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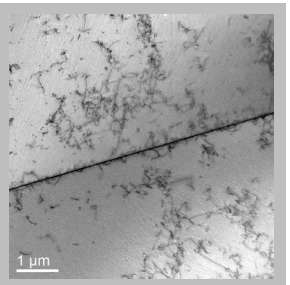

LDRD
LABORATORY DIRECTED RESEARCH & DEVELOPMENT

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Exceptional service in the national interest

Hydrogen Segregation to Vicinal Twin Boundaries in Nickel

C. J. O'Brien
S. M. Foiles
R. A. Karnesky

TMS '15, Computational Thermodynamics and Kinetics

U.S. DEPARTMENT OF ENERGY
NNSA National Nuclear Security Administration

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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 grai ls in reducing embrittlement
- How does the effect H the degree of H se

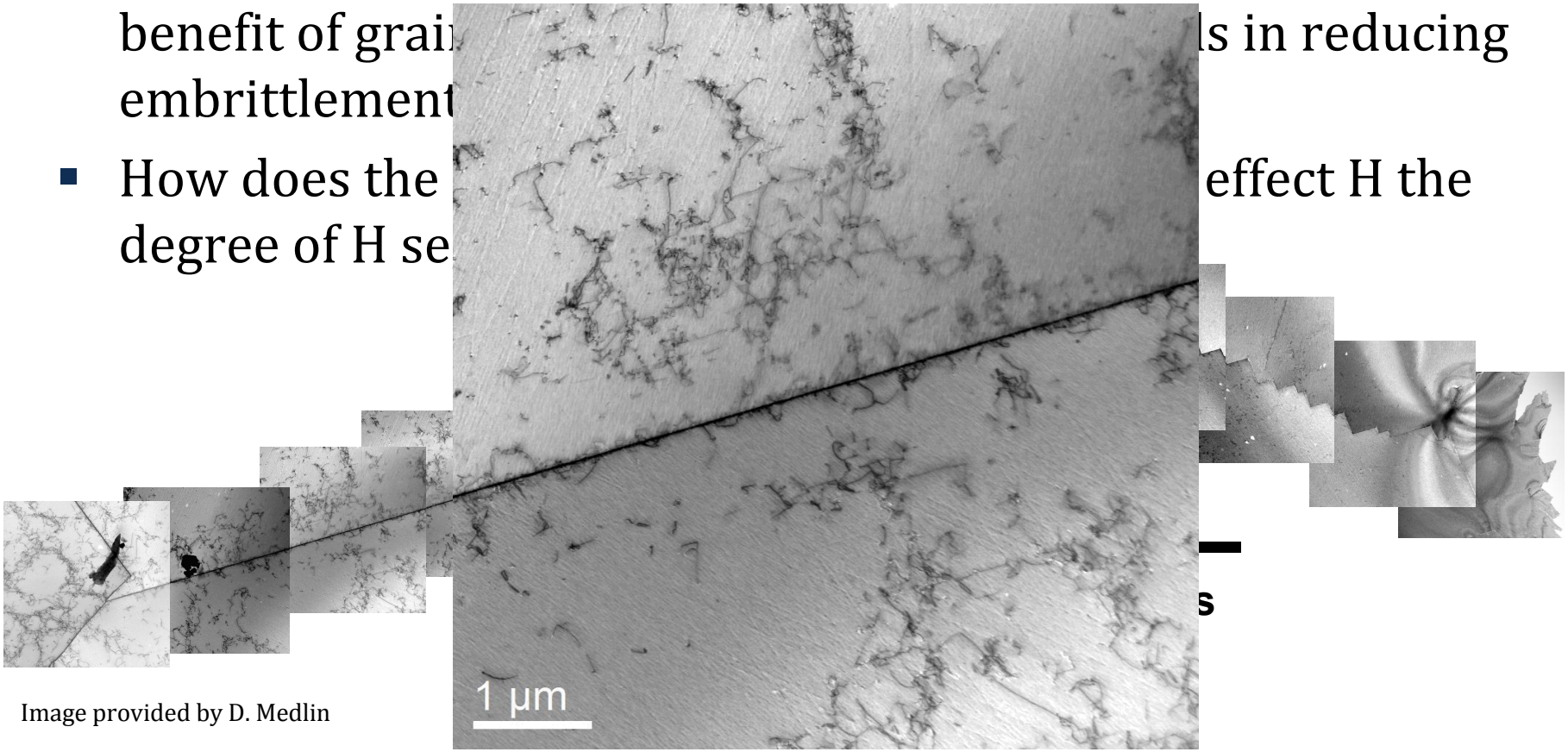

Image provided by D. Medlin

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

Atomistic Models Support Higher Length Scale Modeling Efforts

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Mesoscale and continuum crack growth models rely on many assumptions about hydrogen segregation at grain boundaries

