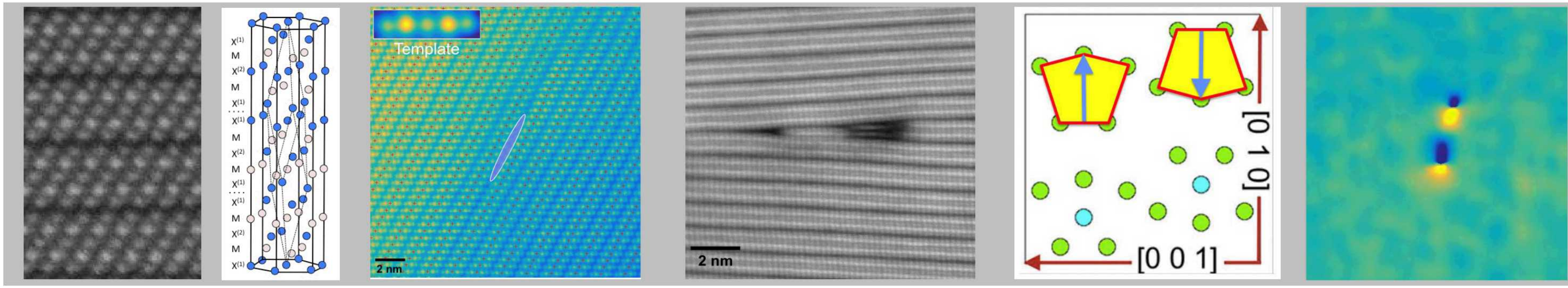
SAND2019-7064C



Extended Crystal Defects in Layered Chalcogenide Materials: Atomic-scale Structural Investigations

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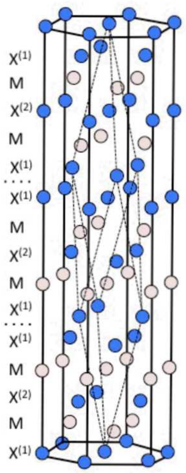
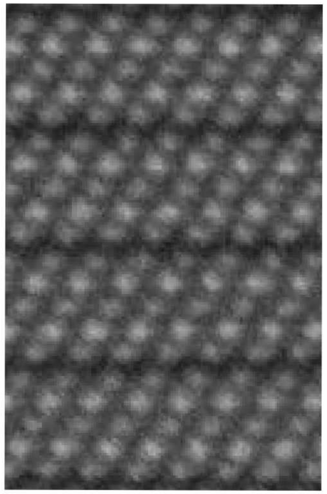
Livermore, California, USA
dlmedli@sandia.gov

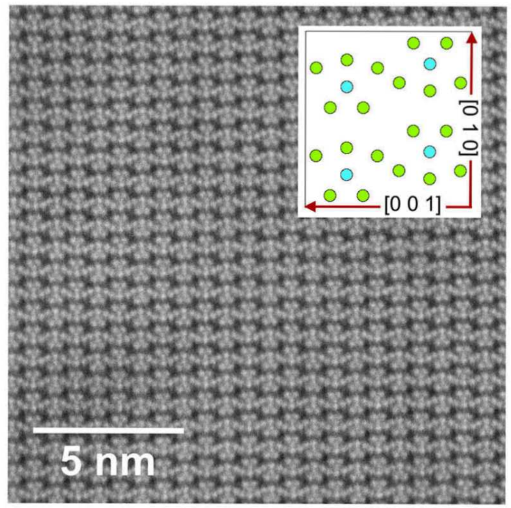
Layered Chalcogenides: Diversity of compositional and structural arrangements

Example: Bi_2Te_3





Example: $ZrTe_5$



Anisotropic, layered structures contribute to useful and interesting thermal, electronic, optical properties:
Thermoelectrics, Photothermoelectric Effect, Topological Insulators, Dirac Semimetals

Focus for today's presentation:

Analysis of dislocation core-structure in these materials

Bismuth Telluride:

-Basal dislocations – core spreading in relationship to gamma surface
-Rhombohedral dislocation – climb-dissociation

Zirconium Telluride:

[001] dislocation – climb dissociation

Collaborators

Sandia

- K. Erickson
- N.Y.C. Yang
- C.Spataru
- M. Siegal,
- S. Limmer
- W.G. Yelton
- W. Pan

George Mason University

- Y. Mishin

National Institute of Standards and Technology (NIST)

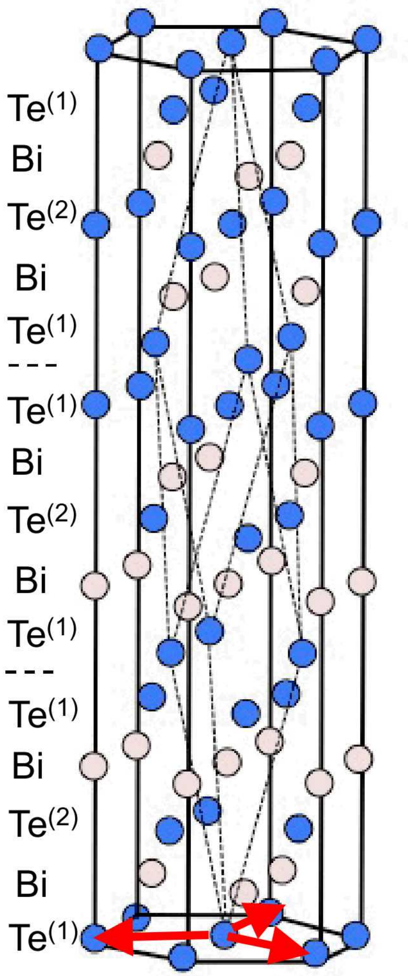
- L. Hale

LBNL/National Center for Electron Microscopy

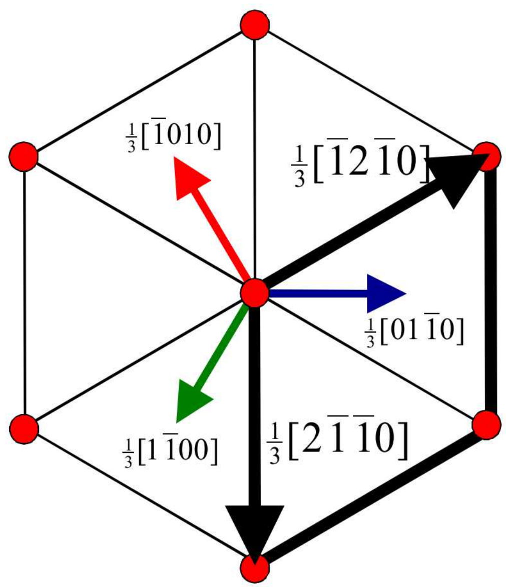
- C. Ophus

Dislocations in Bismuth Telluride (Bi_2Te_3)

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

Weak van der Waals bonding between tellurium planes

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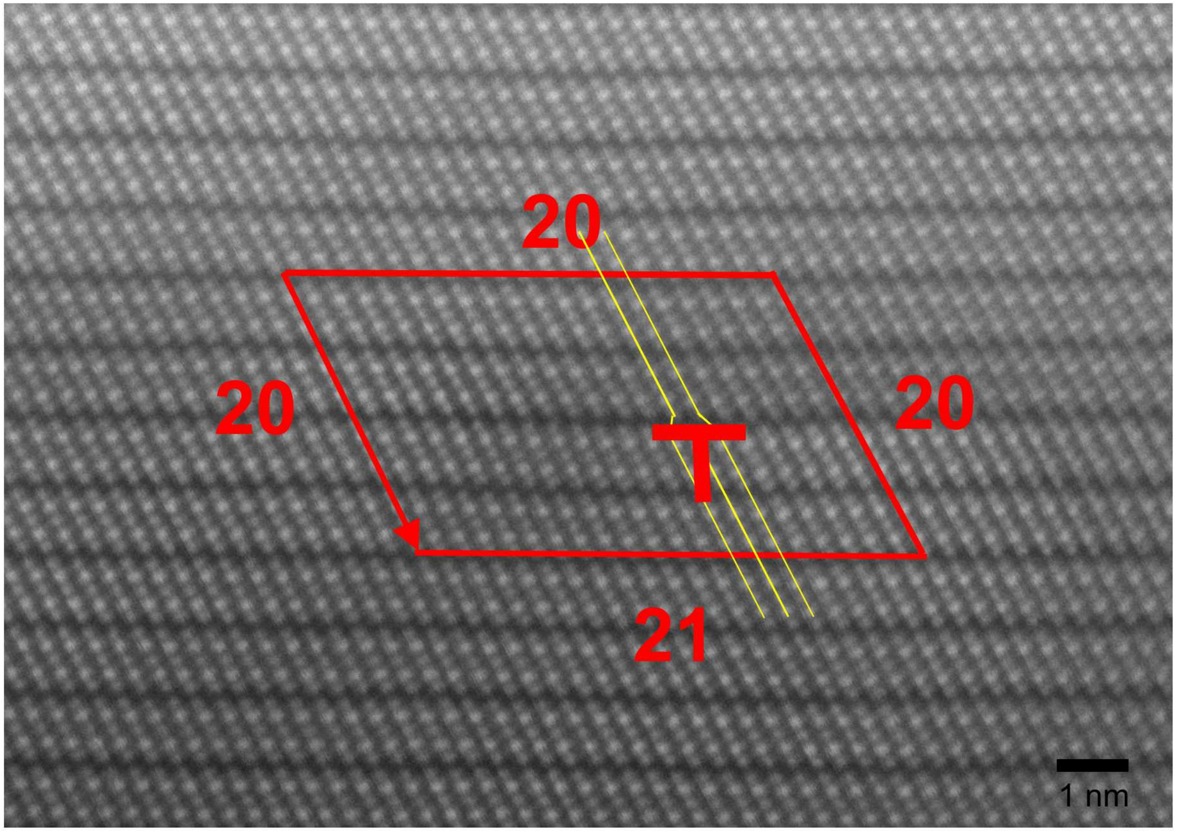
Dislocation Core structure: Termination at $Te^{(1)}$-$Te^{(1)}$ layer

5-layer Bi_2Te_3 "quintet"

[0 0 0 1]



