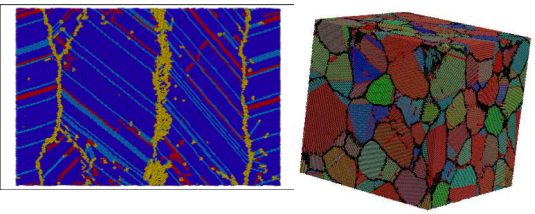
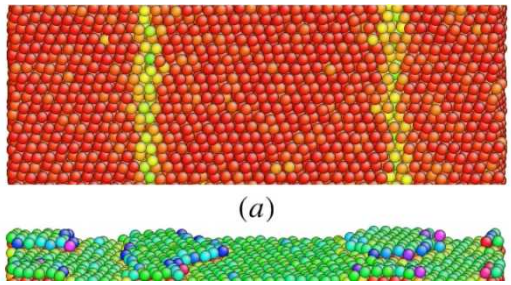
SAND2016-3770PE

# Simulating Grain Boundaries at the Atomic Scale:

## *More Complicated Than You Think*






Stephen M. Foiles
Computational Materials & Data Science
Sandia National Laboratories
Albuquerque, NM

Sandia National Laboratories

*Exceptional service in the national interest*

U.S. DEPARTMENT OF ENERGY

NNSA National Nuclear Security Administration

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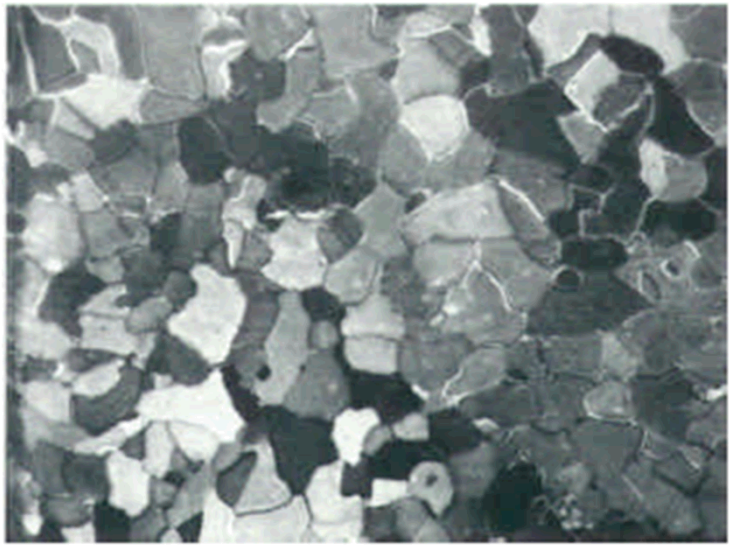
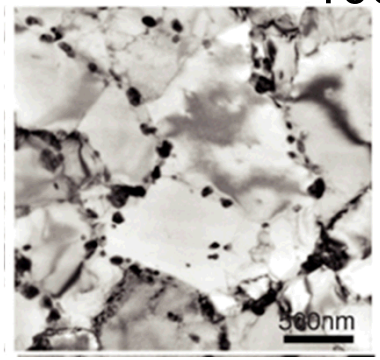
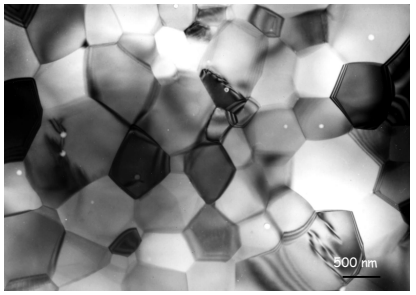
# Why does anyone care about grain growth?

- Grain-level microstructure strongly influences a wide range of materials properties
  - Strength
    - Hall-Petch relationship: $\sigma_y = \sigma_0 + \frac{k_y}{\sqrt{d}}$
  - Toughness and Fracture
  - Corrosion resistance
  - Electrical conductivity
  - Magnetic susceptibility
  - …
- *Controlling the microstructure and relating the microstructure to properties are central problems in materials science.*



1000 μm



# Evolution of grain microstructure is a highly complex multi-scale modeling problem

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- Atomic-scale
  - Boundary properties are determined by atomic-scale structure and dynamics
    - Energy – changes in *atomic-level* bonding/coordination in the boundary
    - Motion – local *atomic-level* rearrangements at the boundary
  - Time-scale: picoseconds – nanoseconds
- Meso-scale
  - Grain sizes: ~10 nanometers - ~100 micrometers
  - Need to consider the 3-D network of grain boundaries
  - Time-scale: seconds to hours
- Conventional strategy
  - Determine the properties of grain boundaries with atomic-scale methods
  - Evolve the grain structure with meso-scale simulations that incorporate the boundary properties – energy, mobility

# What is the big deal about determining grain boundary properties?

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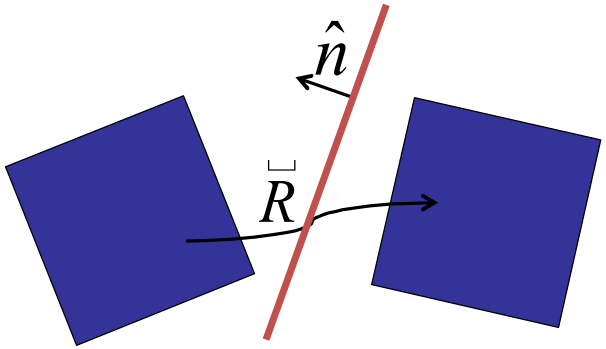
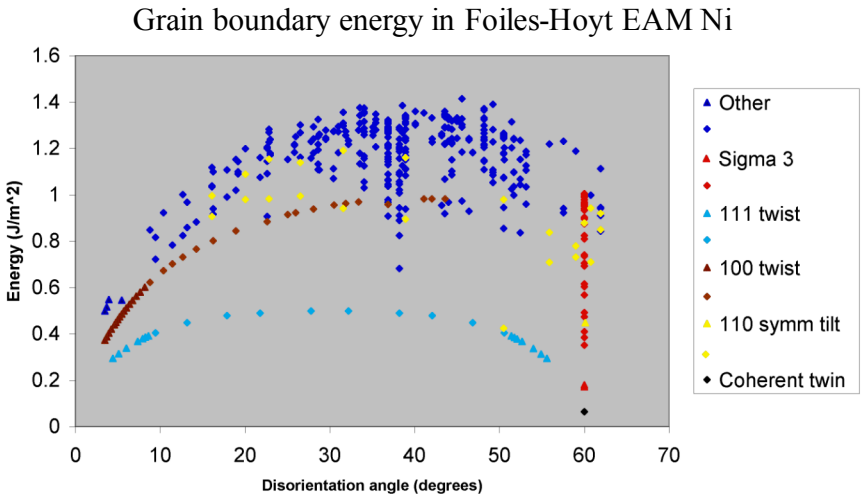
- *"We hold these truths to be self-evident, that all grain boundaries are **NOT** created equal, …"* - apologies to Thomas Jefferson
  - There is a **5-dimensional** space of macroscopic grain boundary structure
  - The properties vary throughout this 5-D space in an, at best, partially understood manner
  - And this does ***NOT*** even consider the effects of temperature, alloying, impurities, second phases, applied stress, …
  - For a given macroscopic configuration, multiple microscopic (atomic-level) grain boundary structures may be present in equilibrium

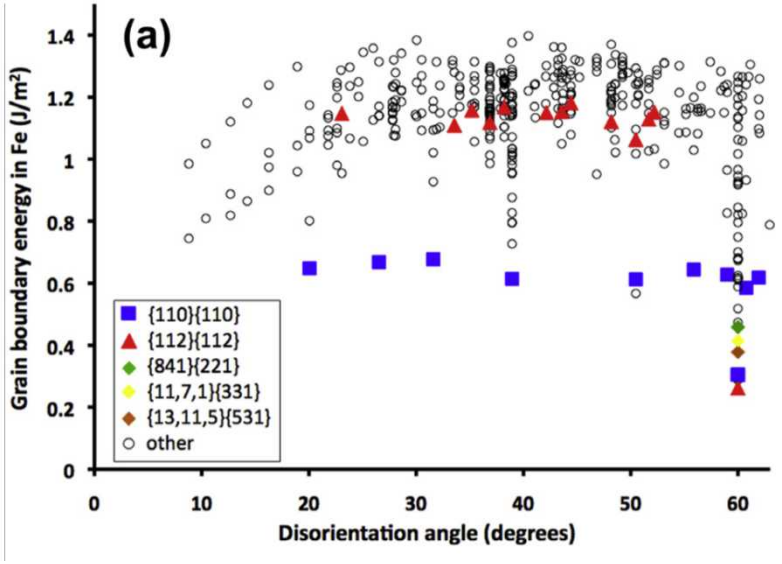


# Grain Boundary Properties have been computed for large catalogs of elemental boundaries




- Energy variations computed for boundaries in FCC metals
  - Olmsted, Foiles, & Holm, Acta Mater 57, 3694 (2009)
- Numerical parameterization of these energies has been developed
  - Bulatov, Reed & Kumar, Acta Mater 65, 161 (2014)

- Similar data has been generated for BCC metals
  - Ratanaphan, Olmsted, Bulatov, Holm, Rollett & Rohrer, Acta Mater 88, 346 (2015)



# Overview of atomistic simulation methods: *'Twitterverse' Version*

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- Representation of energy/forces in terms of atomic positions
  - Better: Computed from *approximate* solution of quantum mechanics of the electron ground state (ie. "DFT")
  - Typical: Interatomic potential
    - Reduced Order Model of the Born-Oppenheimer Surface
- Energy minimization (Molecular Statics)
  - Optimize atomic positions to find an energy minimum
    - *Hopefully*, global minimum but often use local minimization methods
- Molecular Dynamics
  - Follow classical Newtonian trajectory of atoms – "$F = ma$"
  - Let the atoms *"do what they want"* subject to imposed boundaries
- Equilibrium Monte Carlo
  - Adjust atomic arrangements to sample a thermodynamic ensemble

# Molecular Dynamics:

## *What could possibly go wrong?*

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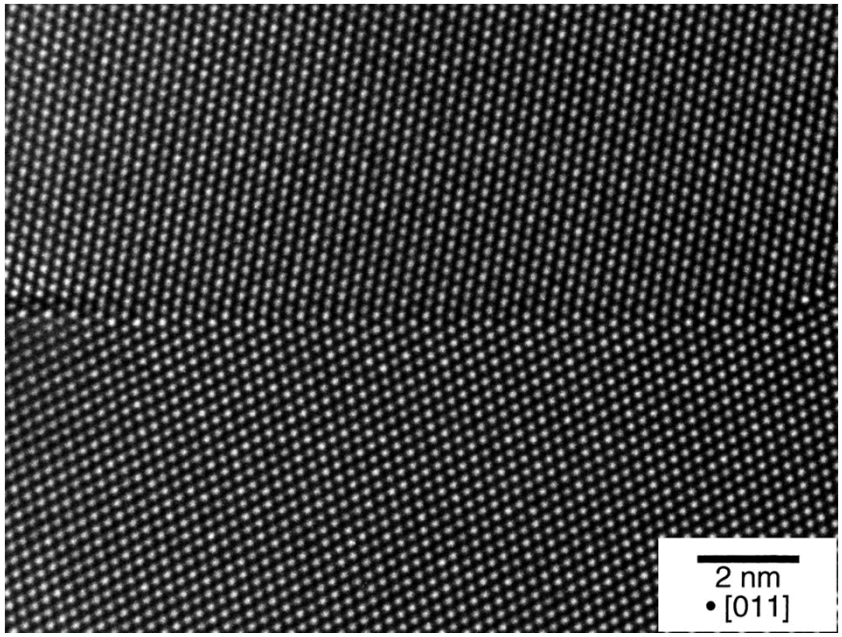
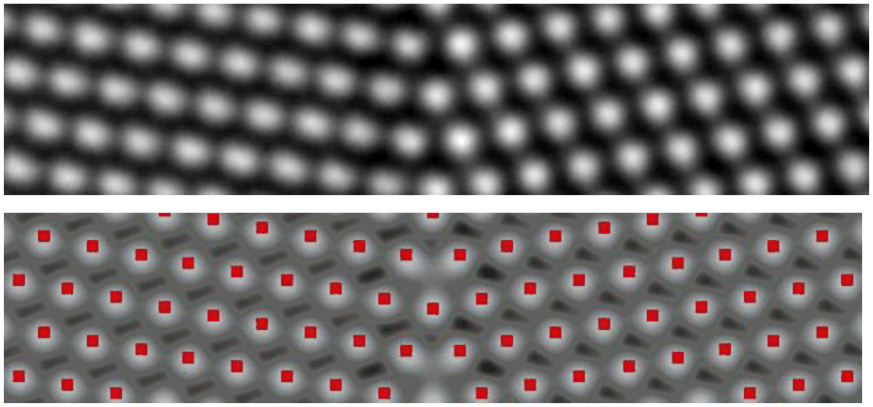
- Deviations from Born-Oppenheimer Approximation
  - Highly dynamic events, charge states, …
- Inadequate Interatomic Potentials
  - Imperfect knowledge of Born-Oppenheimer surface
    - Errors in experimental data
    - Deficiencies of *ab initio* database
  - Assumed potential form – model form error
  - Transferability or lack thereof
- Quantum Mechanical Effects
  - Zero-point energies of light elements
  - Debye Temperature often above room temperature

- Limited time scales
  - High rates and high driving forces
  - Infrequent events
  - Sampling errors - ,metastable states
- Structural approximations
  - Where are the atoms, *really*?
  - Simplification of geometries
  - Boundary conditions
- Multi-component systems
  - Composition and structure coupled
  - Compositional variation - equilibrium or kinetic?
- Information extraction for higher-scale models
  - Millions of coordinates -> ‘Physics’
  - Identification of dominant effects

# MD can reproduce structure of high-symmetry boundaries in Al




- High-resolution TEM of Σ11(1 1 3)/[-1 1 0] boundary in Al



- Top: close-up of boundary
- Bottom: Simulated TEM image based on computed structure using EAM potential for Al
  - Red dots show column positions



King, Campbell, Foiles, Cohen & Hanson, J. of Microscopy 190, 131 (1998)

# *"Great, kid! Don't get cocky!"* – Han Solo

## Boundaries in non-FCC metals are harder to predict

- Central transition metals have partially filled d-bands
  - d-band bonding has an angular character reflecting d-orbital symmetry
  - The trends in equilibrium structures of central transition metals can be rationalized in terms of these interactions
    - David Pettifor's structure maps
- Commonly used potential forms like EAM and Finnis-Sinclair do ***NOT*** incorporate angular dependence
- *Potentials with and without angular terms predict different structures!*

71° [10], which is the nearest-neighbor bond angle in the bcc structure. Model 2 contains a significant number of right angles at the boundary, whereas the other two models do not.

