constrained at junction

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

{111} Planes Offset in Unconstrained Boundary

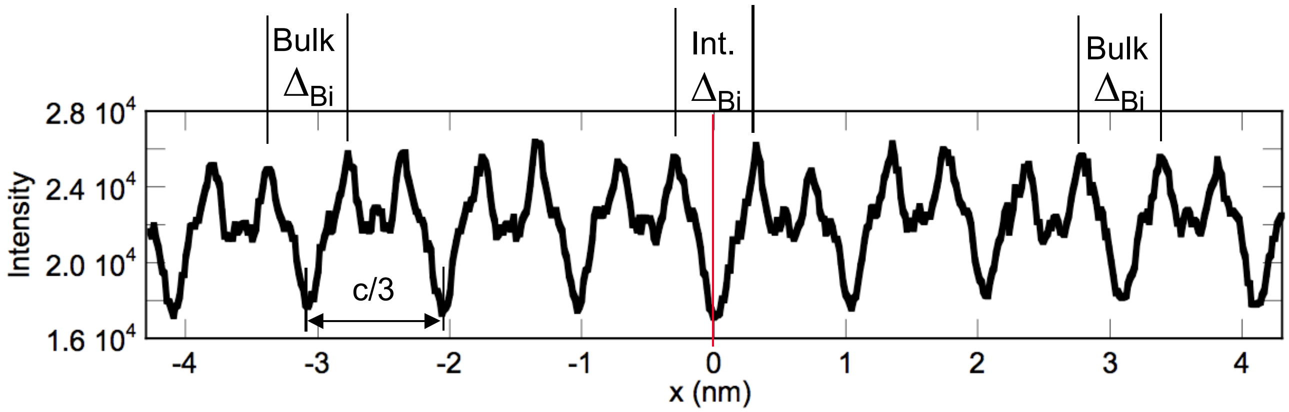


First-principles calculations of GB energy



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:

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

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

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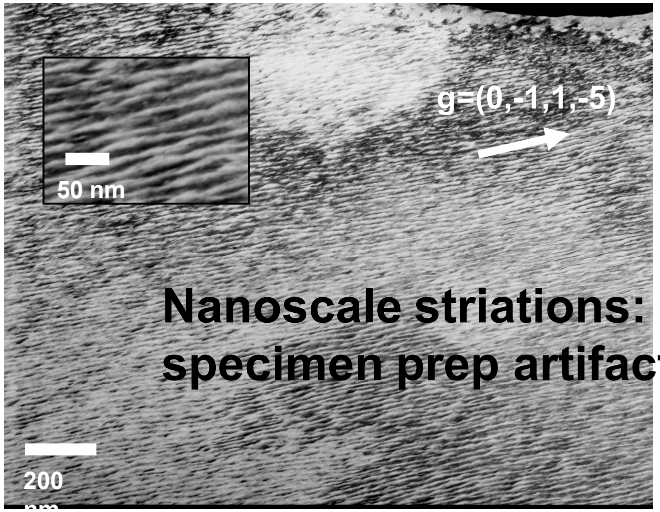
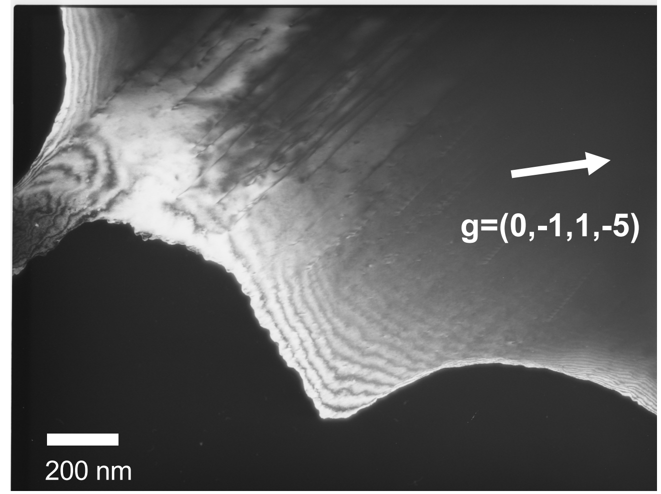
EXTRA

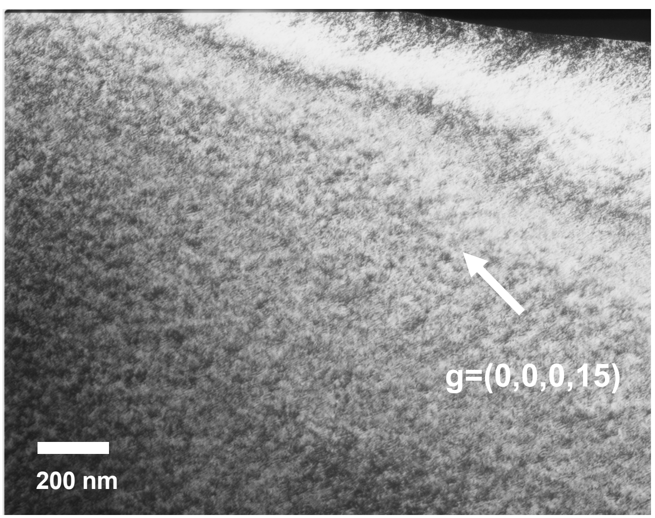
Aggessive ion-milling produces nanoscale artifacts in Bi_2Te_3