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

60˚ mixed dislocation

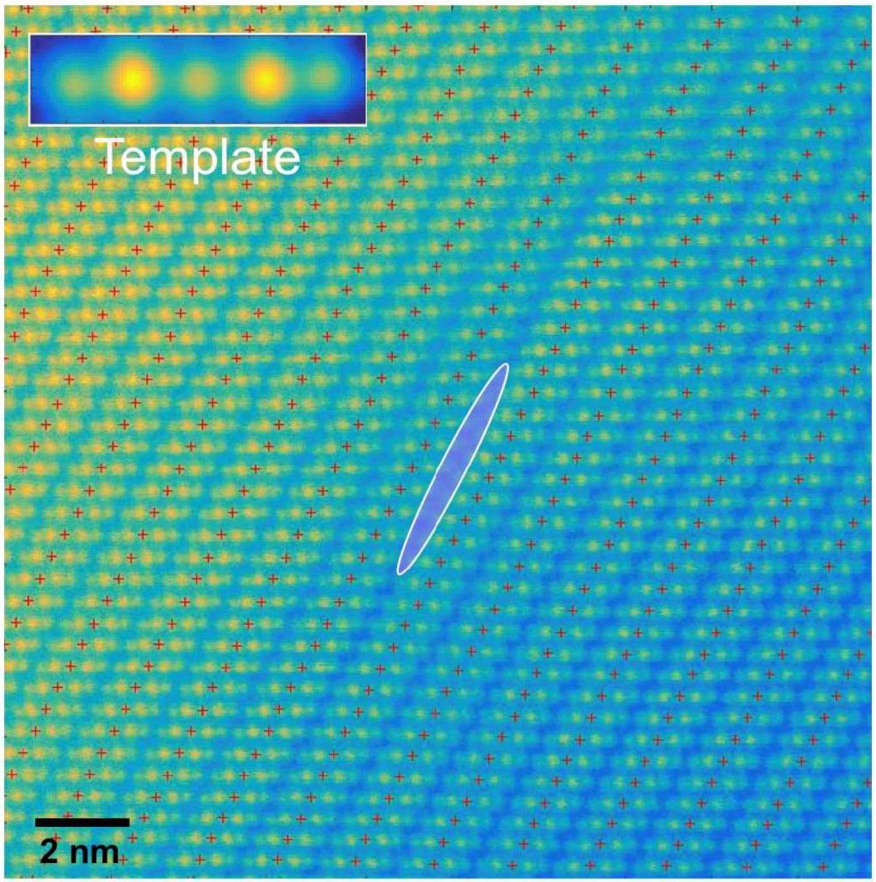
Stoichiometric Core

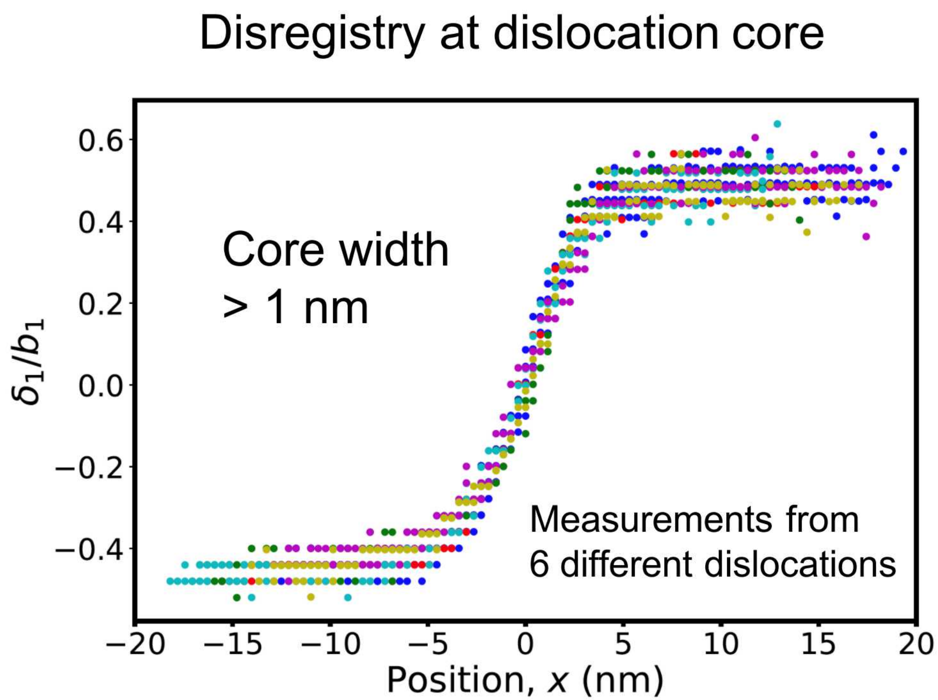
<2 -1 -1 0 > projection

Is dislocation compact or dissociated?

Medlin, Yang, Spataru, Hale, Mishin, Nature Communications 2019

Surprising Result: Broad core, but no dissociation into partial dislocations





Medlin, Yang, Spataru, Hale, Mishin, Nature Communications 2019

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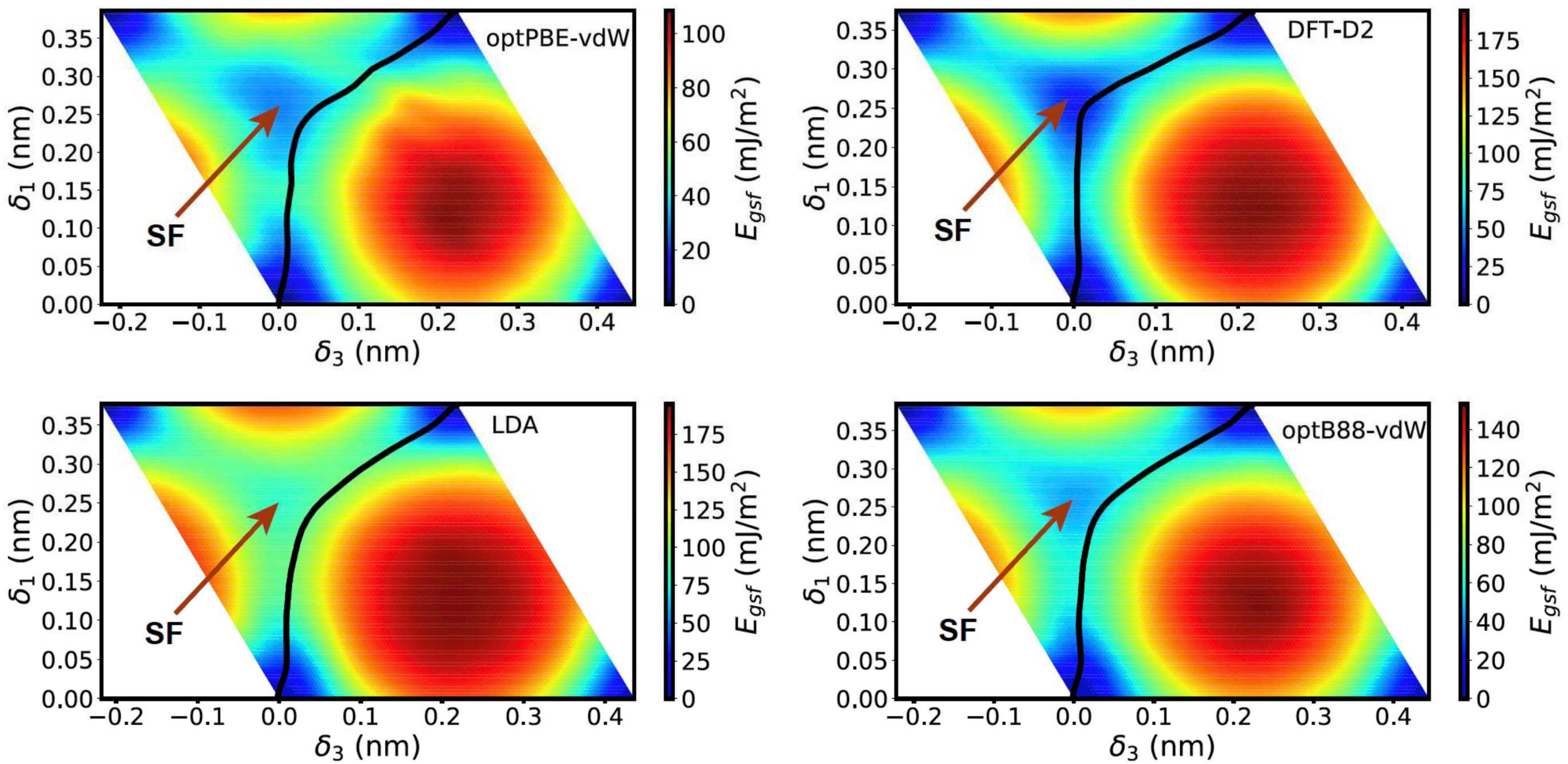
Modeling: combination of ab initio and semi-continuum dislocation theory



DFT calculations for generalized SFE using different van der Waals corrections

Peierls-Nabarro model for dislocation disregistry:

-accounts for anisotropic elastic parameters of Bi_2Te_3

Medlin, Yang, Spataru, Hale, Mishin, Nature Communications 2019

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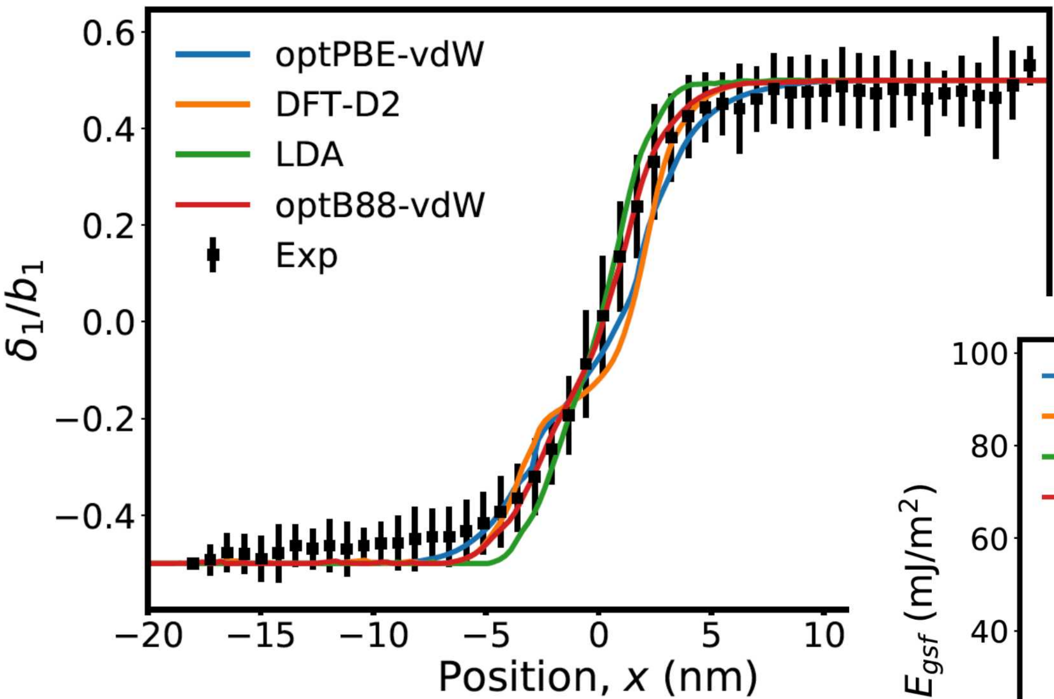
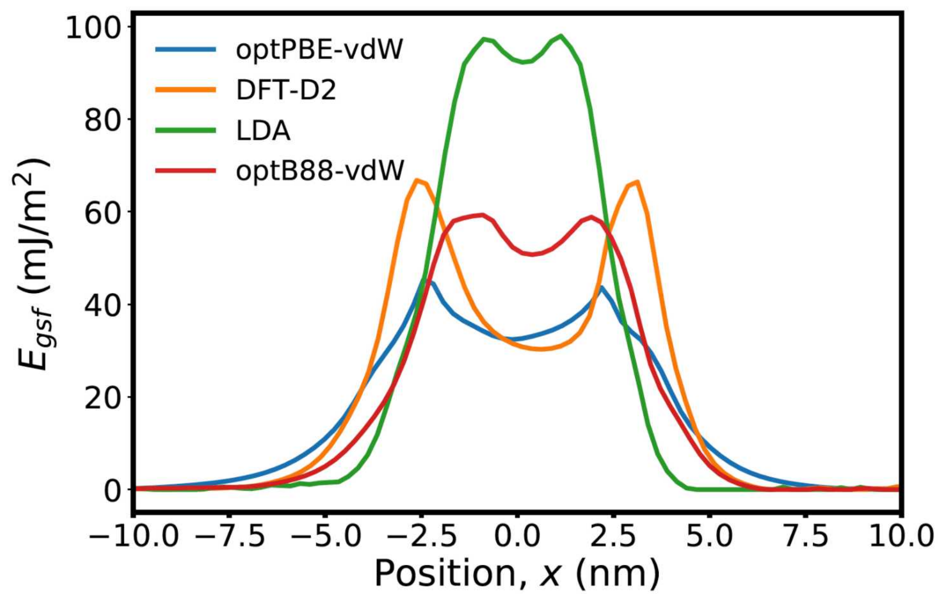
Shallow minimum relative to unstable SFE prevents localization into discrete partials





Medlin, Yang, Spataru, Hale, Mishin, Nature Communications 2019

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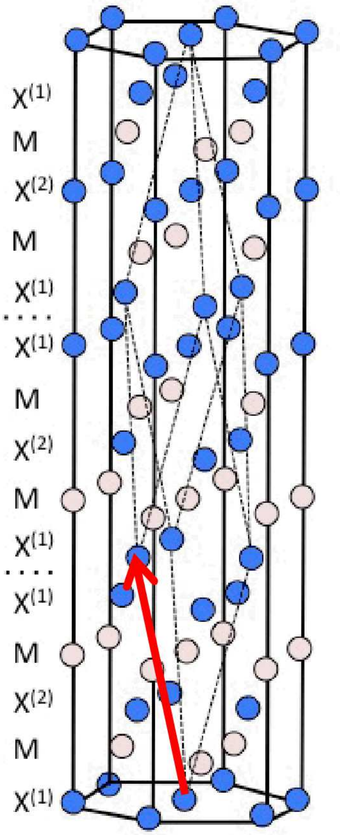
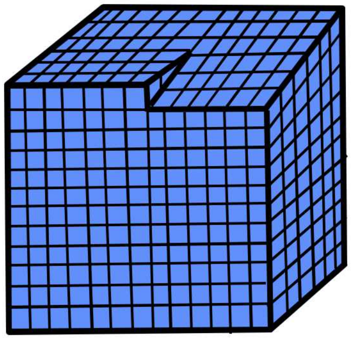
Non-basal dislocations:

Screw dislocations important to crystal growth

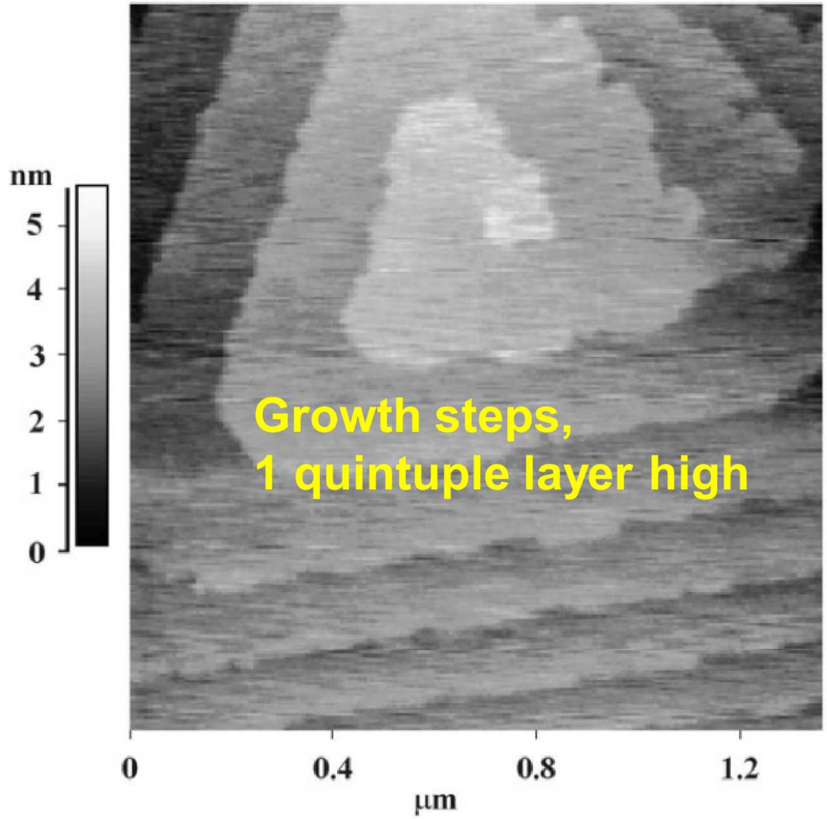


Screw Dislocation



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

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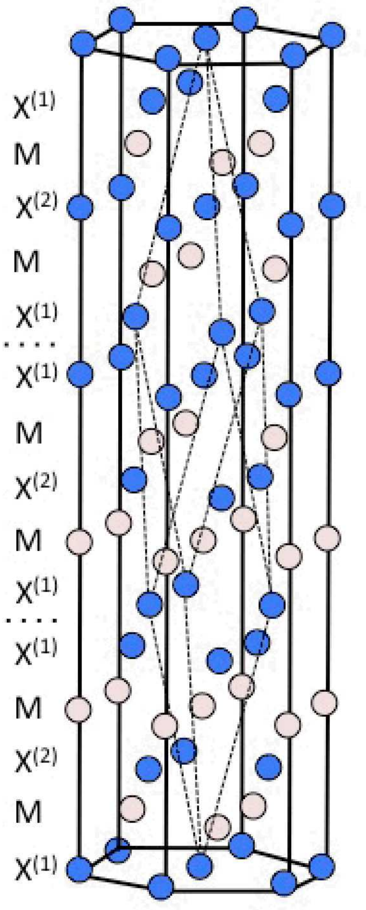
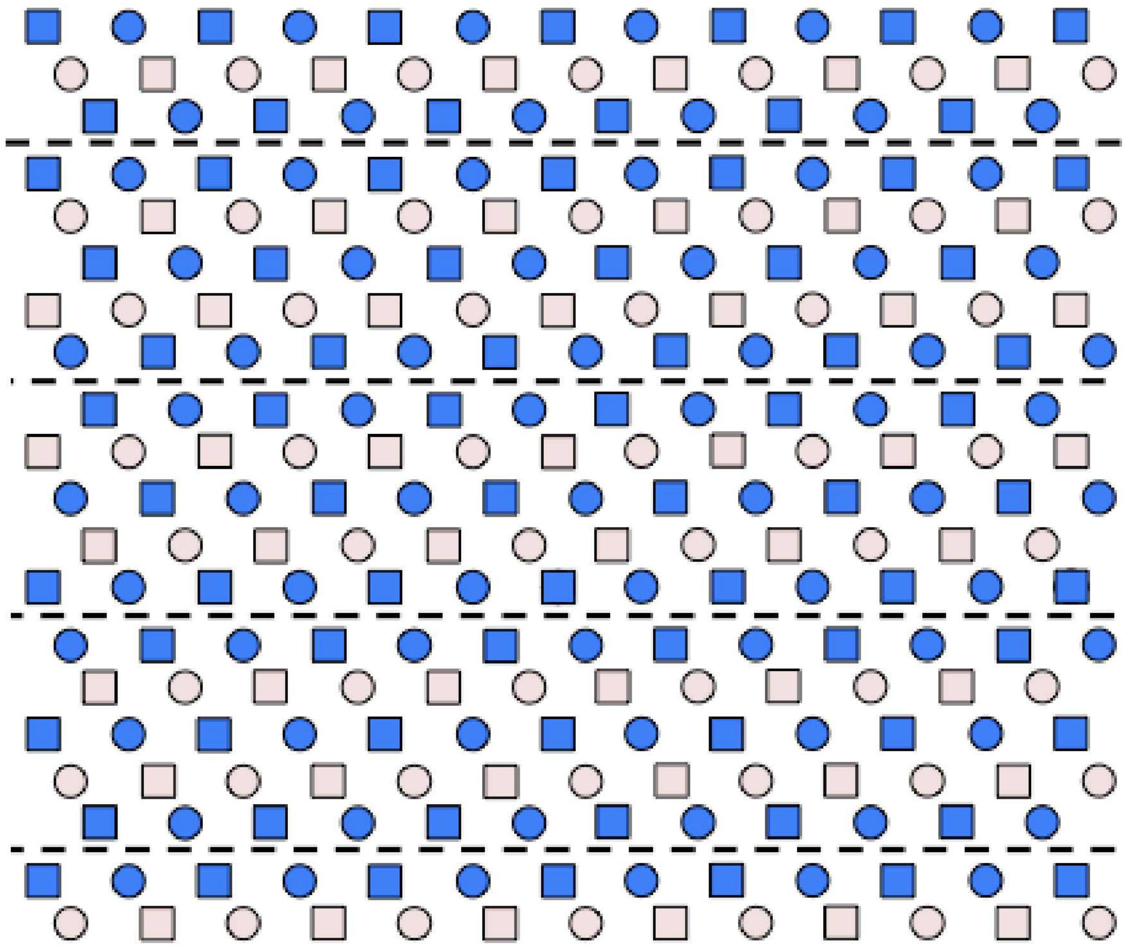
Non-basal edge dislocations:
What happens if we pull out a quintuple unit?