- Thermodynamics
  - The actual dependence of free energy on structural deviations from ideal GBs is unknown
- H Segregation
  - There is little segregation to (111)⟨110⟩ (coherent) twins
  - Degree of hydrogen segregation to non-ideal twins is unknown

Present efforts focus on Σ3-like GBs

1. Misoriented Twins
   - Symmetric rotation of grains about (111)⟨110⟩ (coherent) twin ($-15^\circ < \theta < +15^\circ$)
2. Inclined Twins
   - Fixed grain orientation, with boundary plane rotated from the (111)⟨110⟩ (coherent) to (112)⟨110⟩ (lateral) twin ($0^\circ \leq \Phi \leq 90^\circ$)

- Enthalpies calculated via LAMMPS molecular dynamics code using Angelo, Moody, and Baskes† Ni-Al-H EAM potential

† Mod. Simul. Mater. Sci. Eng. 3 p. 289, 1995

Misoriented Twin Grain Boundaries

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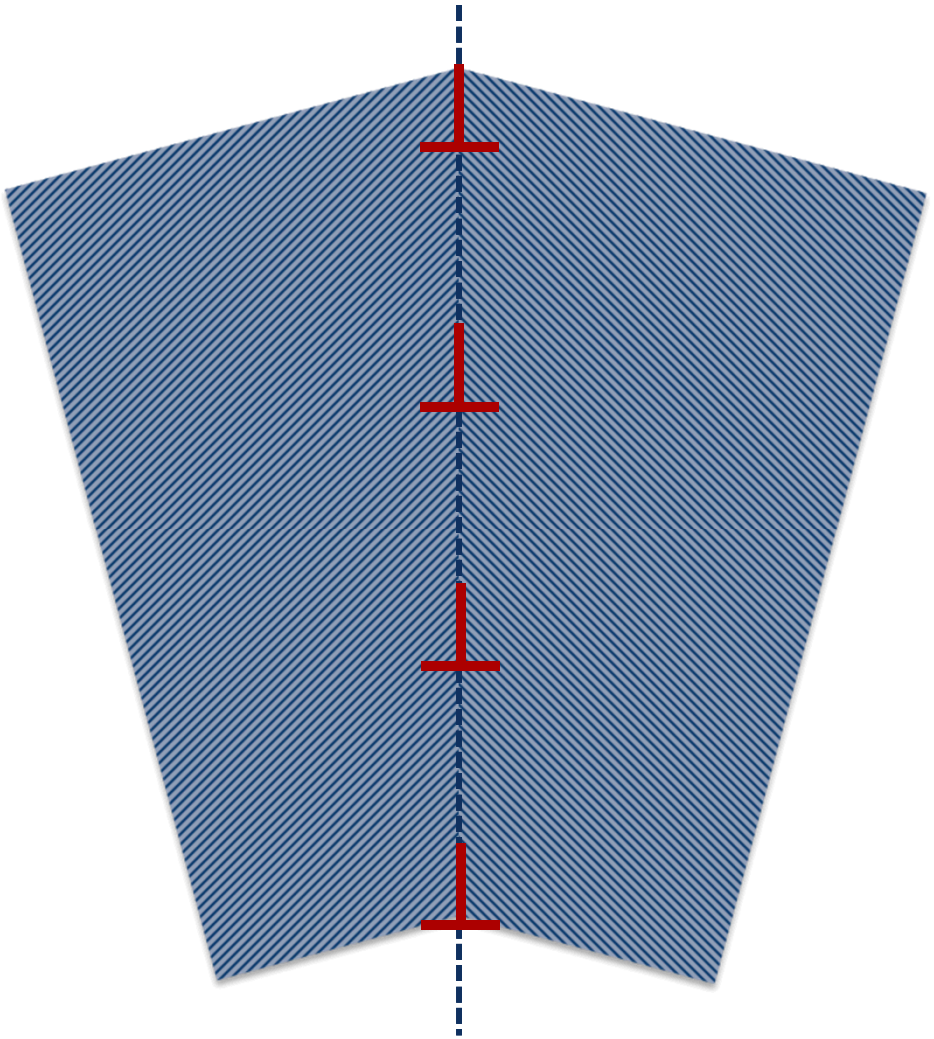
Definition: Misoriented GBs are produced by a symmetric rotation of grains about (111)⟨110⟩ (coherent) twin ($-15^\circ < \theta < +15^\circ$)