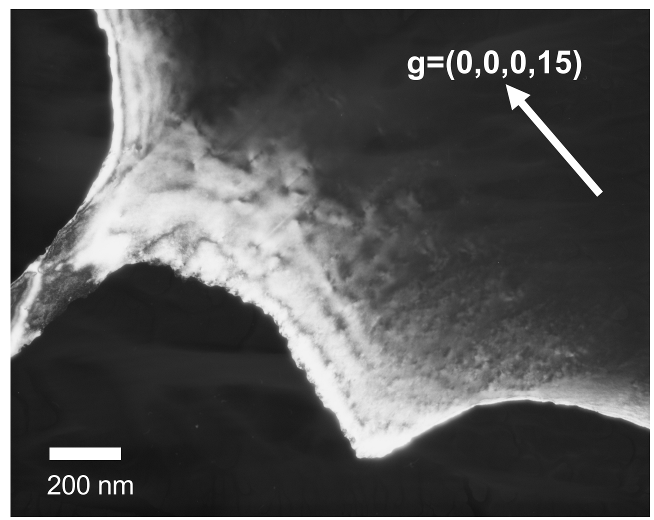
Ion Milled (Gatan DualMill 5 kV Ar+)



Electrochemical Polish







Can avoid artifacts using low-voltage, low-angle ion milling with cryo-cooling

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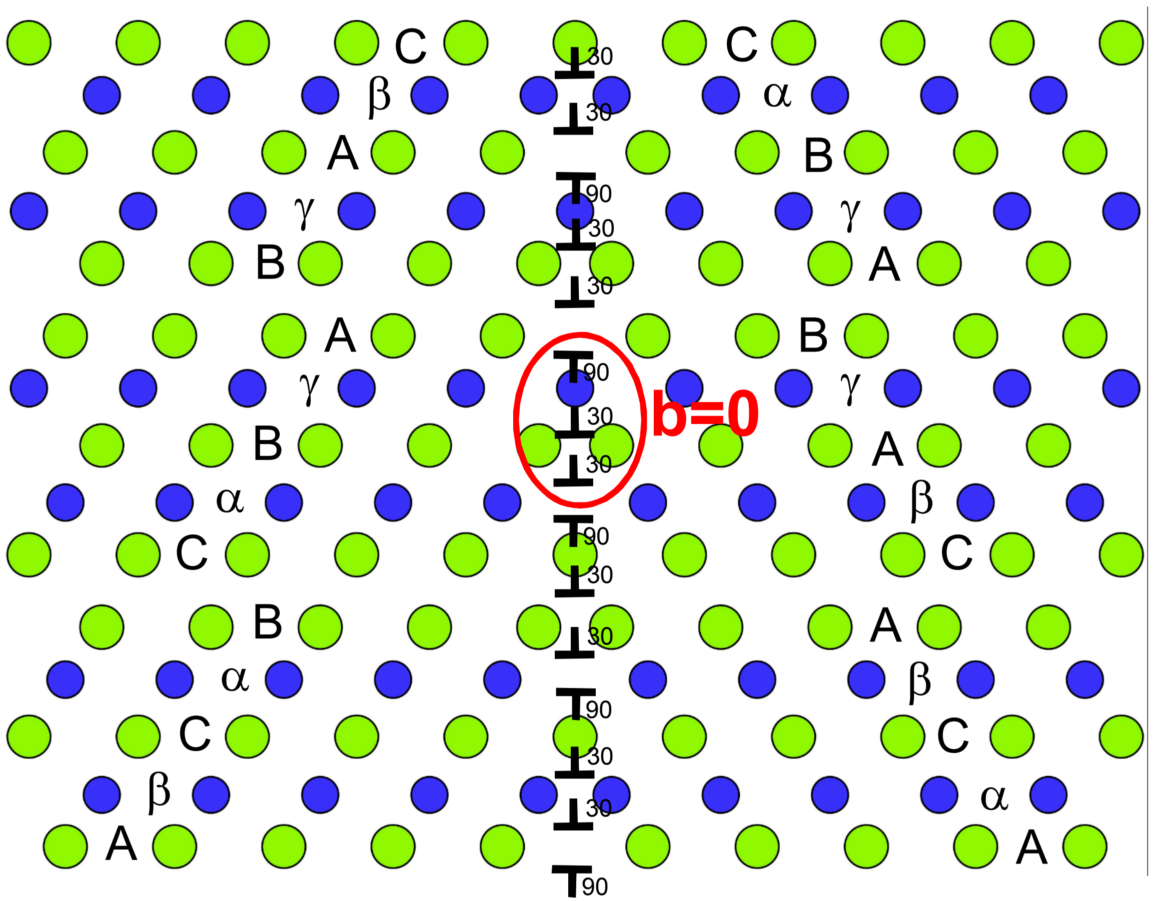
Schematic of Bi_2Te_3 {10-10} twin



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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