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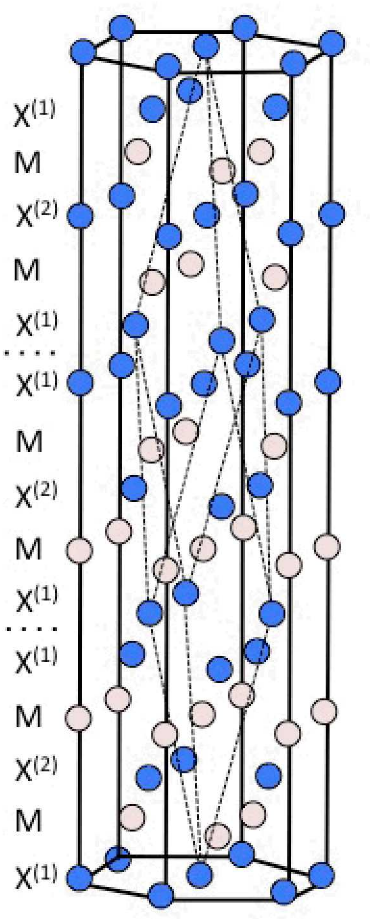
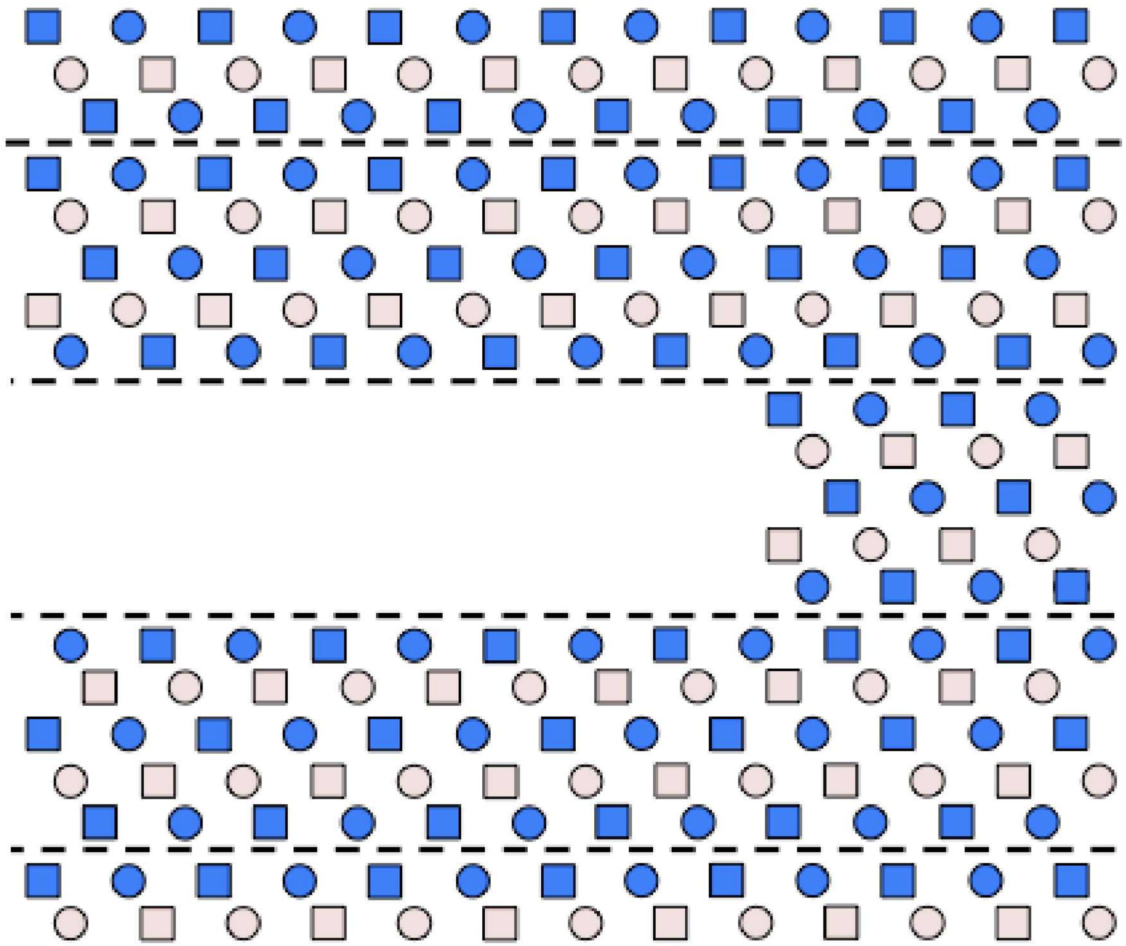
Non-basal edge dislocations: What happens if we pull out a quintuple unit?





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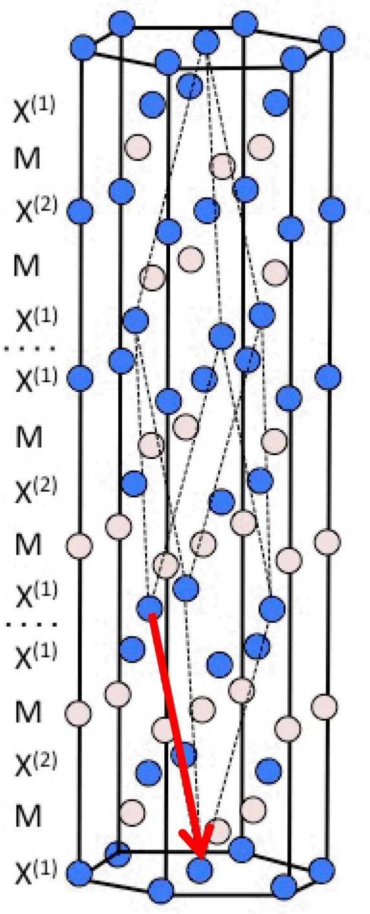
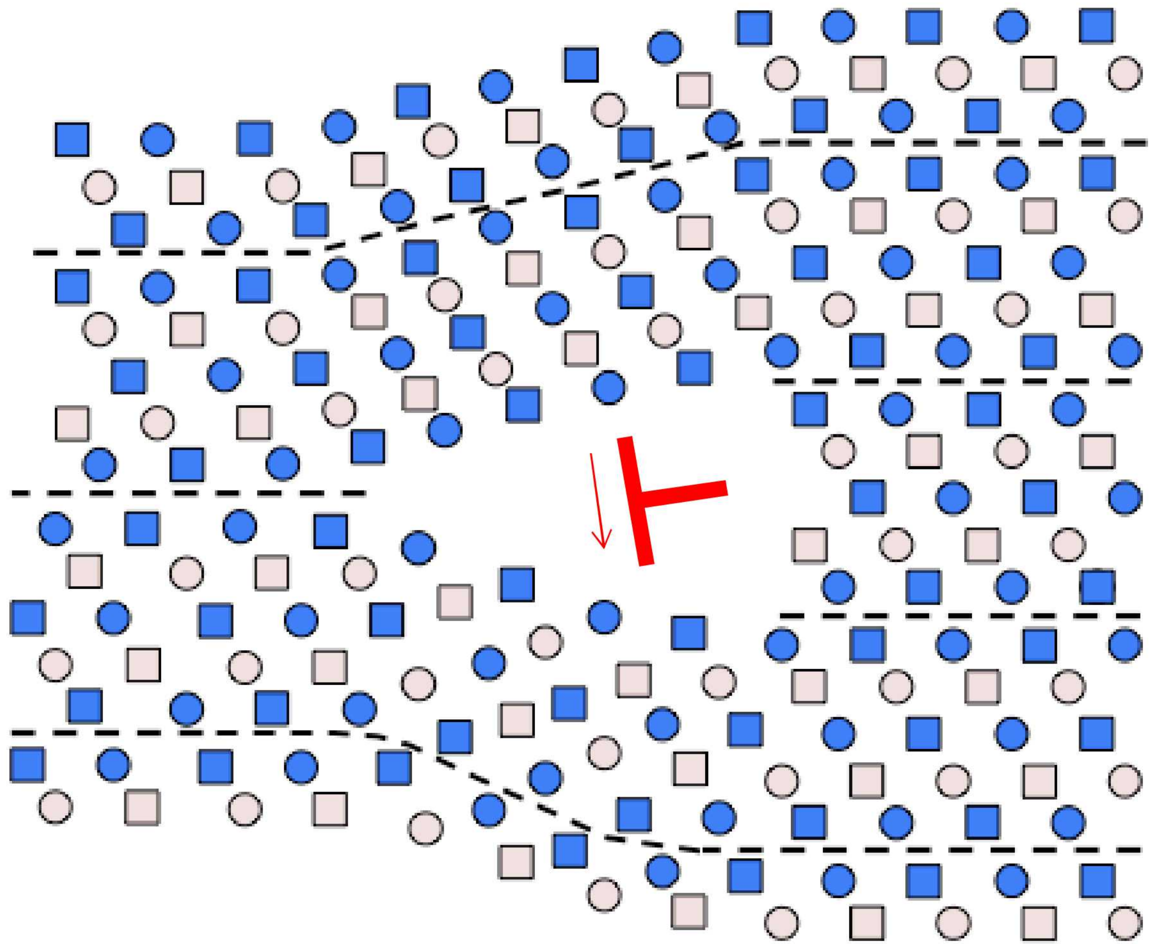
Non-basal edge dislocations:
What happens if we pull out a quintuple unit?