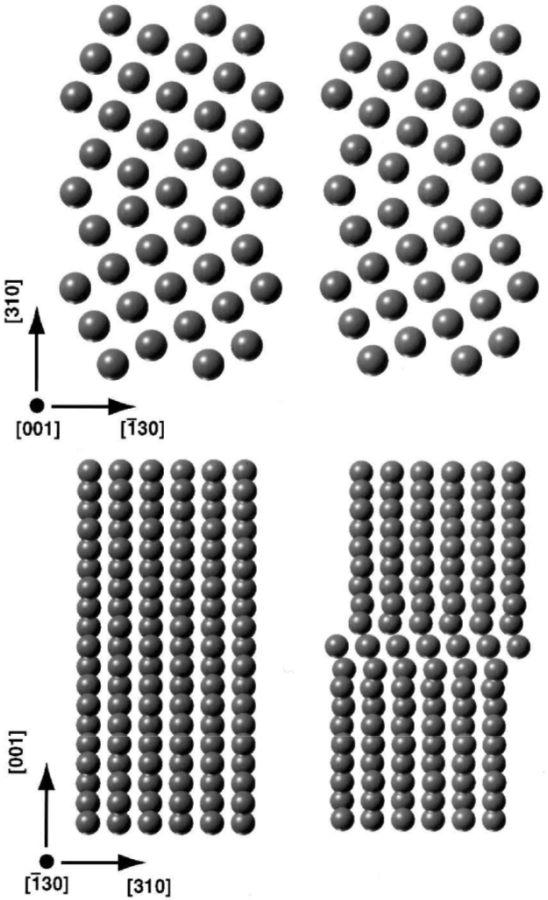
Grain boundaries forming (310) twins in Nb were prepared by diffusion bonding two precisely oriented, to within ±0.1°, Nb single crystals with flat polished (310) surfaces which were misoriented by 180° about [310] rel-

Predicted structures for (310) twin in Nb



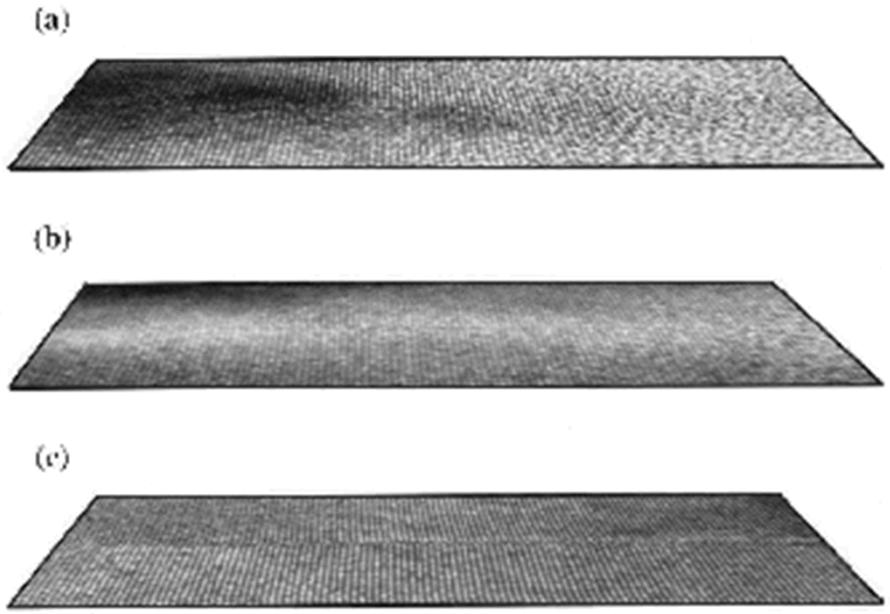
Campbell, Foiles, Gumbsch, Rühle, King, Phys. Rev. Lett. 70, 449 (1993)

# With *sufficiently accurate potentials* the right structures are predicted




Nb Mo, Ta

MGPT predictions




Nb

Mo

Ta

- Modified Generalized Pseudopotential Theory (MGPT) qualitatively predicts which elements possess a shift along tilt axis
  - EAM and FS potentials fail this test



Campbell, Kumar, King, Belak, Moriarty & Foiles, Phil. Mag. A 82, 1573 (2002)

# Cu in Al – bulk substitutional alloy

*Just replace Al by Cu near the boundary, right?*

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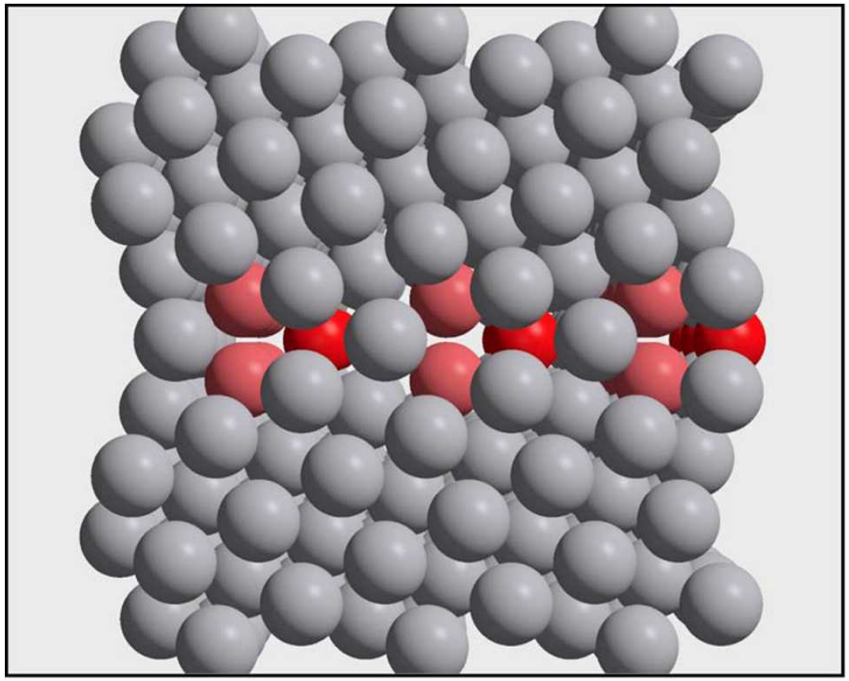
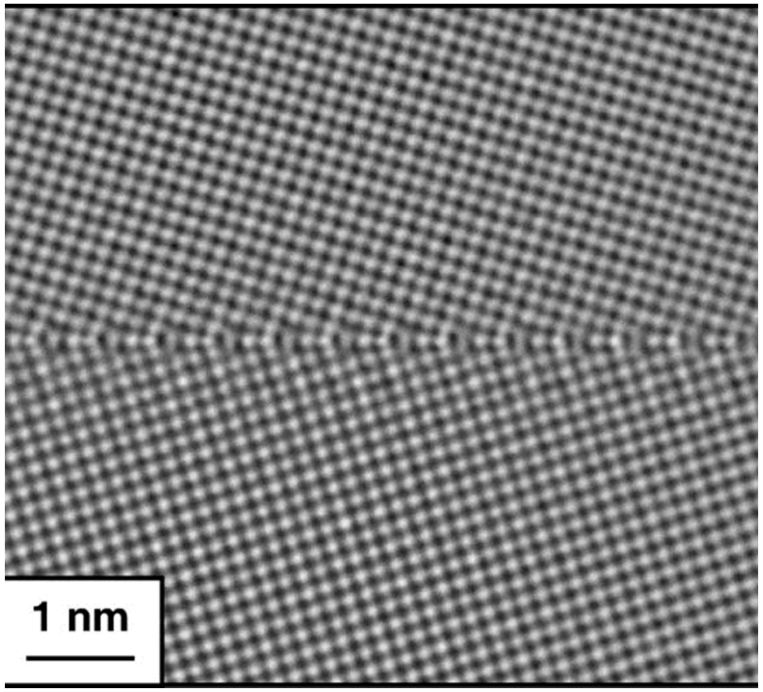


DFT predicted substitutional energies for Cu near Al Σ5 (310)/[001]




HRTEM shows a 3-atom repeat along boundary as opposed to 2-atom repeat in calculations



Campbell, Plitzko, King, Foiles, Kisielowski, Duscher, Interface Science 12, 165 (2004)

# Cu is substitutional in bulk Al
## *but interstitial at this boundary*

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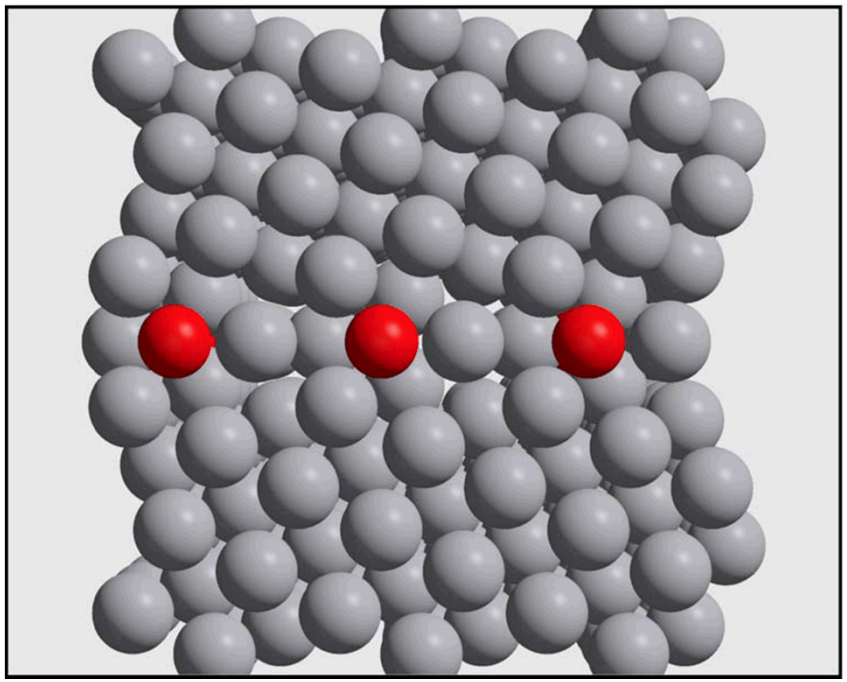
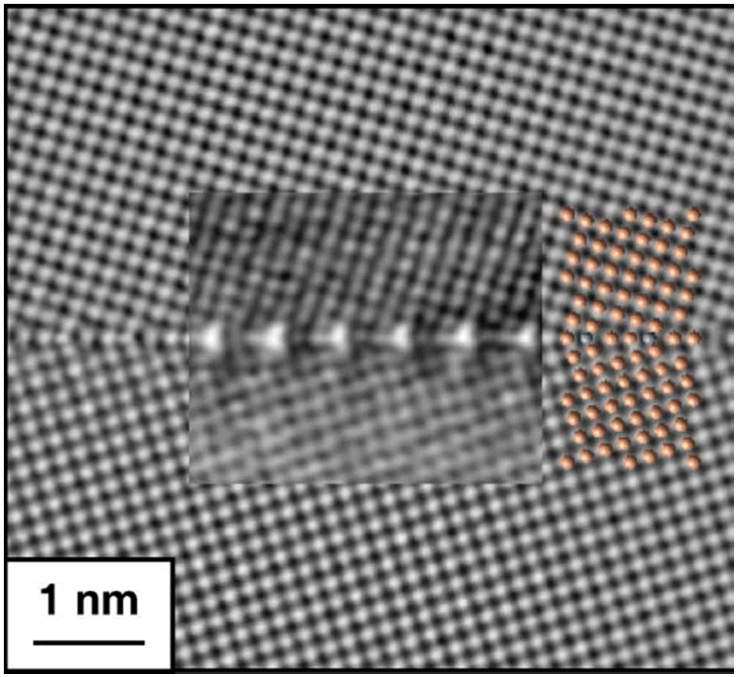


DFT predicts that the segregation to the interstitial site is stronger than to substitutional sites



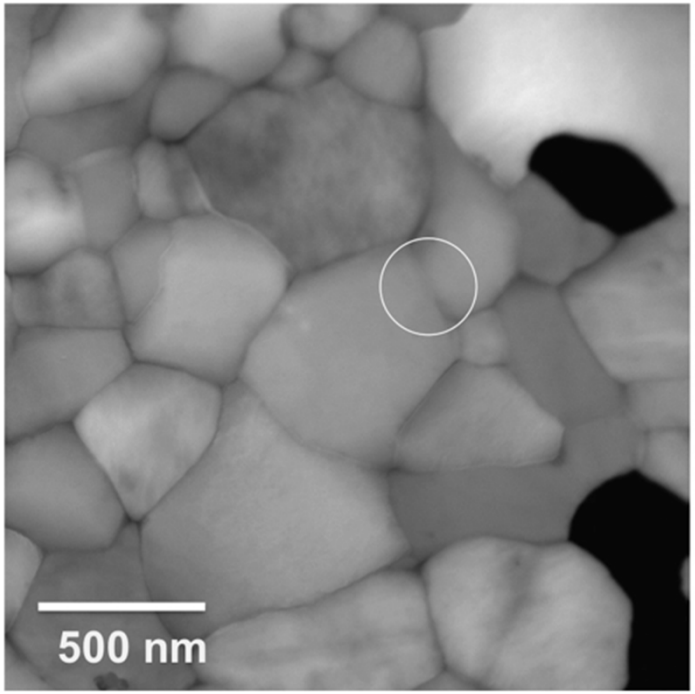

Interstititial Cu agrees with the HRTEM image

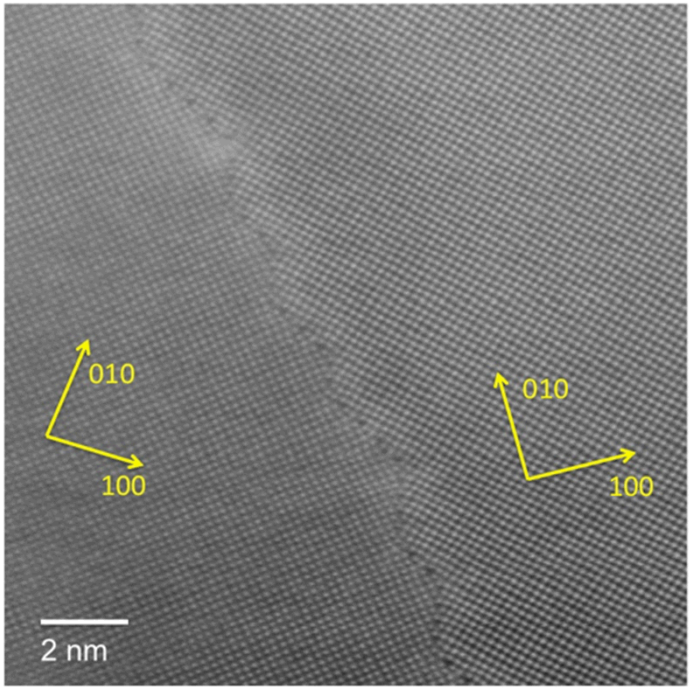
***Be careful where you assume the atoms are!***



Campbell, Plitzko, King, Foiles, Kisielowski, Duscher, Interface Science 12, 165 (2004)