- 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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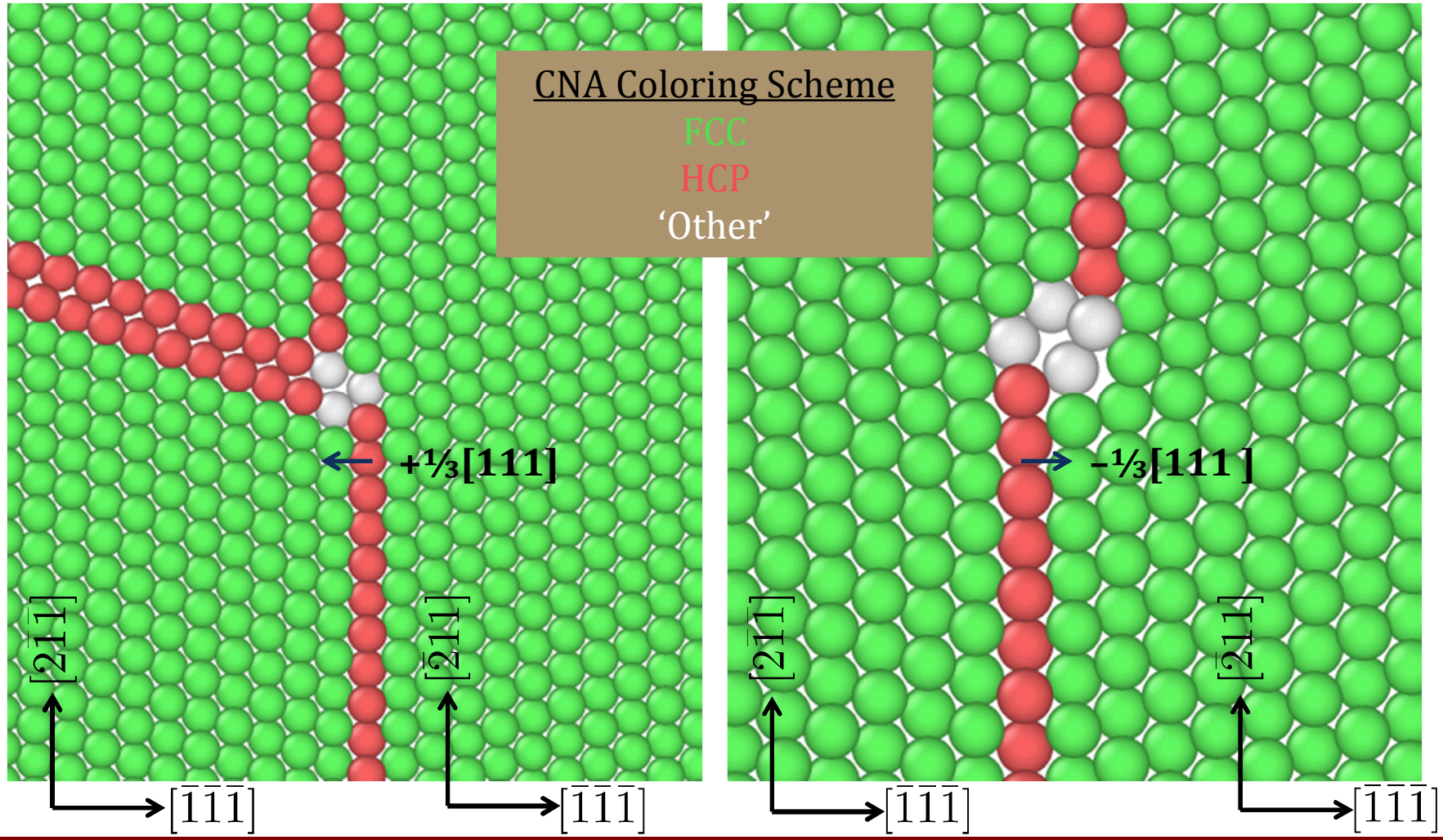
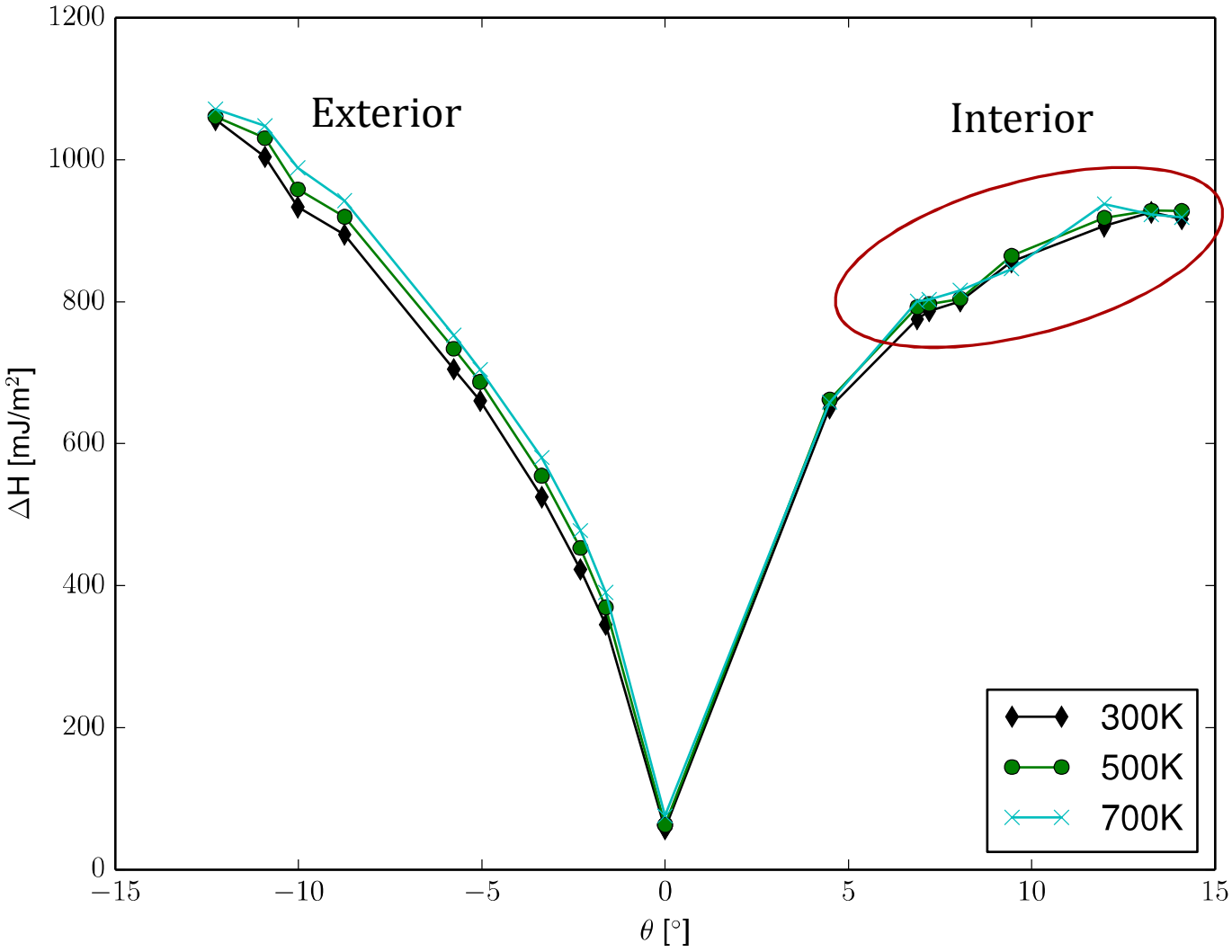
Exterior Disconnection