b = (1/3)[01-1-1)$_H$ = [00-1]$_R$

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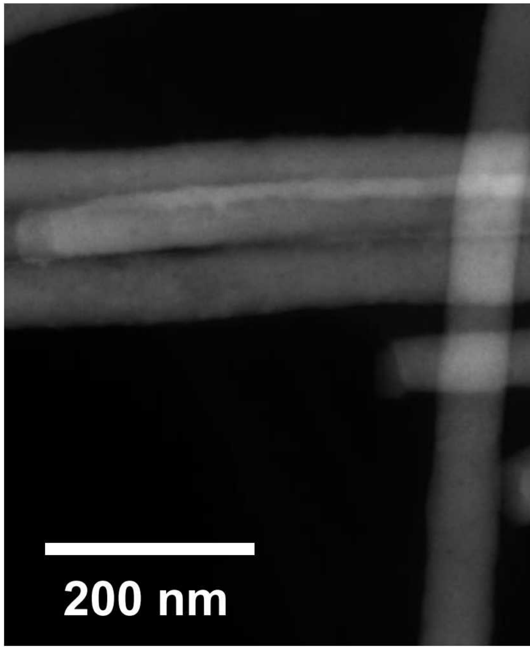
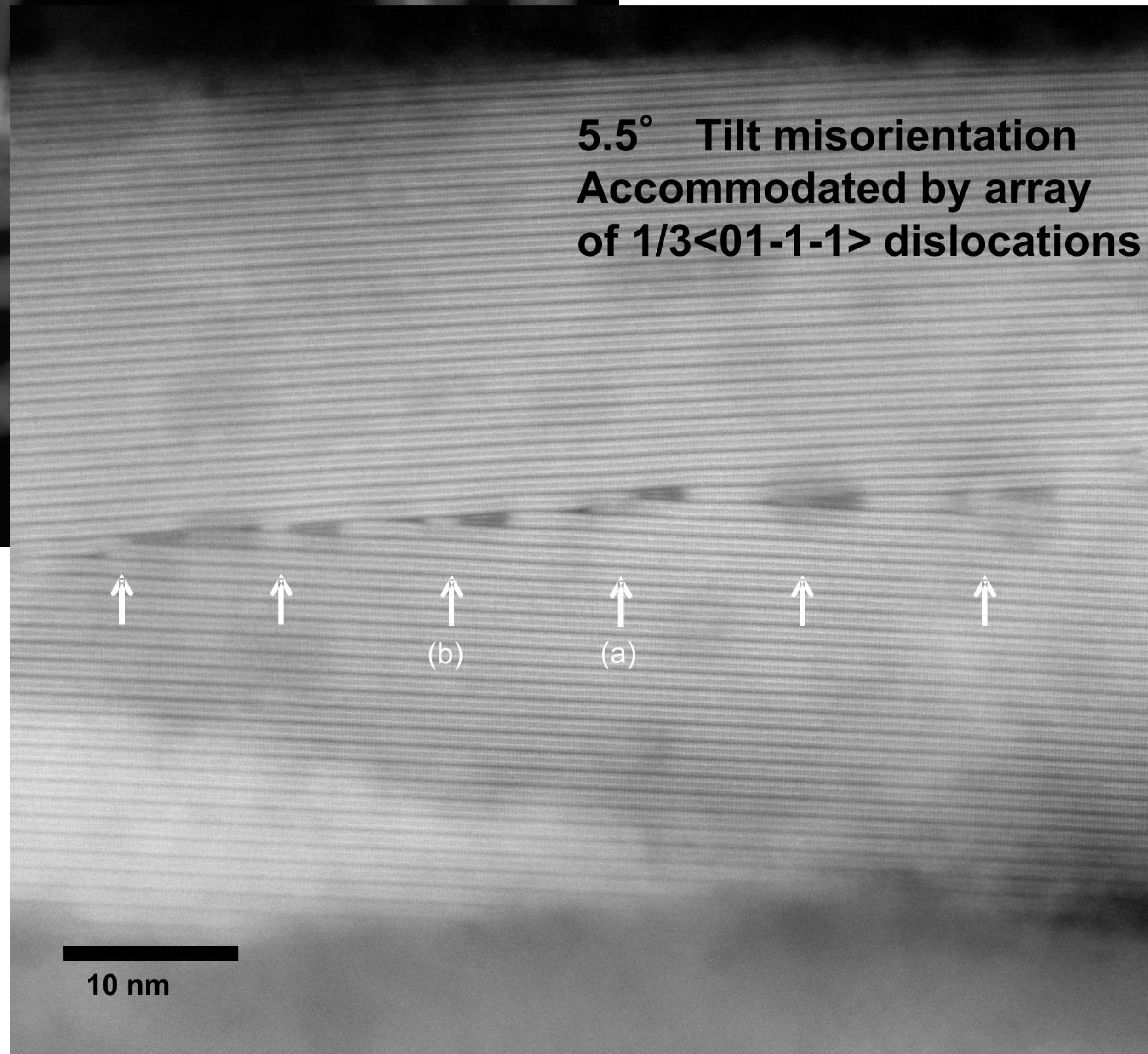
Dislocations in Bi_2Te_3 Nanowires





Wires formed by electrochemical deposition in nanoporous AAO templates.

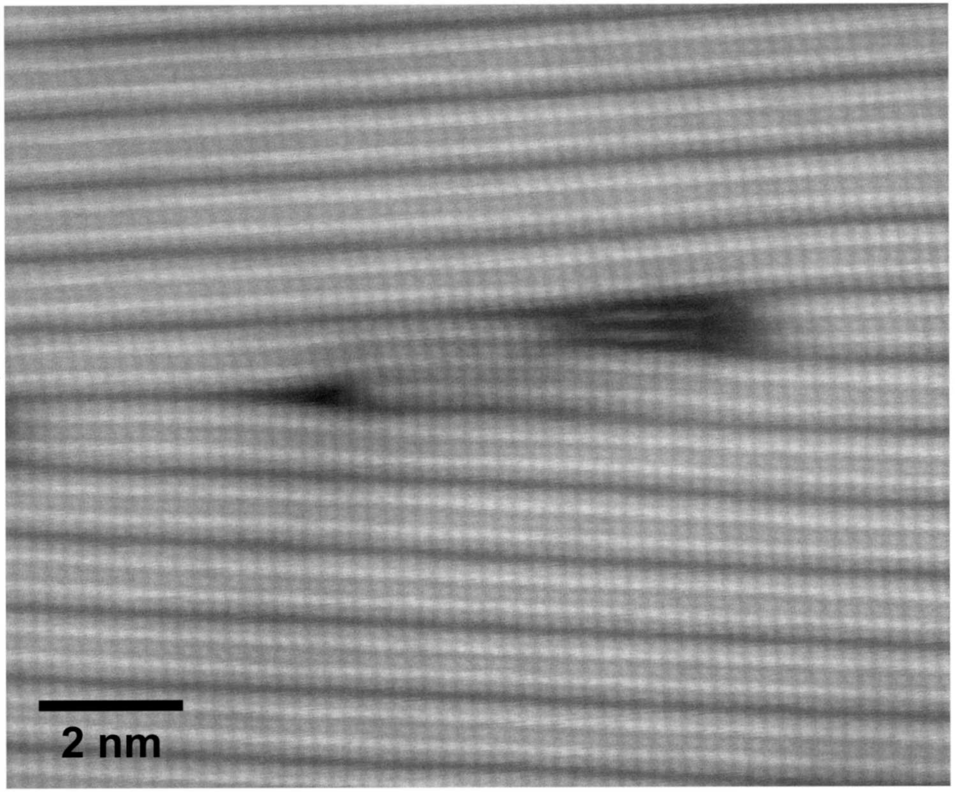
Free standing wires annealed 30 minutes at 300° C in Ar-3%H_2.

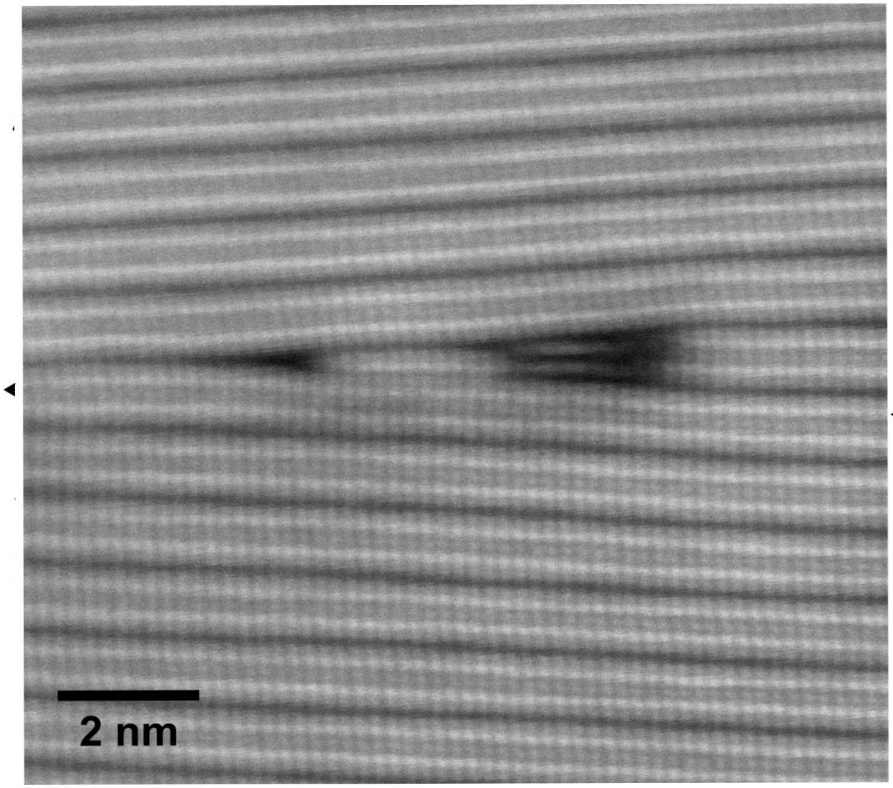
➔ Some loss of Te due to high vapor pressure