# Faceting of Σ5 grain boundary in Fe



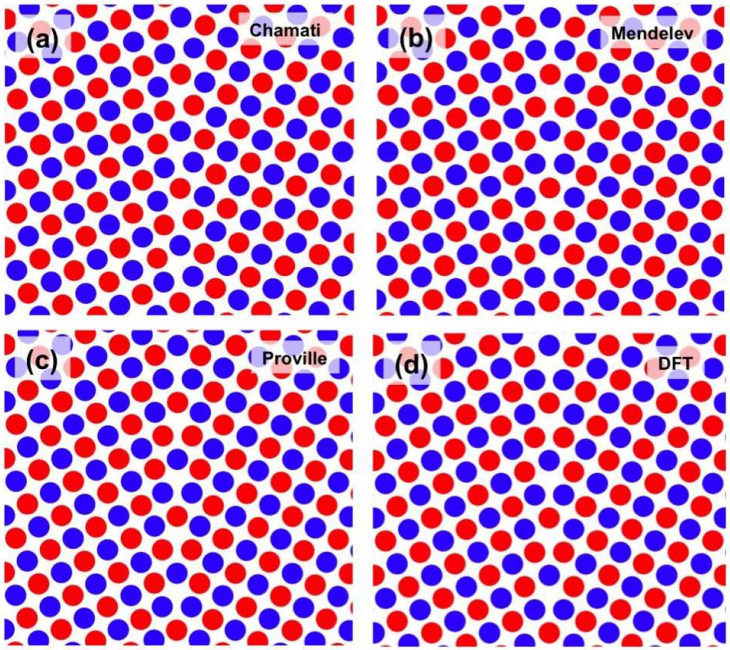




HAADF-STEM images of Fe film

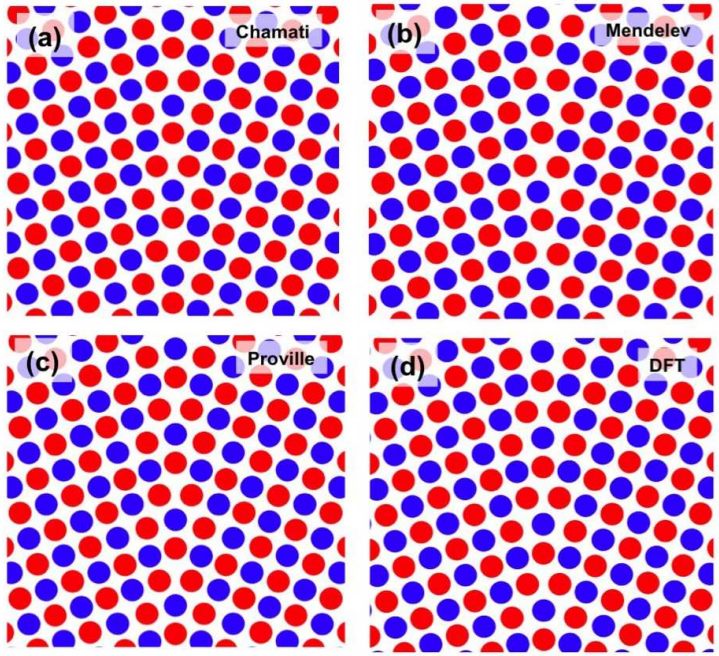
- Overall grain structure
- Atomic resolution detail of the Σ5 boundary

# Faceting of Σ5 grain boundary in Fe: Atomistic prediction for facet geometries

{310} facets




{210} facets




- Subtle differences between structures computed with different empirical potentials
  - Frames (a) - (c)
- DFT (approximate quantum mechanical calculations) are in frame (d)

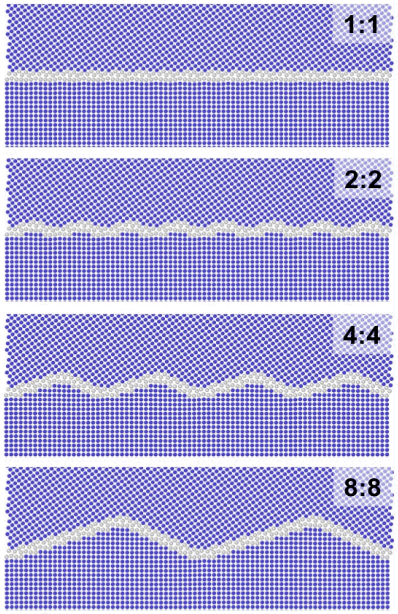


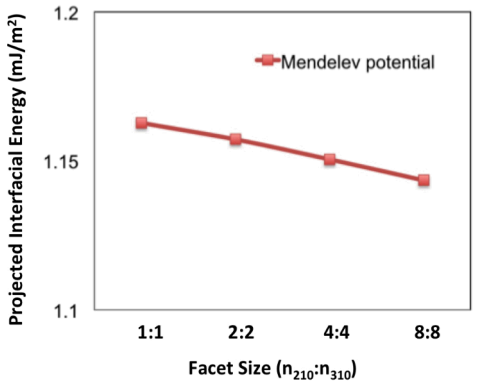
Medlin, Hattar, Zimmerman, Abdeljawad, Foiles, in preparation for Acta Materialia

# Faceting of Σ5 grain boundary in Fe: Atomistic prediction for facet length

Equilibrium facet size depends on

- Energies of facet planes
  - Variation of boundary energy with boundary plane orientation
- Junction energies
- Elastic interactions between junctions
  - Junctions have dislocation-like strain fields



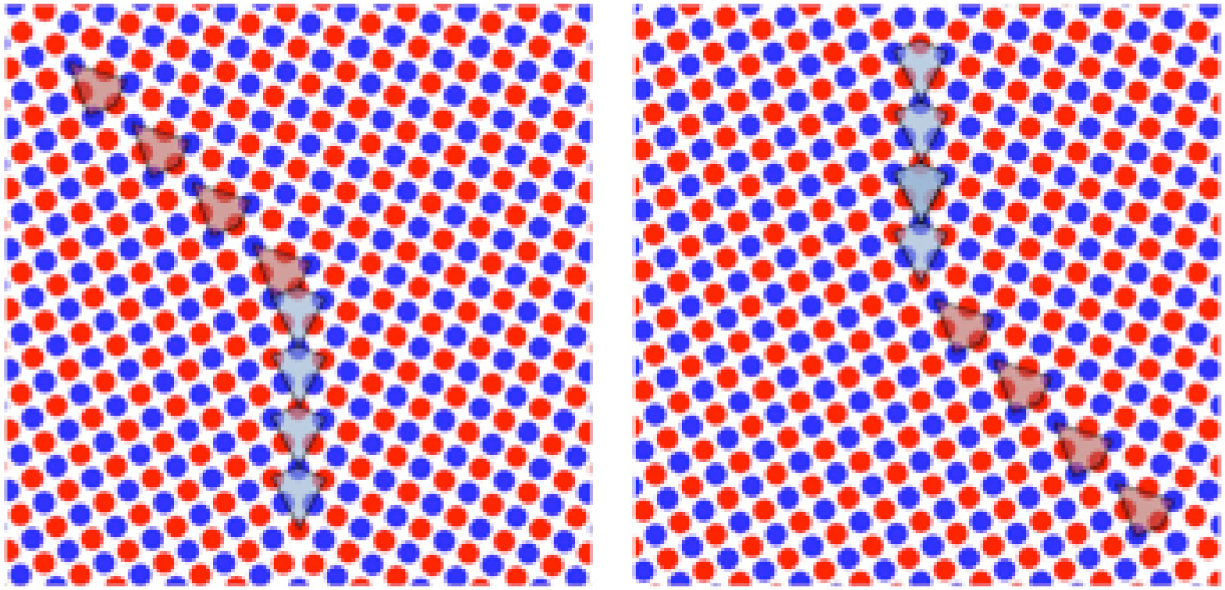




**Computed energies using empirical potentials predict that facets should grow arbitrarily large**



Medlin, Hattar, Zimmerman, Abdeljawad, Foiles, in preparation for Acta Materialia

# Faceting of Σ5 grain boundary in Fe: Atomistic prediction for junction geometry



- Predicted structures of the junctions based on simulation of boundary using an empirical potential (Mendelev)
- Computed junction structure consistent with DFT calculations for Σ5 (710) boundary which contains both of these junctions

# Do Calculations and Experiment Agree?

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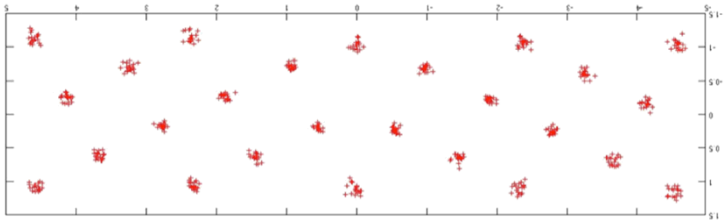
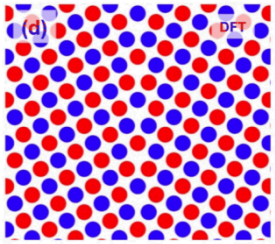
Structures of individual facets ***OK***






Equilibrium Facet Length ***WRONG***

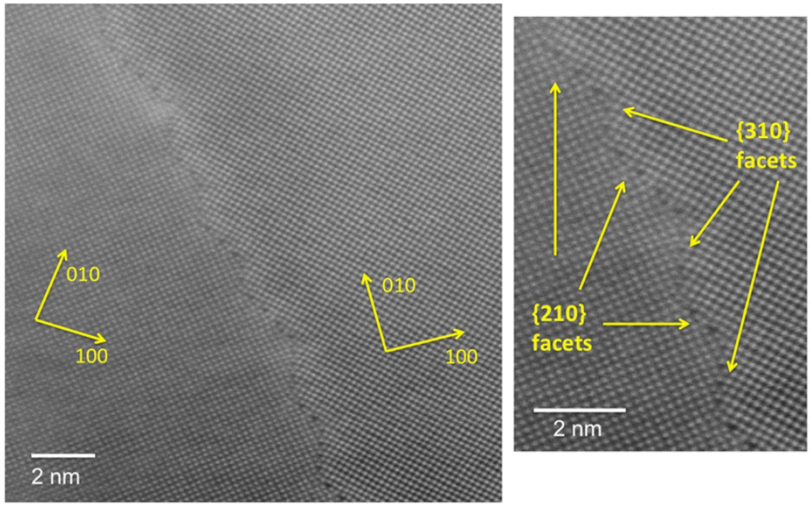
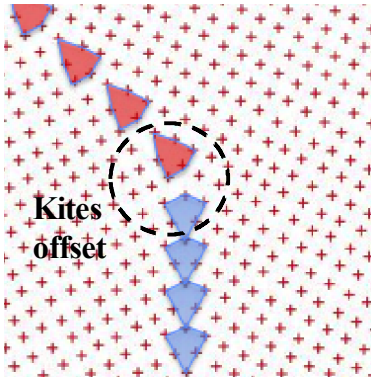


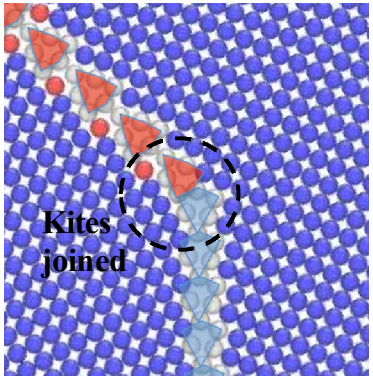

Figure 3

Junction Structure ***WRONG***

**Experimental Junctions b=(1/5)(120) and (1/5)(310)**




**Relaxed Periodic Atomistic Structure**

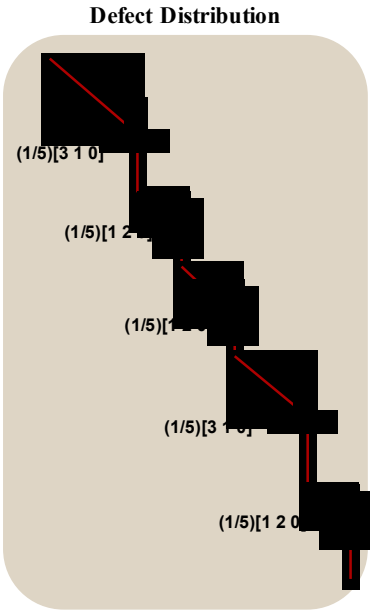


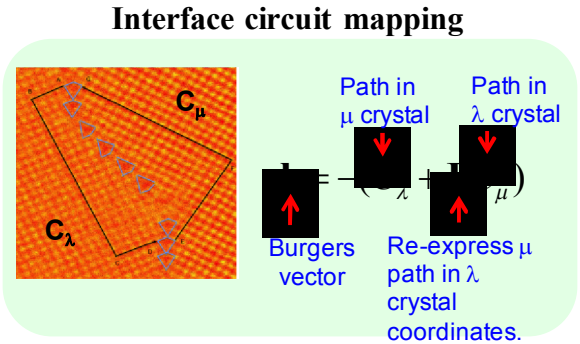


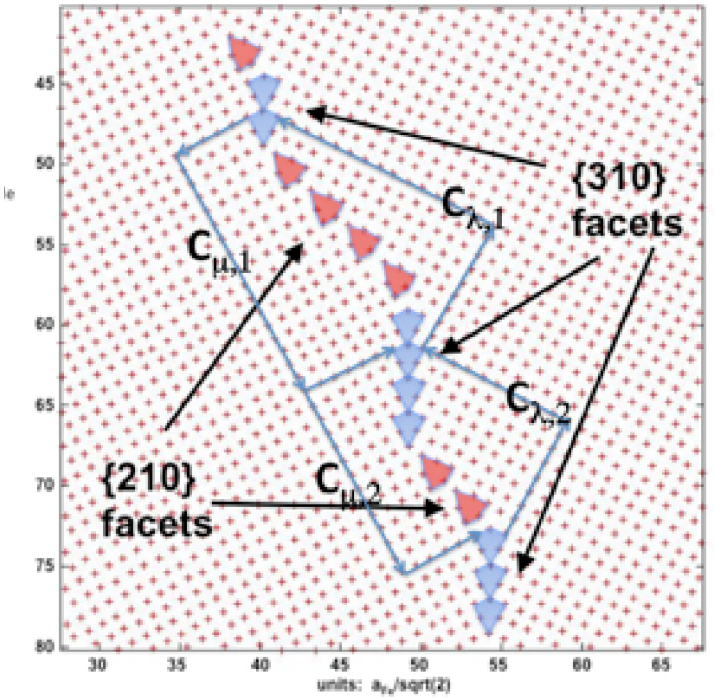

Medlin, Hattar, Zimmerman, Abdeljawad, Foiles, in preparation for Acta Materialia

# What went wrong!?!

- Simulations are Experiment are for ***DIFFERENT STRUCTURES***
  - Simulation: ***Ideal*** Σ5 misorientation
  - Experiment: ***Real-world*** Σ5 misorientation
    - $\Delta\Theta = 2.4 \pm 0.8$