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

Laboratories

Dislocations have dissociated core: two configurations





<1 0 -1 0> Projection

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

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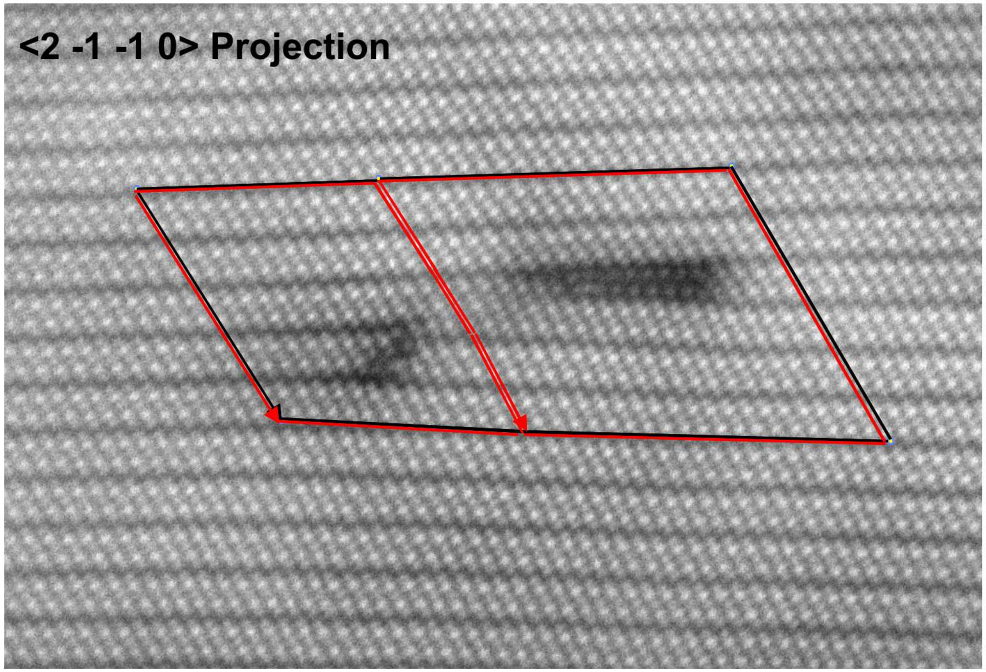
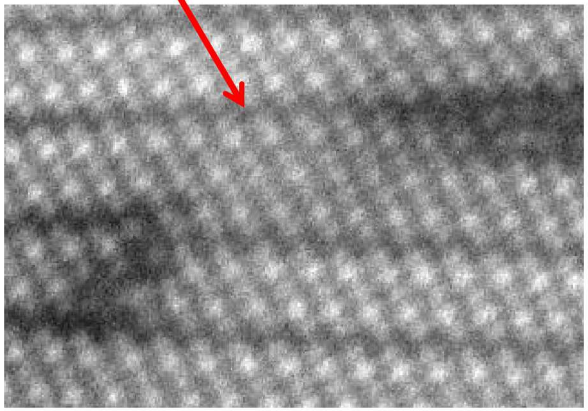
(1/3)[0 1 -1 -1] Dislocation in Bi_2Te_3:



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

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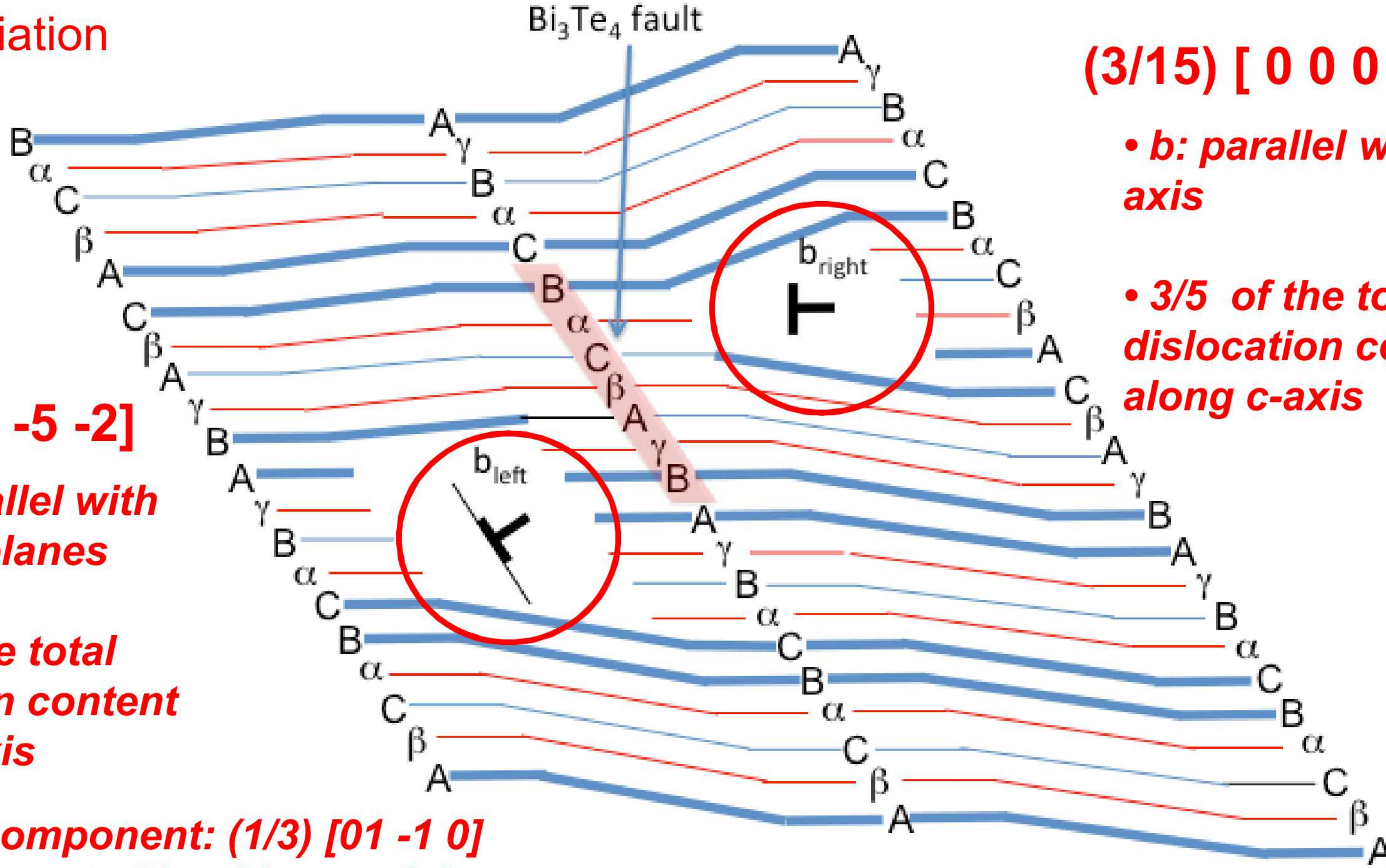
Medlin, Erickson, Limmer, Yelton, Siegal, J. Mat. Sci. 2014

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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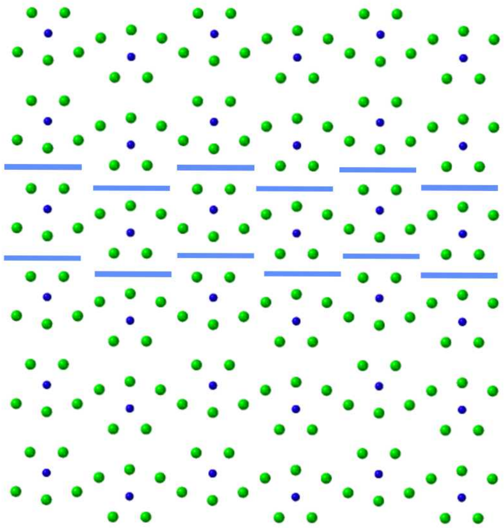
$ZrTe_5$: A complex, layered chalcogenide

Material of interest as a Dirac Semimetal

Corrugated layering structure

Orthorhombic, *Cmcm*

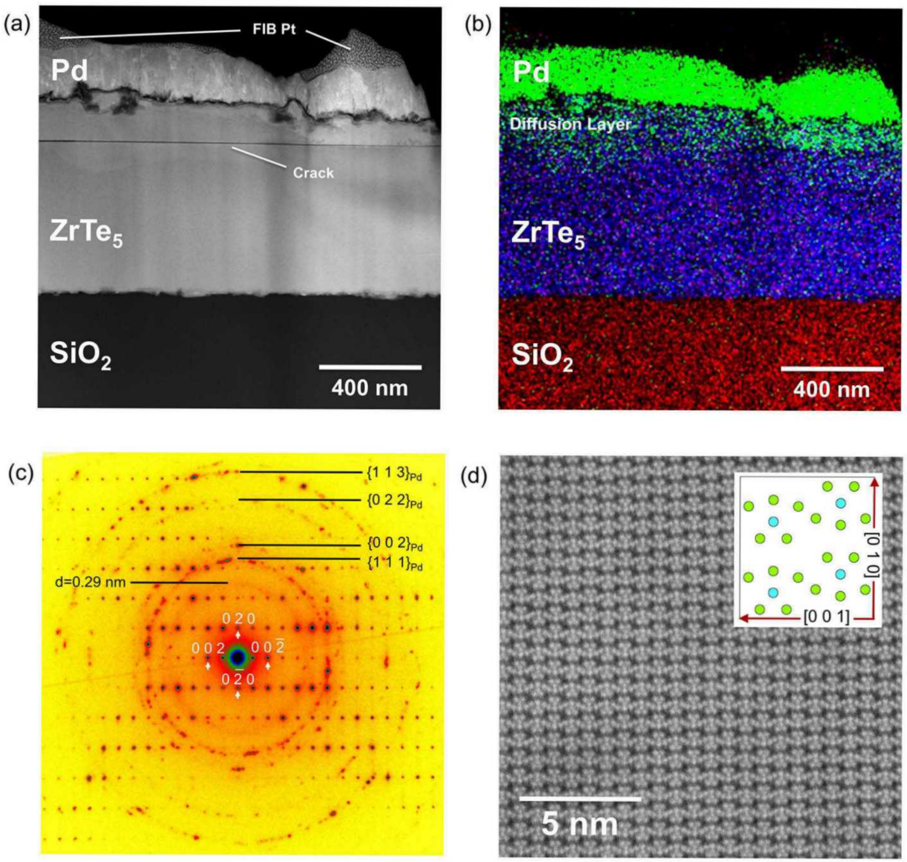


[1 0 0] projection

a=3.9875Å, b=14.530Å, c=13.724Å

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

Interdiffusion of contact metallization causes large strains



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

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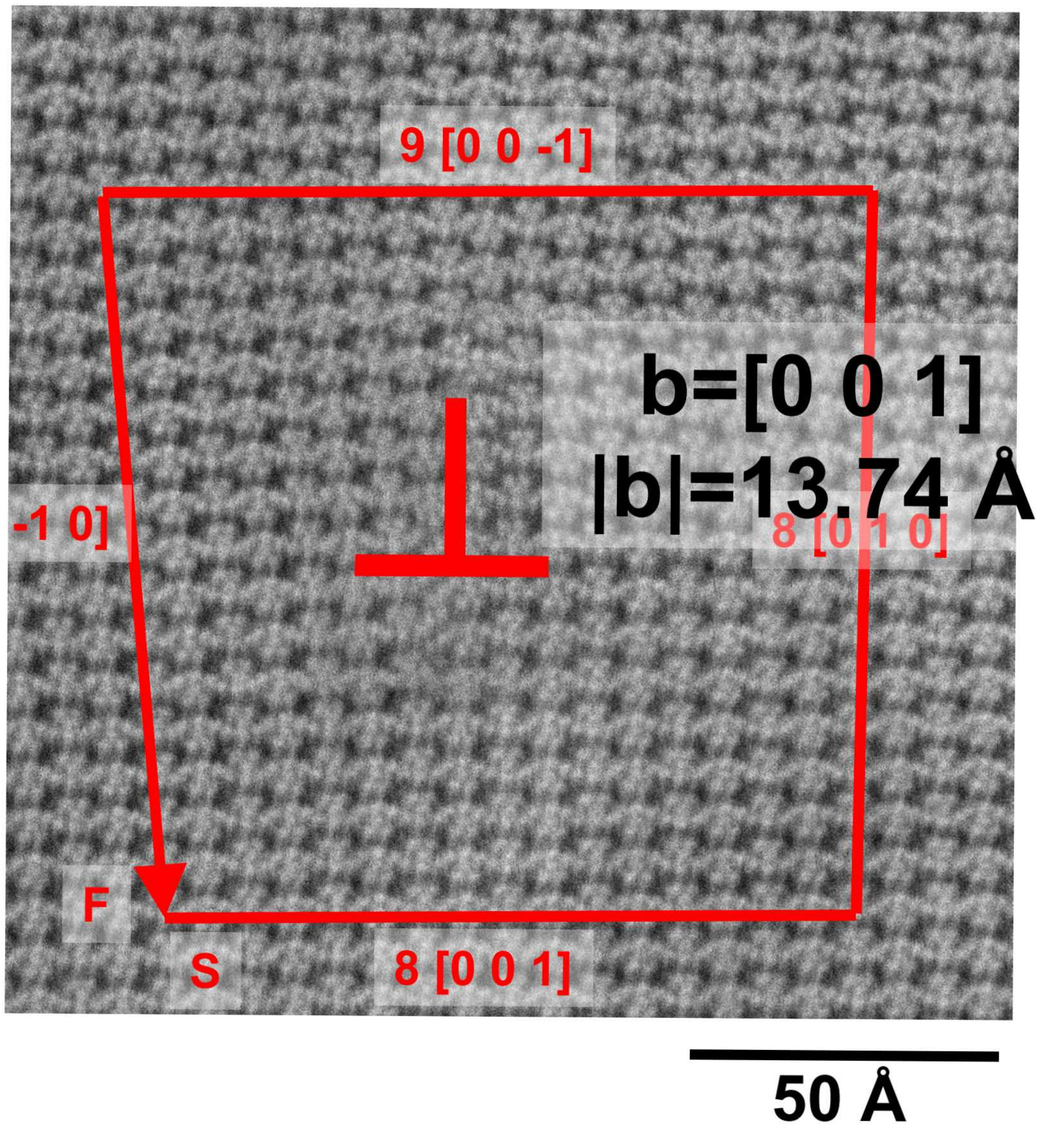
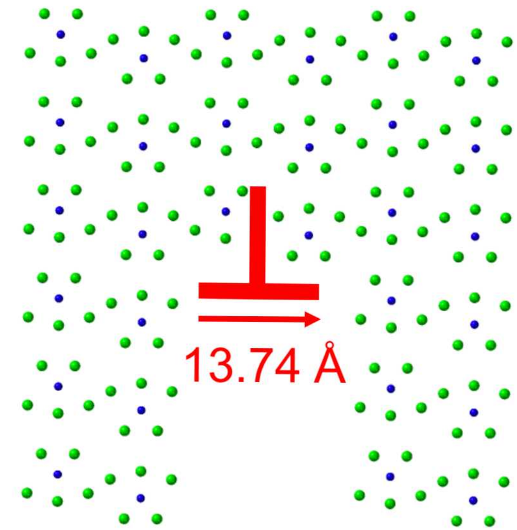
Dislocation Structure in Zirconium Telluride

HAADF-STEM



$ZrTe_5$ Crystal structure

Orthorhombic, *Cmcm*



[1 0 0] projection

a=3.9875Å, b=14.530Å, c=13.724Å

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

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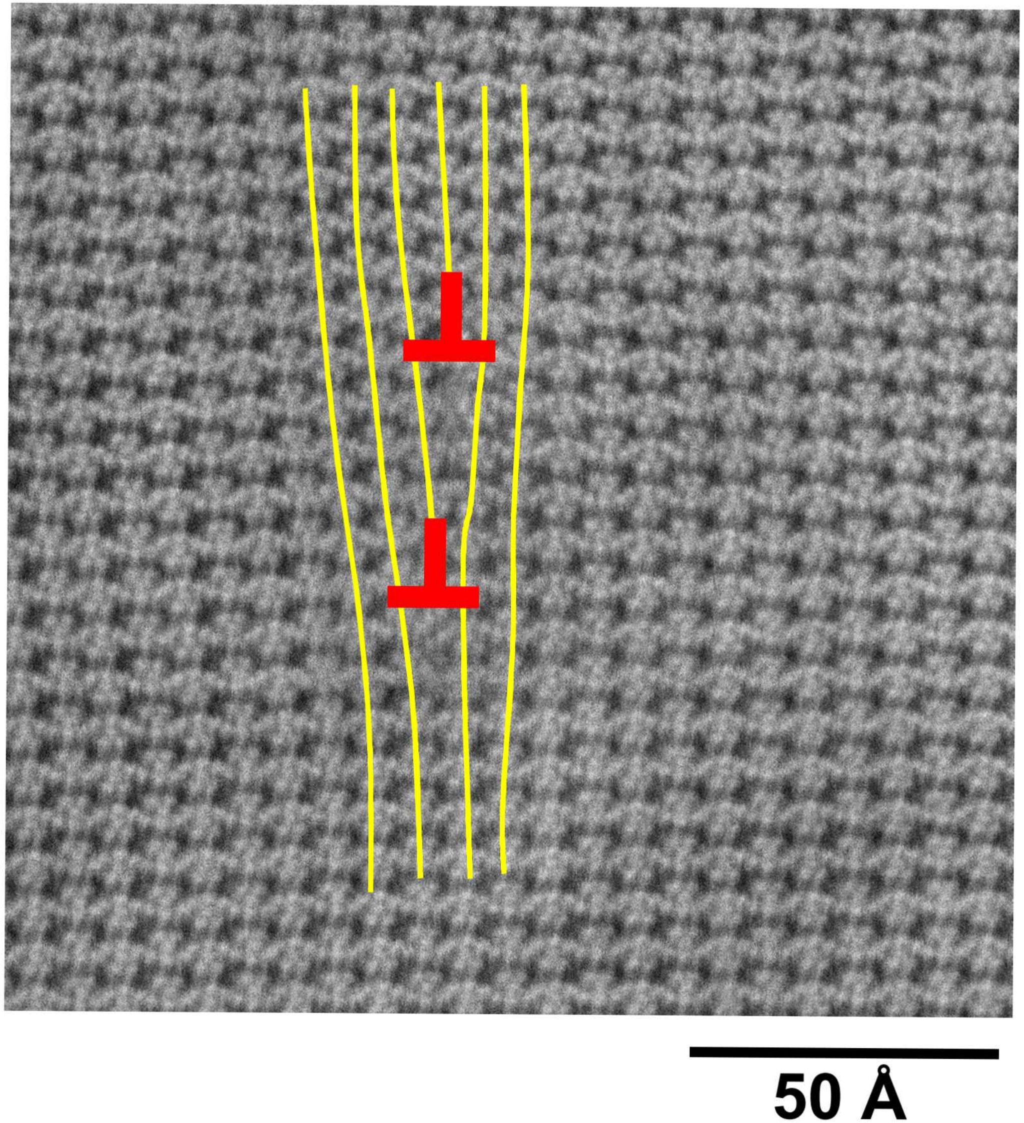
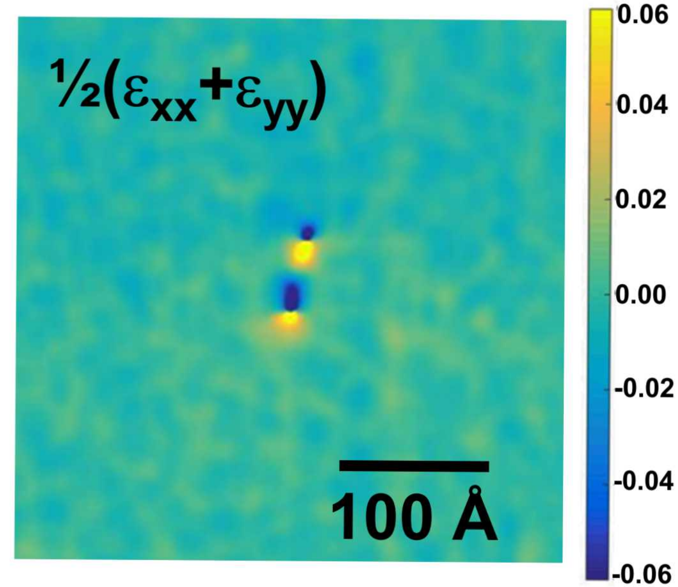
Dislocation Structure in Zirconium Telluride