Interfacial dislocations required by Frank-Bilby equation

# Secondary grain boundary dislocations convert computed junction to observed

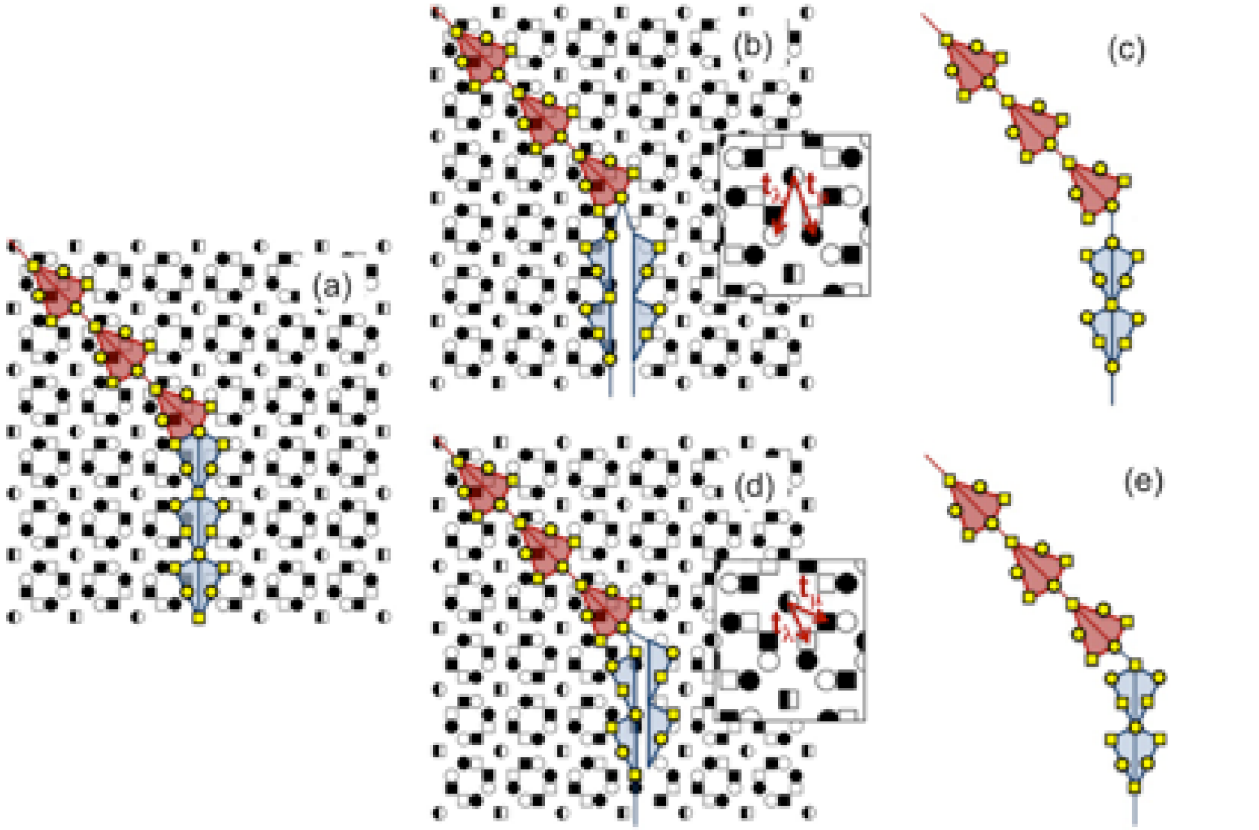



Figure 16

# H in GB Engineered Materials

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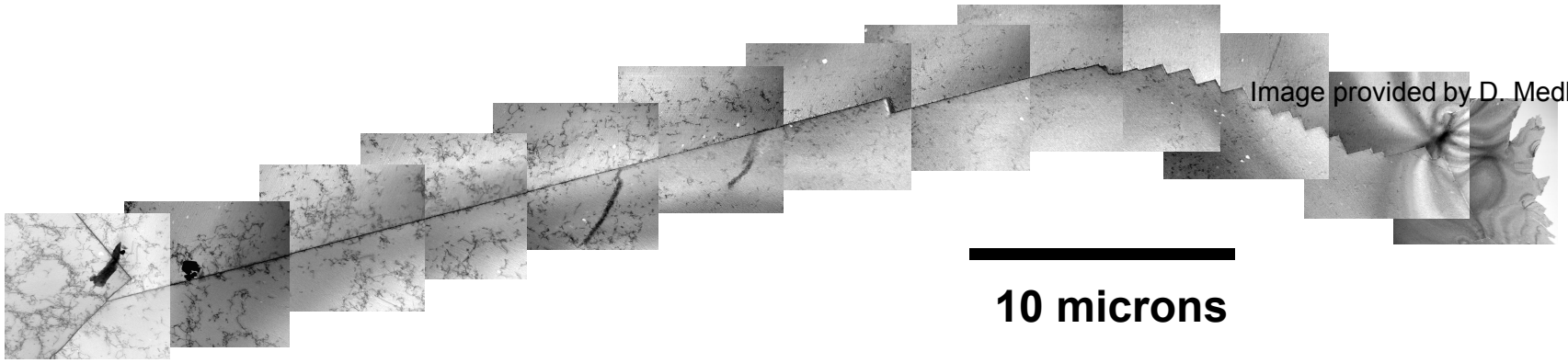
Grain boundary engineered materials offer a promising route to mitigate hydrogen embrittlement

- Recent work by Bechtle[†], and Oudriss[‡], demonstrate the benefit of grain boundary engineered materials in reducing embrittlement
- While H segregation at ideal coherent twins is thought to be small, what is the role of interfacial defects for H interactions?




†Acta. Mat. 57(14) p. 4148, 2009 ‡Acta Mater. 60(19) p. 6814, 2012

# Misoriented Twin Grain Boundaries

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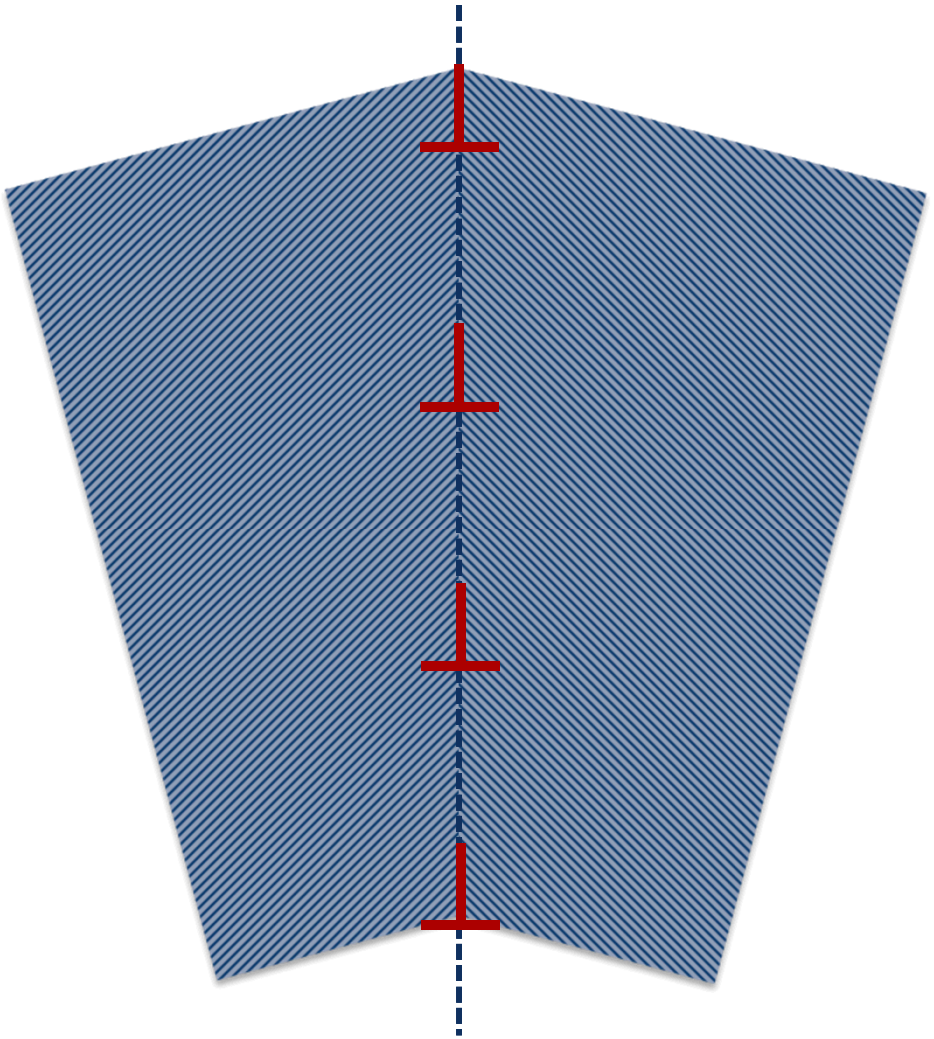
Definition: Misoriented GBs are produced by a symmetric rotation of grains about (111)⟨110⟩ (coherent) twin ($-15^\circ < \theta < +15^\circ$)

- Misoriented GBs are generated by disconnections that come in two classes:
  1. Exterior
  2. Interior
- This terminology, due to Marquis & Medlin,† refers to the decomposition of the $\pm\frac{1}{3}\langle 111\rangle$ disconnection.
  - *Exterior* disconnections disassociate and emit extended stacking faults
  - *Interior* disconnections retain compact core



†Phil. Mag. Lett. 85 (8), 387–394, 2005

# Fundamental Structural Difference Between ±⅓⟨111⟩ Disconnections

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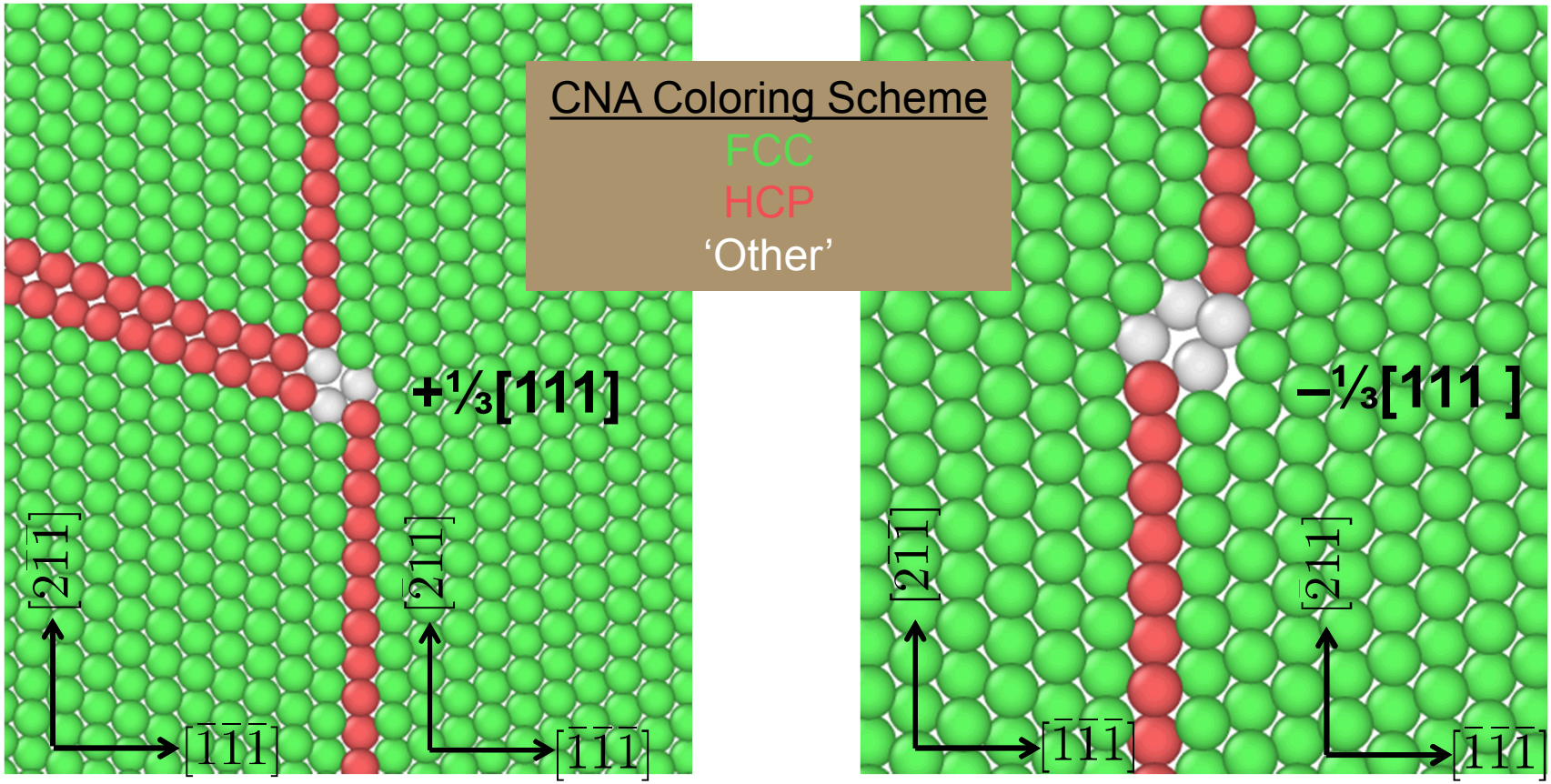
**Exterior Disconnection**

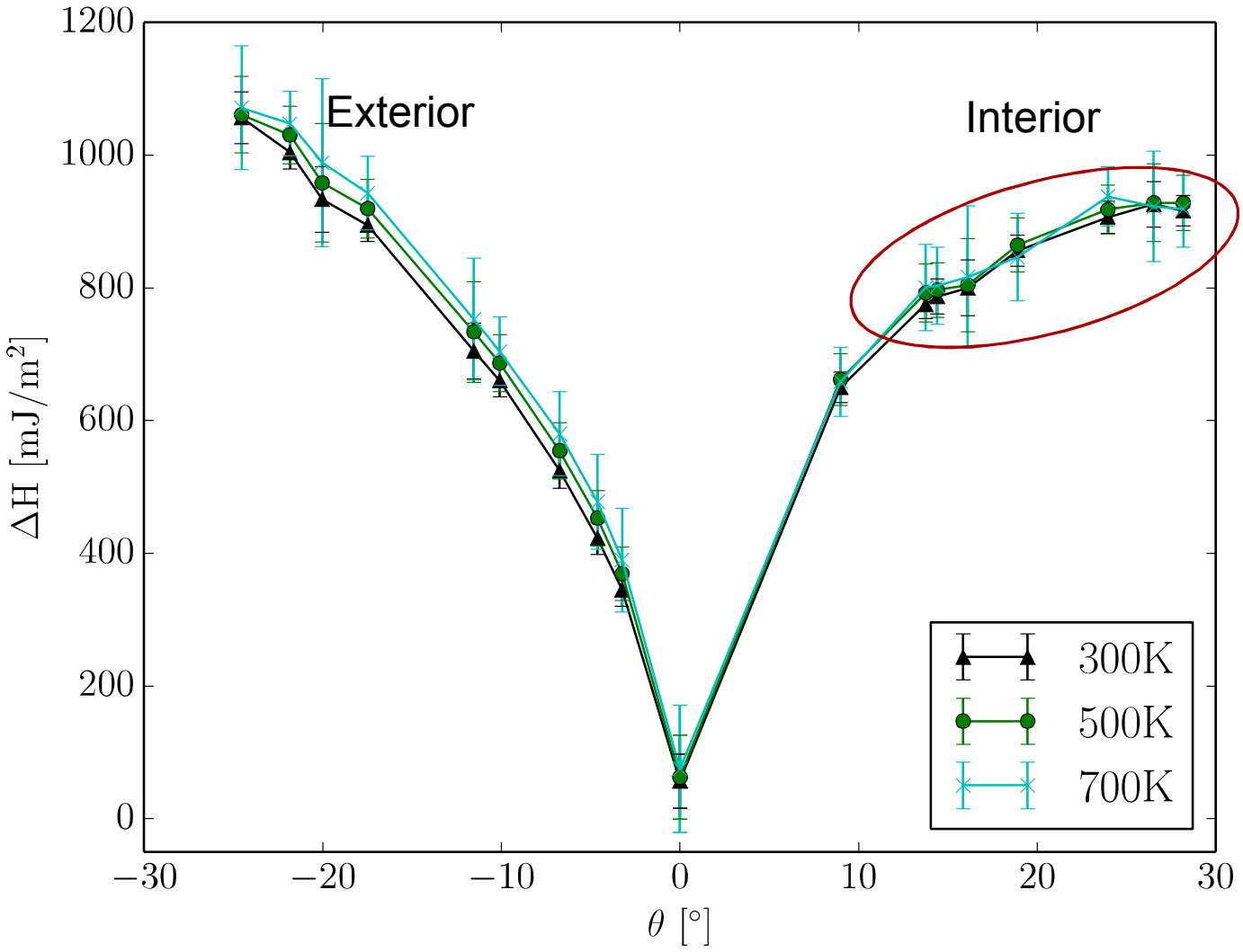
**Interior Disconnection**




Superposition of these disconnections allows for the rotation of the grains or GB plane