HAADF-STEM



GPA Strain Map



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

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Elongation of shear strain along c-axis

HAADF-STEM | ε_{xy} (measured, GPA) | ε_{xy} (calculated, isotropic elasticity)

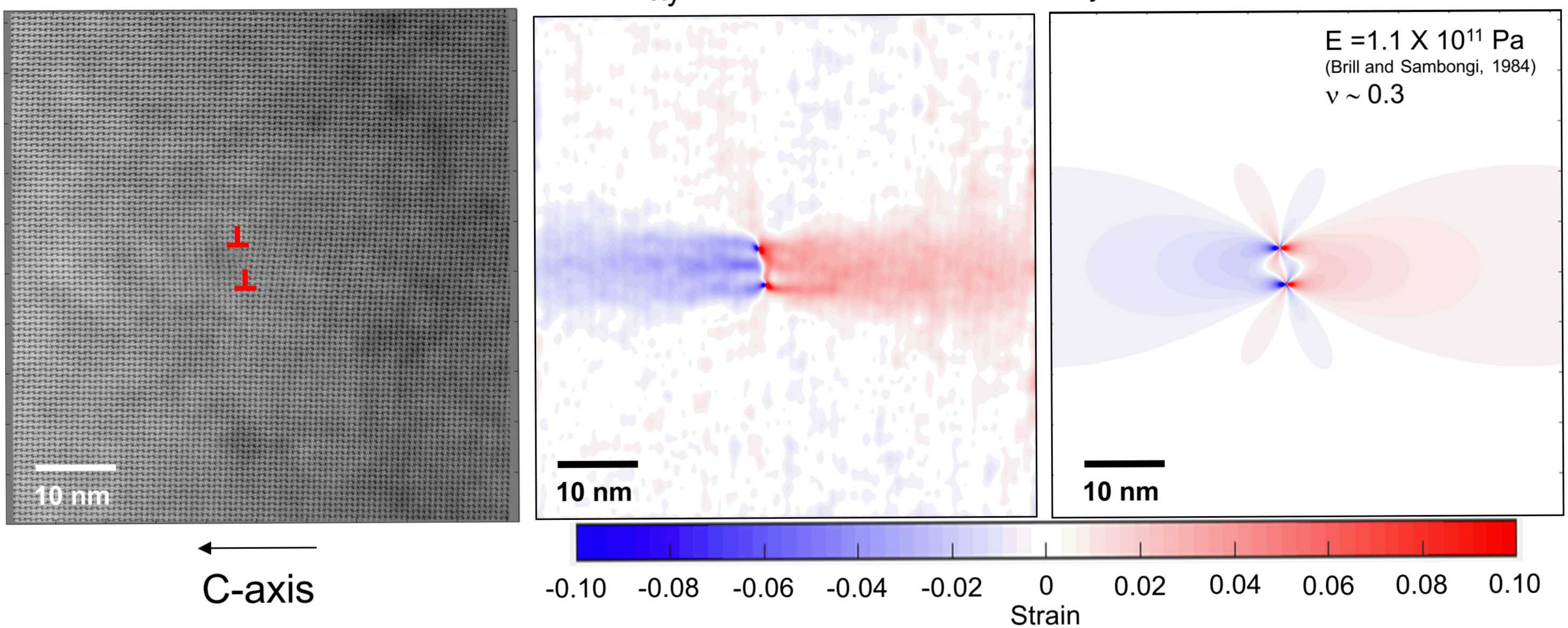
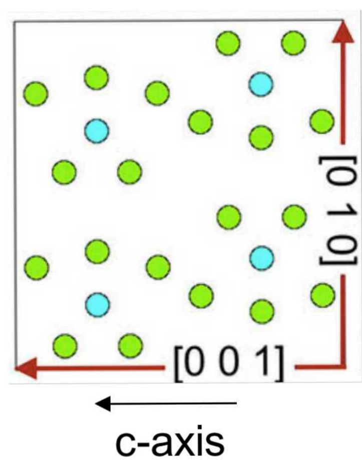


Image correction for non-linear scan distortion
C.J. Ophus, J. Ciston, C.T. Nelson, Ultramicroscopy (2016)

5 images collected at 90° scan rotation increments

GPA: Gaussian masks with σ=0.12 nm^{-1}



Measurement shows greater elongation of ε_{xy} region parallel to c-axis compared with isotropic elasticity solution.

Easier shear in direction parallel with double-tellurium layers?

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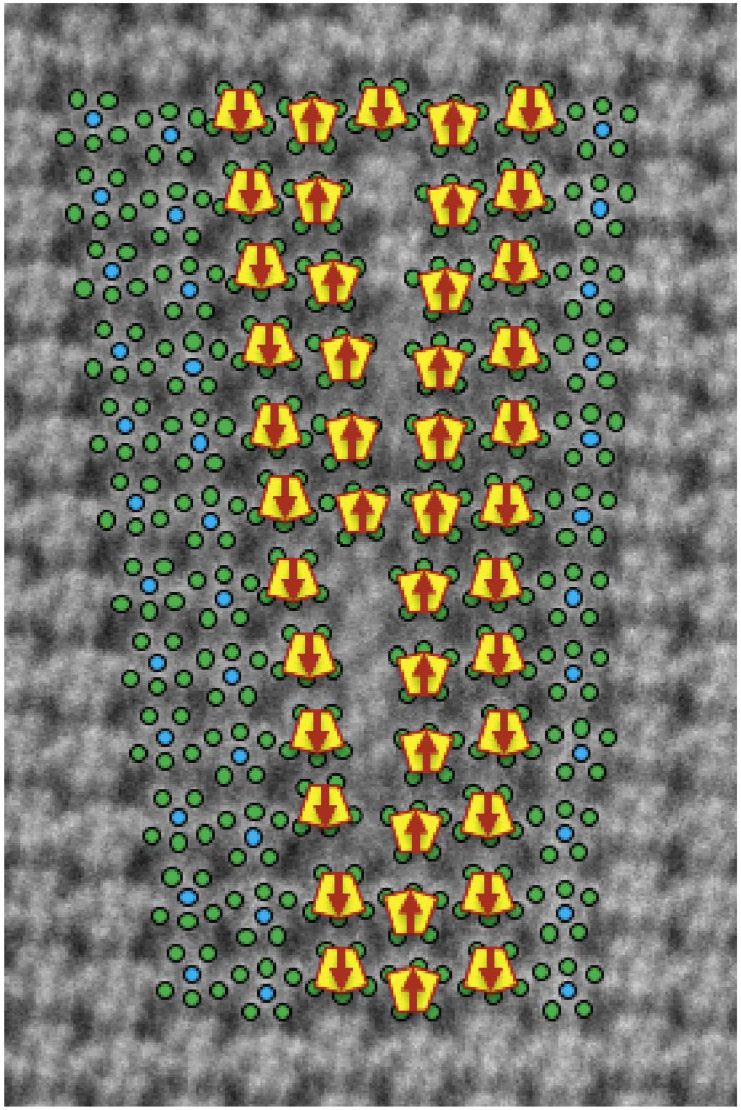
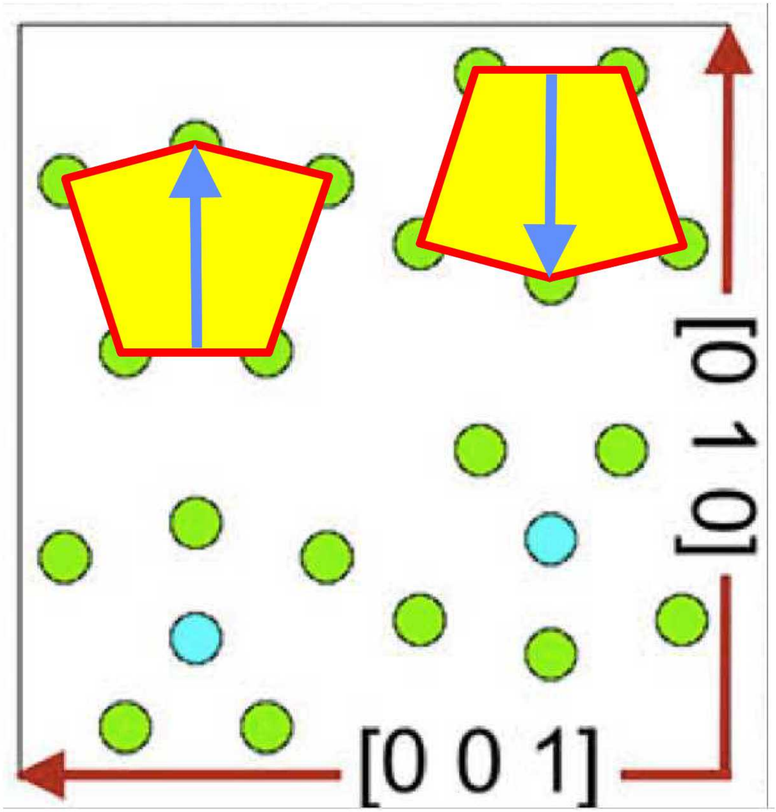
Partial dislocations separate varying transition region: no well-defined fault





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Conclusions

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

Weak, van der Waals bonding across double chalcogenide layers

Ability to accommodate non-stoichiometry through altering the layer stacking

Atomic scale microscopy is clarifying the core structure of dislocations, interfaces, and interfacial line defects

Complex, dissociated core structures observed in Bi_2Te_3 and $ZrTe_5$

Theoretical treatments for transport behavior at such defects should not neglect the possibility for such dissociation.

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