O'Brien, Medlin, & Foiles, Philosophical Magazine, in press

# Asymmetric Enthalpy Dependence






O'Brien, Medlin, & Foiles, Philosophical Magazine, in press

# Temperature Dependence of GB Structure

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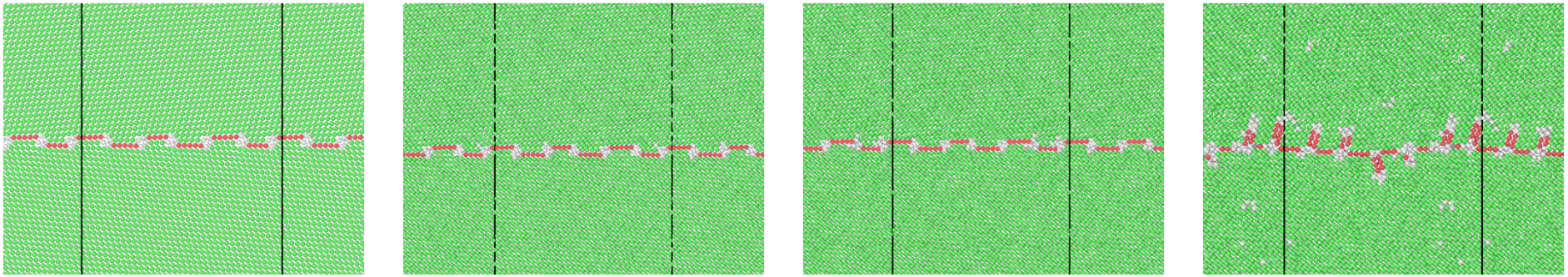
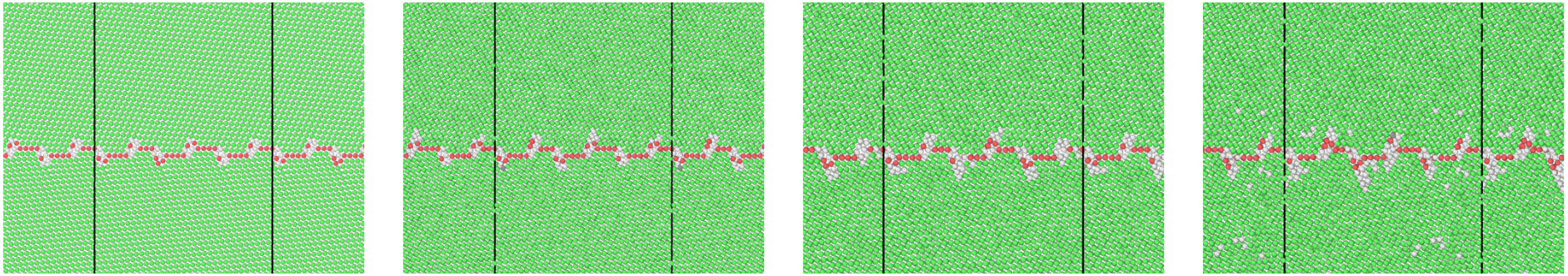
**Interior (θ = +9.0°)**

0K 300K 500K 700K



**Exterior (θ = –10.1°)**

0K 300K 500K 700K





O'Brien, Medlin, & Foiles, Philosophical Magazine, in press

# Stability of Extended Stacking Faults in Interior GBs

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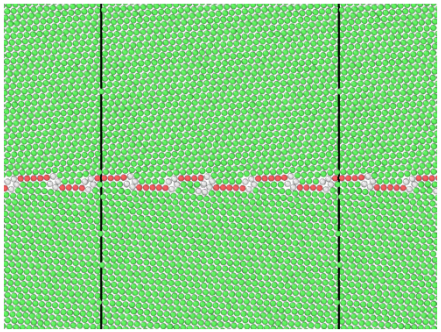
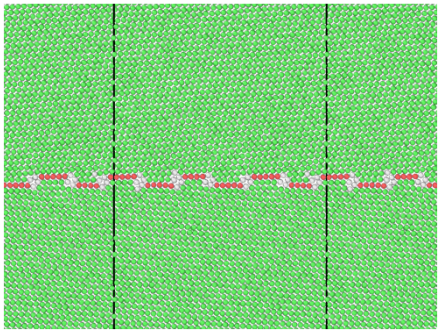
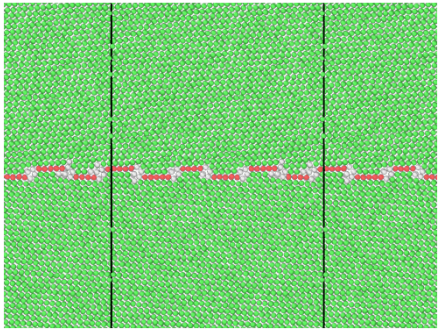
0K→100K



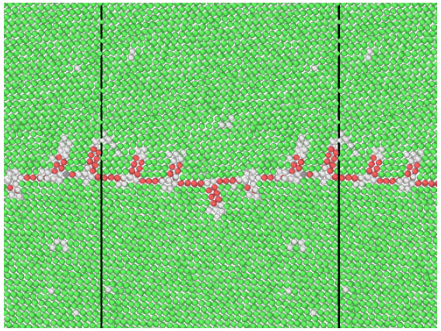
0K→300K



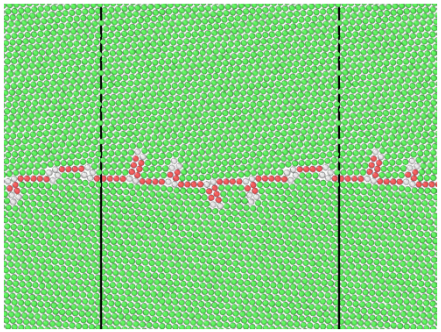
0K→500K



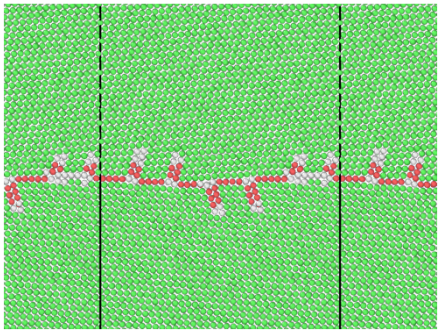
0K→700K



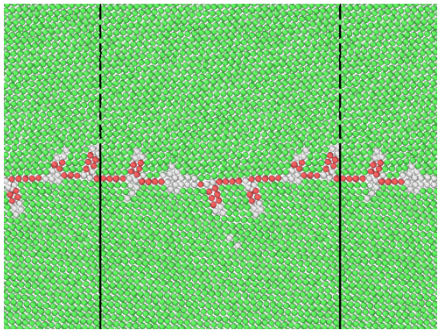
700K→100K



700K→300K



700K→500K



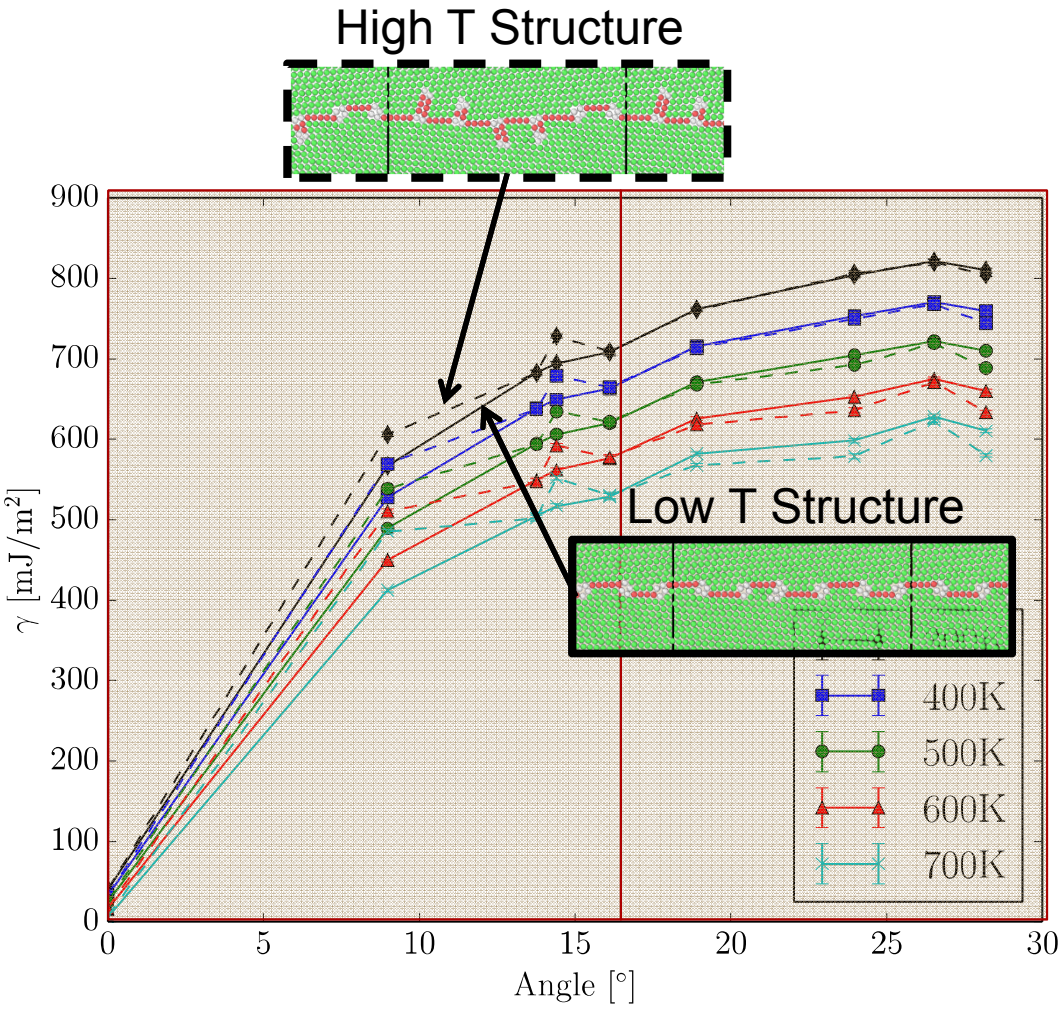
Faults are frozen in upon cooling, but are they stable?



O'Brien, Medlin, & Foiles, Philosophical Magazine, in press

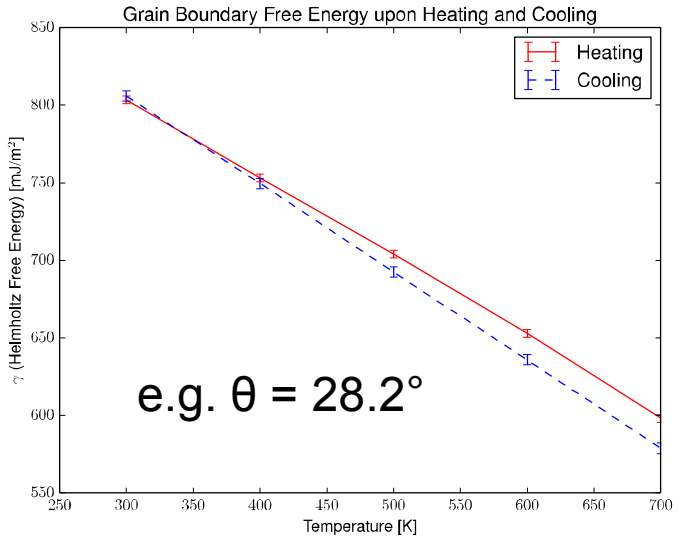
# Compact Core Structure of Interior Disclinations Favored At Low Misorientation Angles

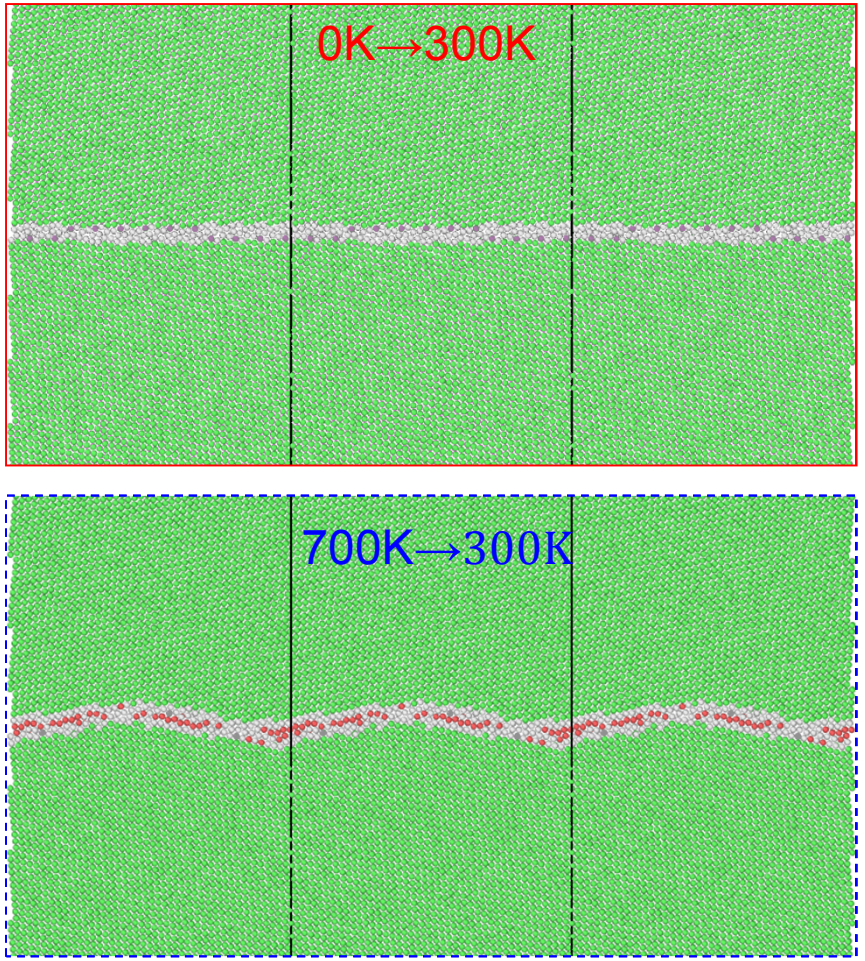
- $\theta \leq 16^\circ$
  - Low temperature structure of interior disconnections (compact cores) favored
- $\theta > 16^\circ$
  - High temperature structure favored
  - Change in character of boundaries
- Transition temperature for favorability of high temperature structures is unknown
  - Thermodynamic integration is used to calculate free energies above 300K
  - Change from low to high temperature form occurs occurs at 500–600K in MD simulations
  - High temperature structures could form during during realistic processing conditions



# Faceting occurs at larger misorientation angles

- Higher angle boundaries facet, which decreases their free energy
- Facets lie along (111) planes

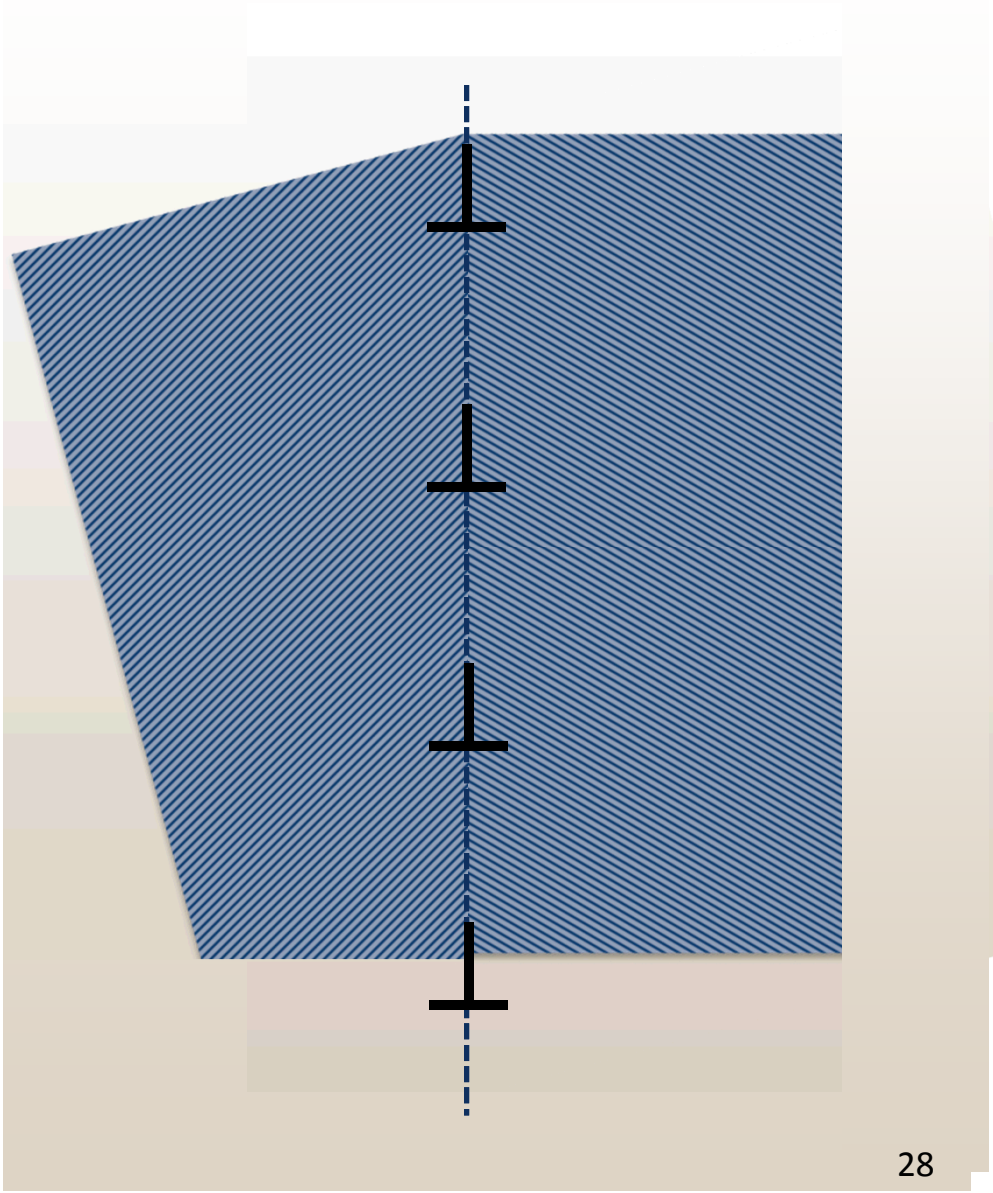


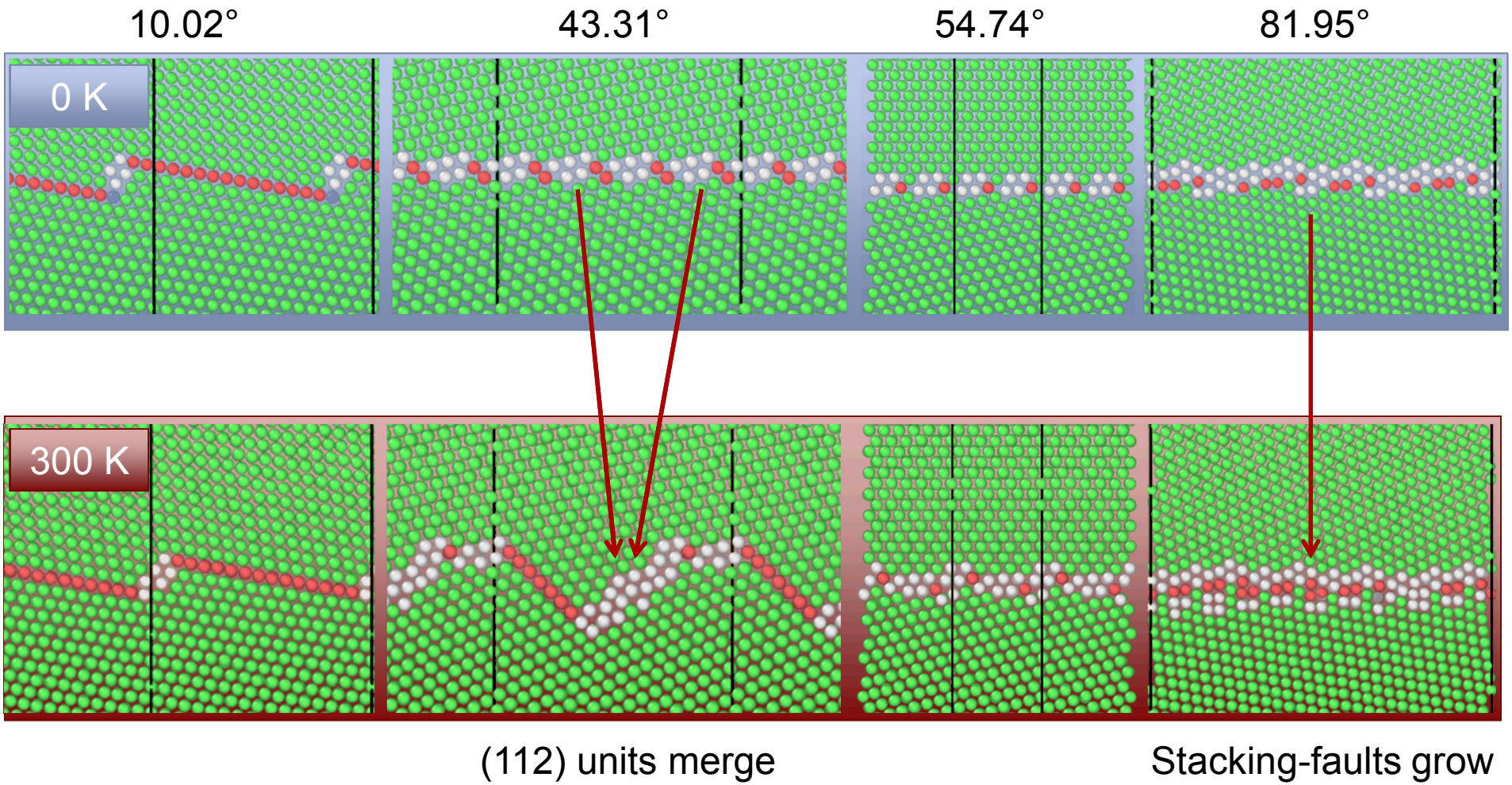
# Inclined Twin Grain Boundaries

Definition: Inclined GBs are produced by a change of grain boundary plane orientation

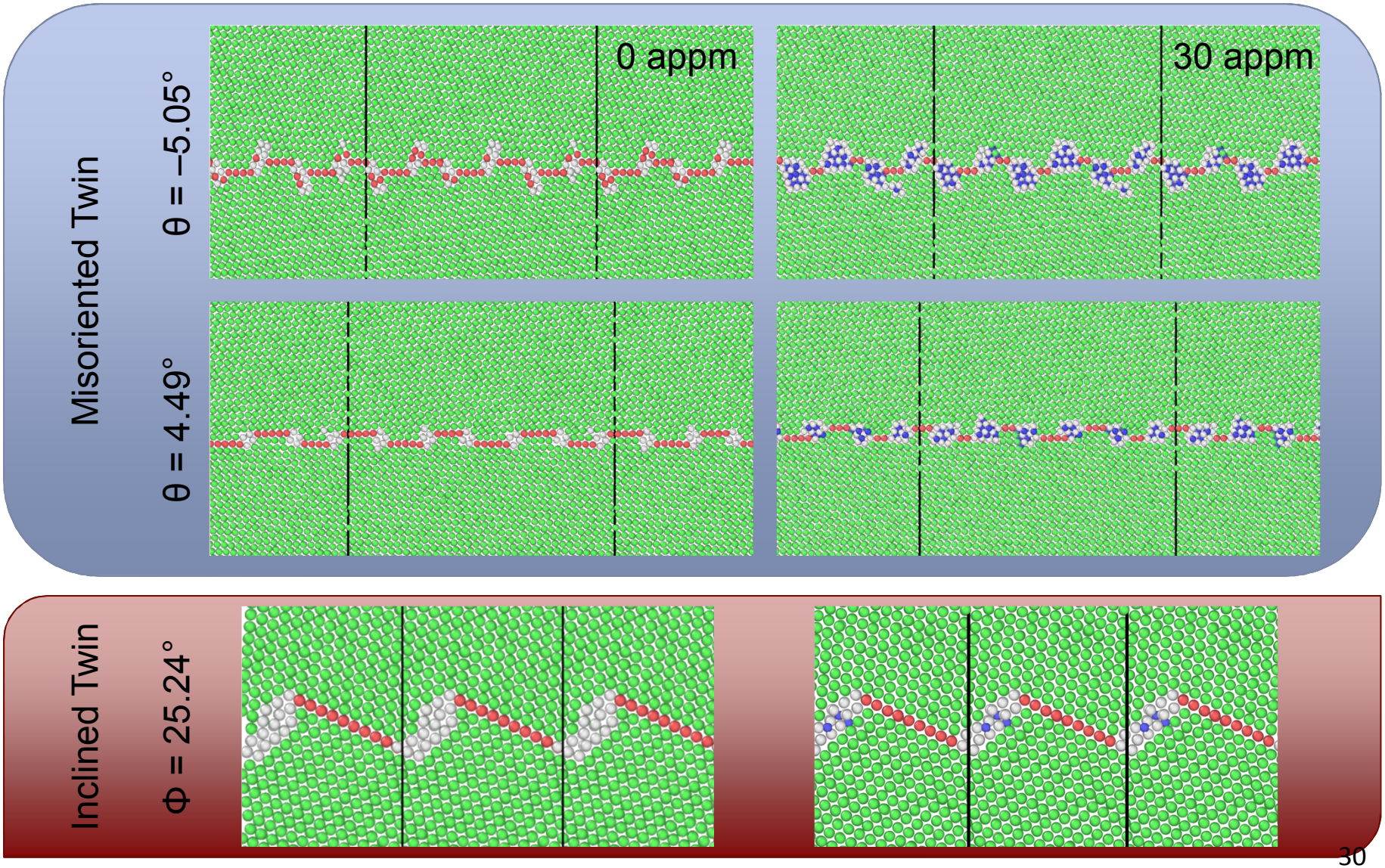
Inclination (Φ) range:
0° (111) ⟨110⟩ (coherent)
to
90° (112) ⟨110⟩ (lateral)



# Inclined Twin Boundary Structure



# Hydrogen Segregates Defect Cores





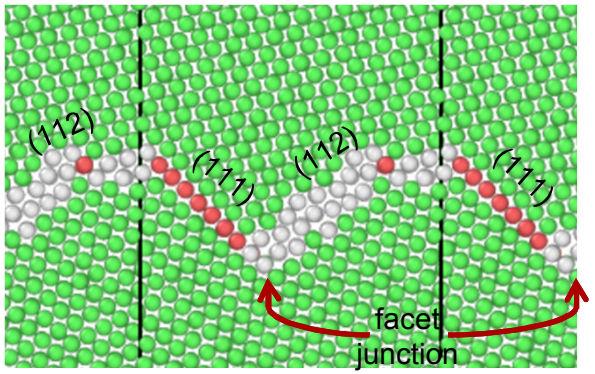

O'Brien & Foiles, Philosophical Magazine, in press

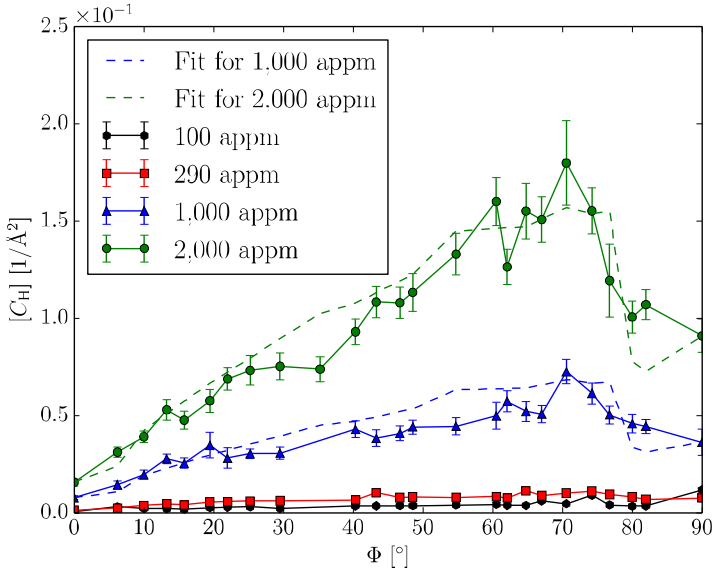
# Analytical Model – Defect Densities

- Facet description of inclined GB employed
  - Assume H segregates to junctions and twin facets
    - $(C_H)_{LTB}$ : Concentration on (112) facet
    - $(C_H)_{CTB}$: Concentration on (111) facet
    - $(C_H)_S$ : Concentration at junction

$$[C_{\mathrm{H}}] = \frac{1}{A}\left\{N_{\mathrm{s}}\,(C_{\mathrm{H}})_{\mathrm{s}} + N_{\mathrm{CTB}}\,(C_{\mathrm{H}})_{\mathrm{CTB}} + N_{\mathrm{LTB}}\,(C_{\mathrm{H}})_{\mathrm{LTB}}\right\}$$

junction (111) Twin (112) Twin



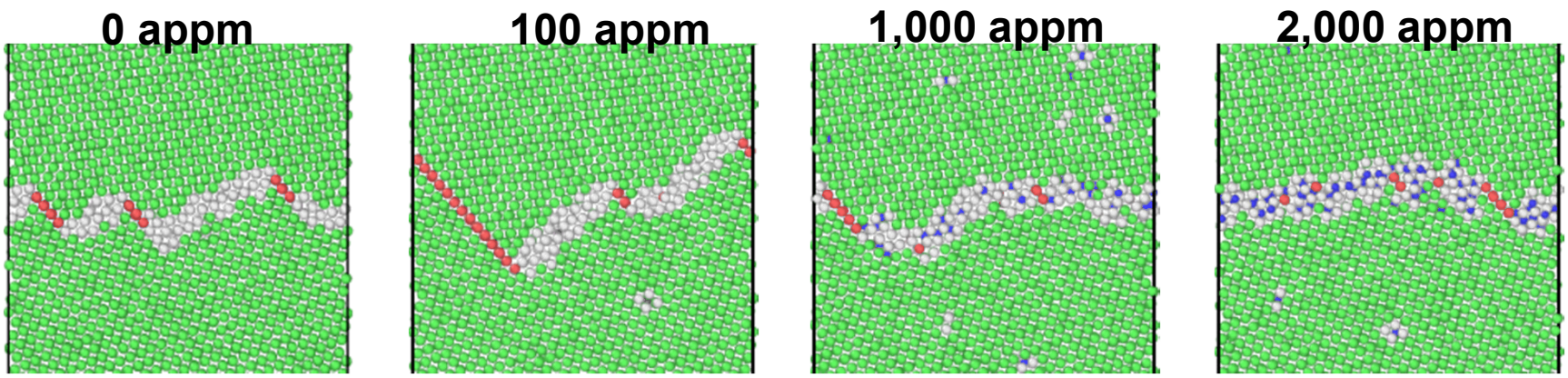




| Φ [°] | Width [Å] | $N_s$ | $N_{CTB}$ | $N_{LTB}$ | $[C_H]$ at 500 K [$10^{-3}$/Å$^2$] 100 | 290 | 1,000 | 2,000 |
|---|---|---|---|---|---|---|---|---|
| 0.00 | 17.384 | 0 | 8 | 0 | 0.5730 | 1.2362 | 7.6976 | 15.6347 |
| 6.21 | 1711.121 | 2 | 24 | 0 | 3.0848 | 2.3978 | 14.3273 | 31.1476 |
| 10.02 | 531.527 | 1 | 16 | 0 | 2.1946 | 3.7843 | 19.5592 | 39.0457 |
| 13.26 | 403.315 | 1 | 12 | 0 | 2.0831 | 4.5375 | 27.7196 | 52.9100 |
| 15.79 | 679.930 | 2 | 20 | 0 | 1.7180 | 4.0819 | 25.4872 | 47.6061 |
| 19.47 | 555.160 | 2 | 16 | 0 | 2.5771 | 5.4291 | 34.6411 | 57.5481 |
| 35.26 | 320.522 | 2 | 8 | 0 | — | — | 42.8791 | 73.8064 |
| 40.32 | 858.058 | 6 | 12 | 0 | 3.4301 | 6.6104 | 42.8791 | 93.0184 |
| 48.53 | 987.915 | 8 | 12 | 0 | 3.6199 | 8.1369 | 44.0075 | 107.9027 |
| 54.74 | 1063.052 | 10 | 20 | 0 | 3.9765 | 7.8516 | 44.3655 | 132.8865 |
| 64.76 | 613.753 | 6 | 8 | 0 | 3.7710 | 11.3393 | 52.0809 | 155.0783 |
| 70.53 | 392.558 | 4 | 8 | 0 | 4.5404 | 10.0850 | 72.5827 | 179.8277 |
| 74.21 | 480.783 | 5 | 4 | 0 | 8.9526 | 11.1193 | 61.4026 | 155.1813 |
| 76.74 | 570.373 | 6 | 4 | 0 | 3.9797 | 9.4398 | 50.2594 | 119.3123 |
| 79.98 | 751.691 | 4 | 2 | 0 | 3.3890 | 8.1005 | 45.8036 | 100.5943 |
| 81.95 | 934.475 | 4 | 4 | 1 | 3.4500 | 6.8524 | 44.4450 | 106.9386 |
| 90.00 | 185.053 | 0 | 0 | 2 | 11.7221 | 7.4934 | 36.2329 | 90.9561 |



O'Brien & Foiles, Philosophical Magazine, in press

# Structure and H Segregation are coupled




Inclined Boundary at 500 K

***Increasing H concentration changes boundary structure with increasing concentration!***



O'Brien & Foiles, Philosophical Magazine, in press

# H segregation also changes in structure in some misoriented boundaries

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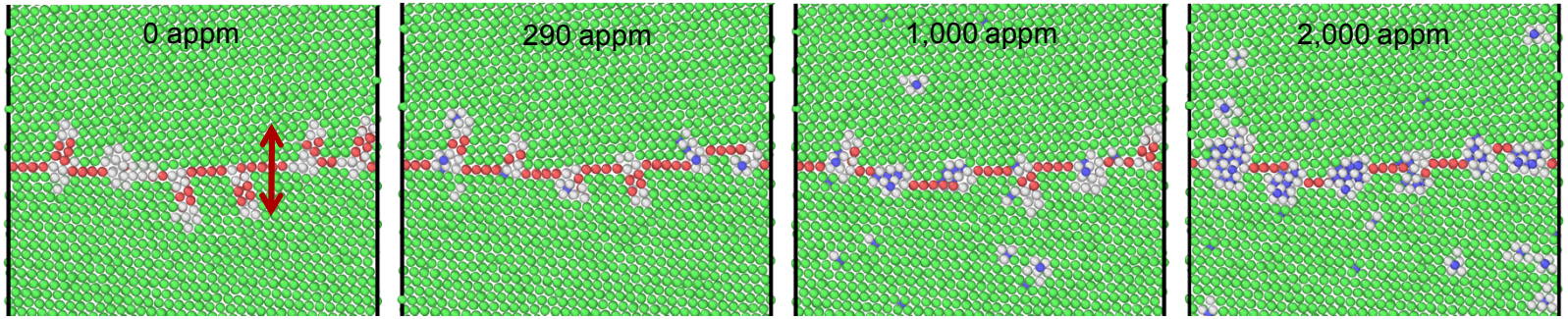
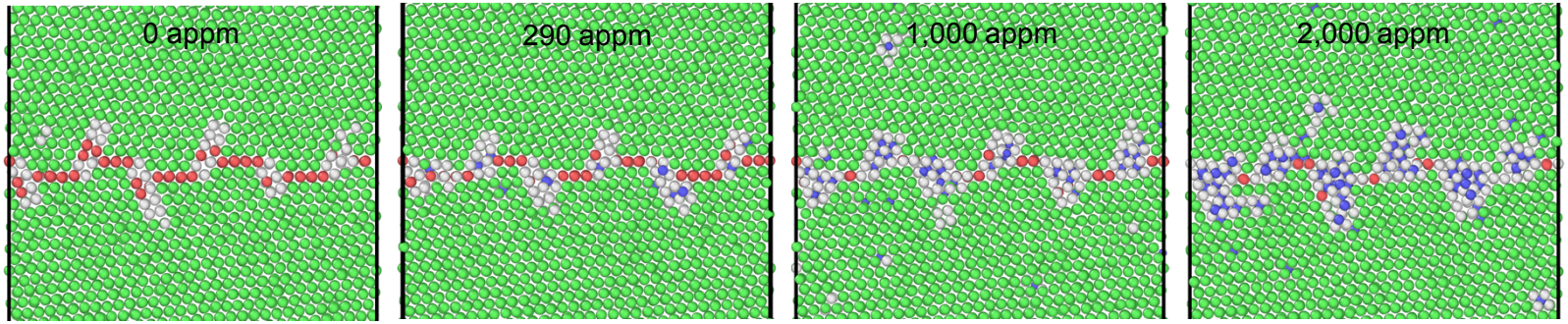
**θ = 4.49°**




**Stacking fault length reduced by increasing H concentration**

**θ = –5.05°**

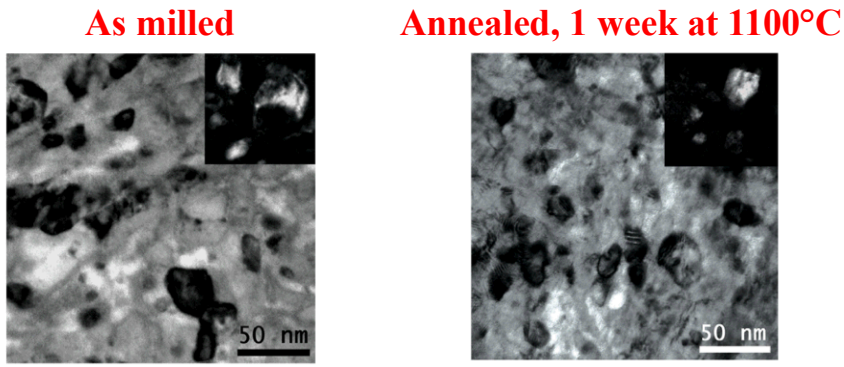





O'Brien & Foiles, Philosophical Magazine, in press

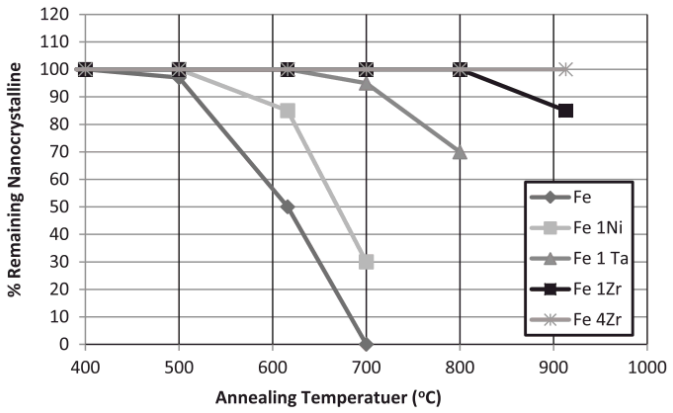
# Alloying can stabilize nanocrystalline grain structures

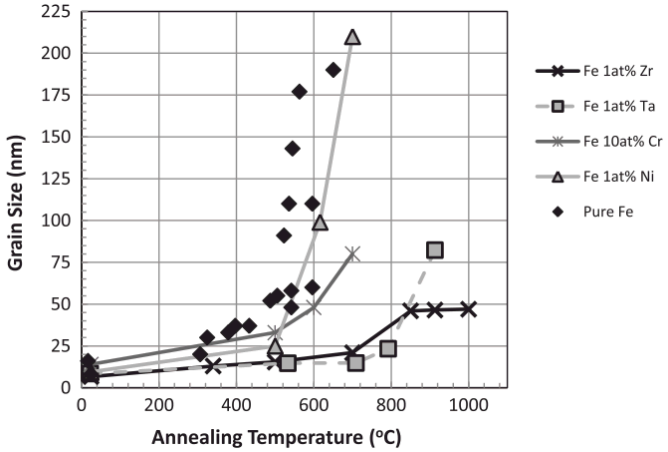
- Sluggish growth dynamics: W – 20at. % Ti




T. Chookajorn et al., Science. **337** (2012)
T. Chookajorn et al., Acta Mater. **73** (2014)

- Alloy selection in Fe-based system
  - Additions of Ta, Cr, NI and Zr

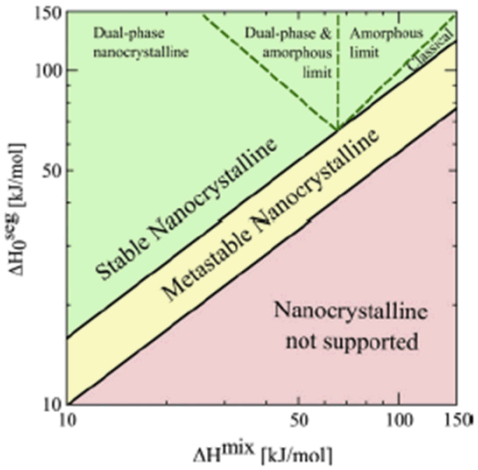


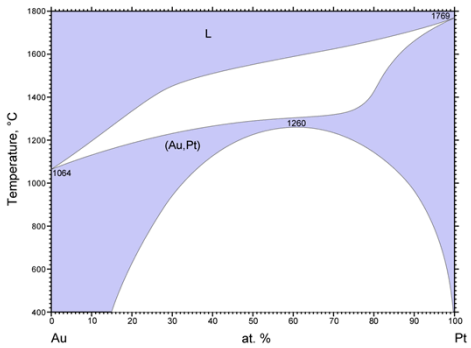

K. Darling et al., Mat. Sci. Eng. A **528** (2011)

# Alloy stabilization of nanocrystals could have multiple origins

- Grain boundary segregation can strongly reduced interfacial free energy, a driving force for grain growth
  - Schuh and co-workers
- Solute segregation to boundaries may reduce the mobility of the boundaries
- Precipitation of second phase particles can act as pinning sites
  - Zener pinning
- Pt-Au is being examined as a model system to elucidate the relative importance of these effects
  - O'Brien has developed DFT-based EAM potentials for Pt-Au
  - Experimental observations of this system are in progress
    - No oxide formation & high purity




Murdoch, Schuh, Acta Mat 61 (2013) 2121-2132



# Higher Au content in Pt-Au appears to slow grain growth

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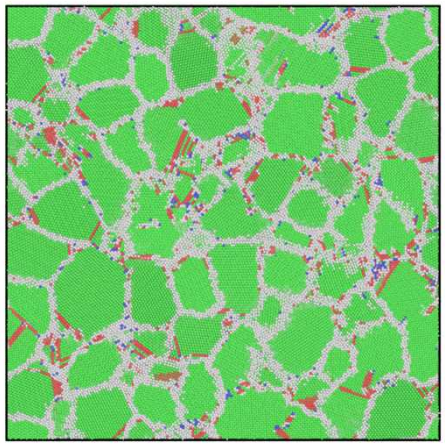
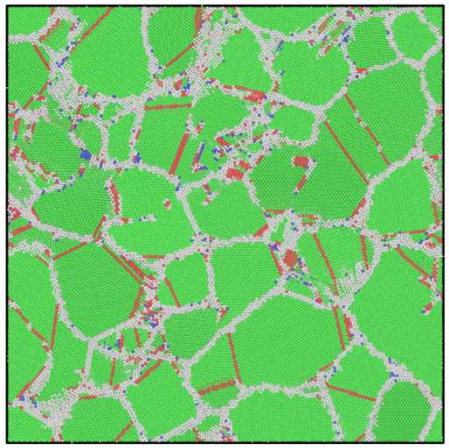
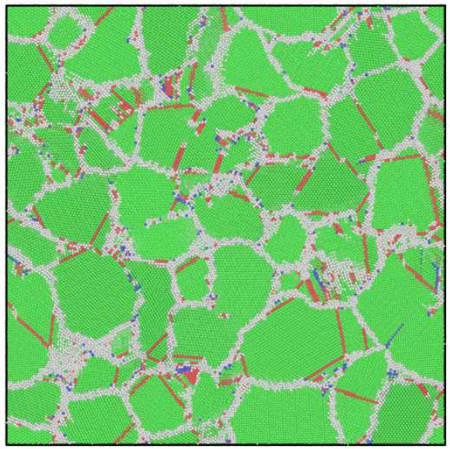
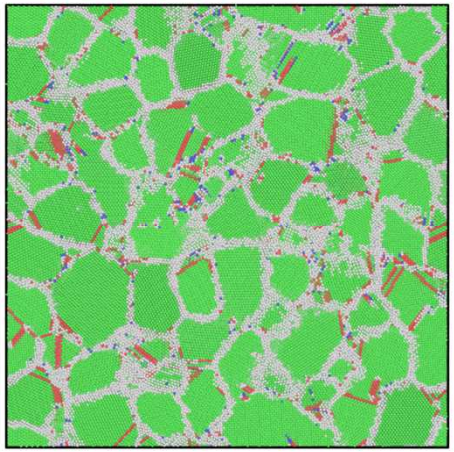
**0.0 nsec**

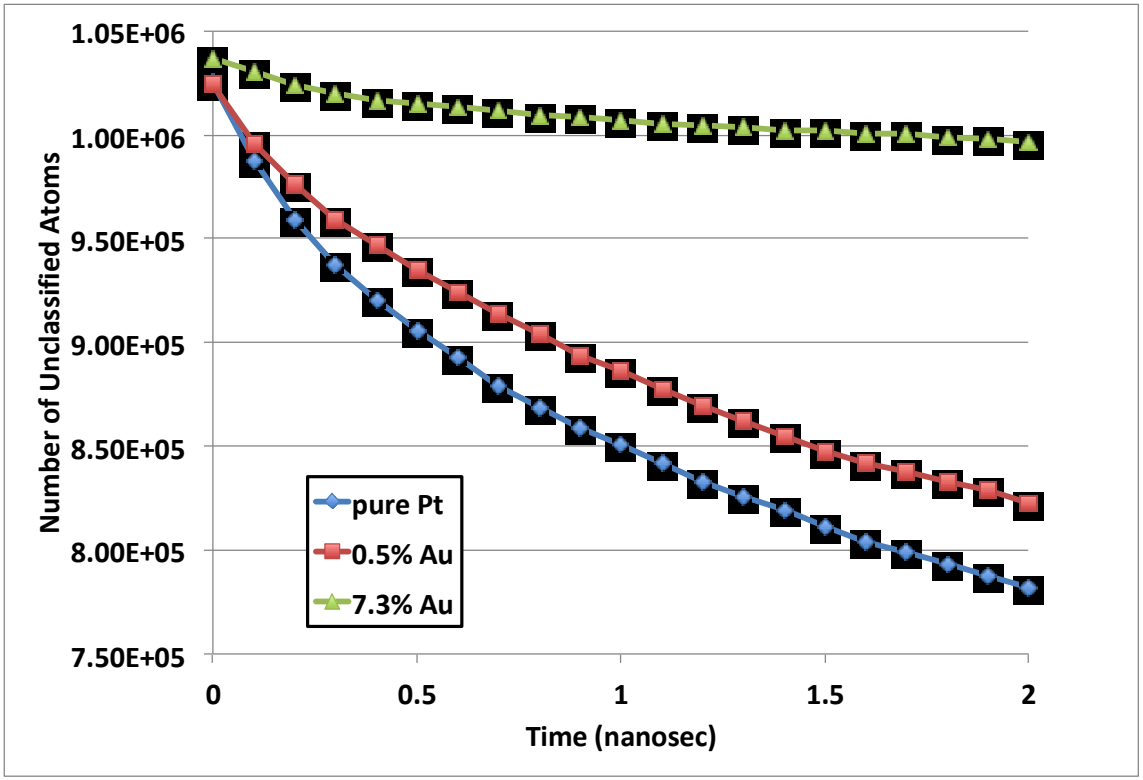


FCC
HCP
BCC
Other

- *Annealed* Voronoi grain structure at 1000K
  - 600 grains
  - Computational cell size: 39 nm
- Monte Carlo simulations employed to determine initial distribution of Au

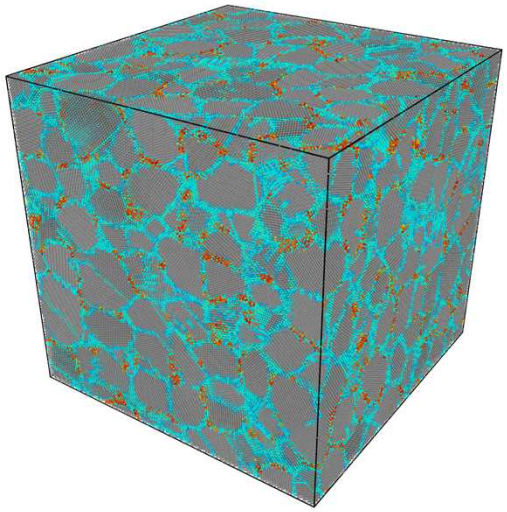
| | Pure Pt | 0.5% Au | 7.3% Au |
|---|---|---|---|
| **2.0 nsec** |  |  |  |

# Simple analysis confirms impression: High Au slows grain growth

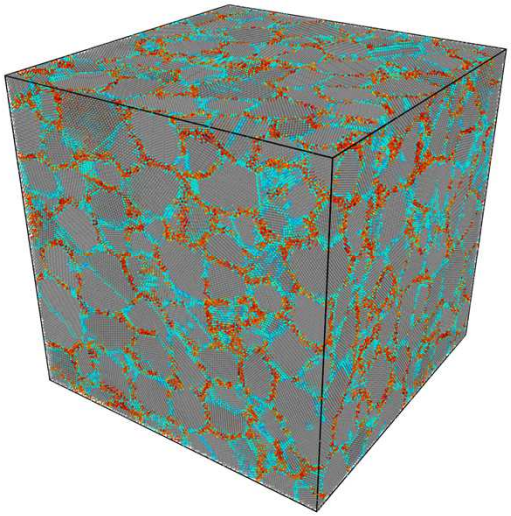



- Common Neighbor Analysis classifies atoms as FCC, HCP, BCC, and 'other'
- Use number of unclassified atoms as rough measure of grain boundary area

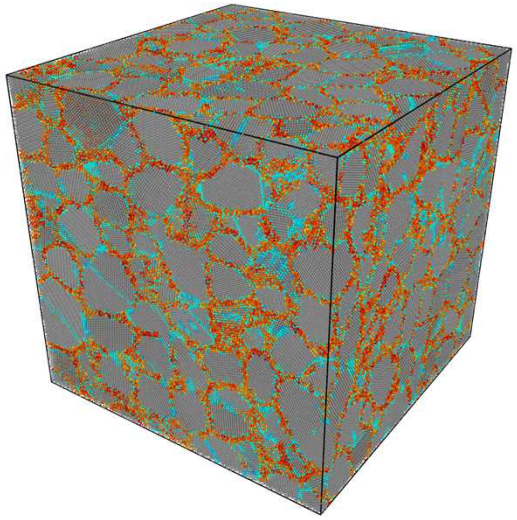
# Au is located almost exclusively at boundaries and triple junctions



Pt-5%Au



Pt-15%Au



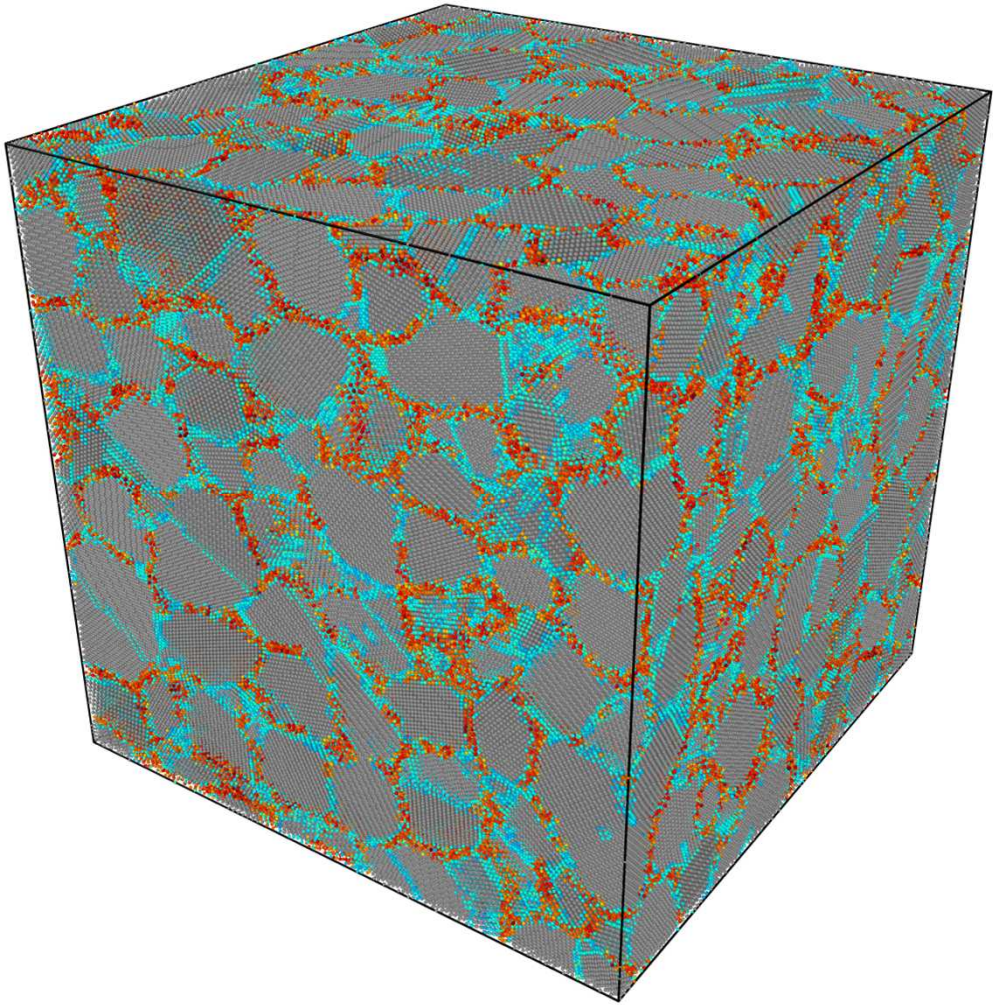
Pt-25%Au

Equilibrium Monte Carlo snapshots at 500° C

- Bulk Au concentrations: ~ 0.1%
- Coloring: combination of atomic element and centrosymmetry parameter
  - Gray: bulk Pt
  - Cyan: Pt interfaces
  - Orange→ Red: Au

# Heterogeneous Segregation

*" all grain boundaries are **NOT** created equal"*

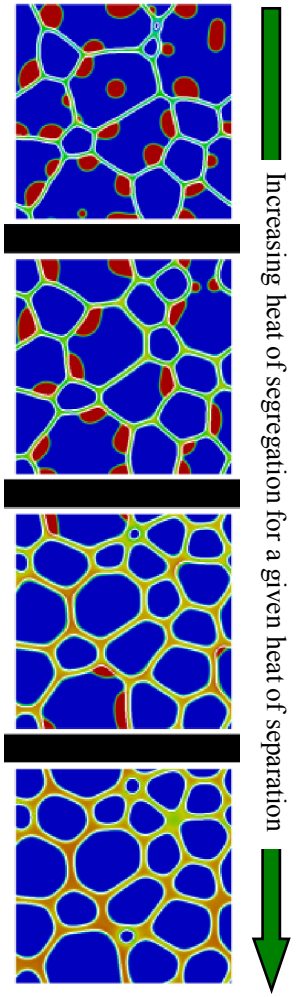


Does it matter that only some of the boundaries are segregated and so probably pinned?

- Pinning a subset of boundaries should be sufficient to stabilize the grain size
  - Holm, Foiles, Science 328, 1138 (2010)

# Future work on Pt-Au nanocrystals

- Bi-crystal simulations of representative boundaries
  - Degree of segregation for comparable bulk compositions
  - Mobility of grain boundaries
    - Segregated & unsegregated moving insolute field
- Use results to motivate introduction of varying boundary properties into phase field simulations
  - Bare energy, heat of segregation
  - Mobility with and without segregants
- Comparison with experiment
  - *"Coming soon to a conference near you!"*



# Molecular Dynamics:

## *What could possibly go wrong?*

Sandia National Laboratories

- Deviations from Born-Oppenheimer Approximation
  - Highly dynamic events, charge states, …
- Inadequate Interatomic Potentials
  - Imperfect knowledge of Born-Oppenheimer surface
    - Errors in experimental data
    - Deficiencies of *ab initio* database
  - Assumed potential form – model form error
  - Transferability or lack thereof
- Quantum Mechanical Effects
  - Zero-point energies of light elements
  - Debye Temperature often above room temperature

- Limited time scales
  - High rates and high driving forces
  - Infrequent events
  - Sampling errors – metastable states
- Structural approximations
  - Where are the atoms, *really*?
  - Simplification of geometries
  - Boundary conditions
- Multi-component systems
  - Composition and structure coupled
  - Compositional variation - equilibrium or kinetic?
- Information extraction for higher-scale models
  - Millions of coordinates -> ‘Physics’
  - Identification of dominant effects

**Issues encountered in this talk**

# Acknowledgements


- Funding sources
  - US DOE Office of Basic Energy Sciences
  - Sandia National Laboratories Laboratory Directed Research & Development (LDRD)
  - US DOE Advanced Simulation and Computing (ASC)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  - Garritt Tucker, Drexel U.
  - Christopher O'Brien, SNL
  - Doug Medlin, SNL
  - Fadi Abdeljawad, SNL
  - Elizabeth Holm, Carnegie Mellon U.
  - Geoff Campbell, LLNL