Interior Disconnection



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

Asymmetric Enthalpy Dependence



Temperature Dependence of GB Structure

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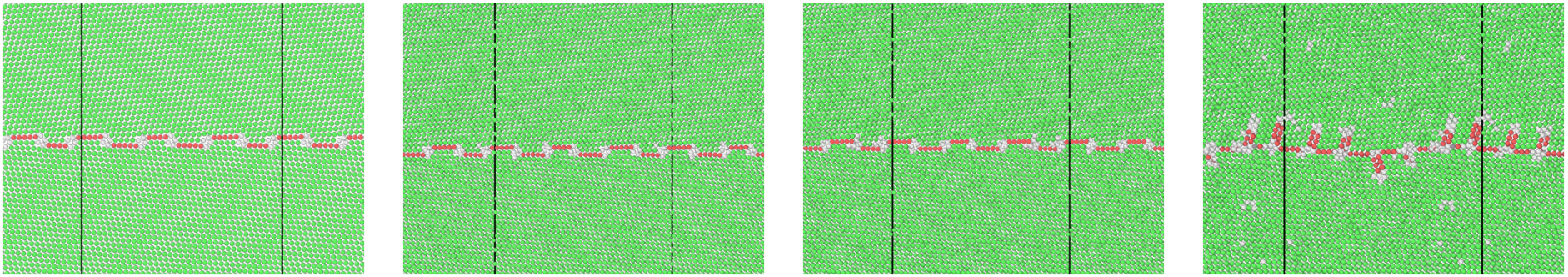
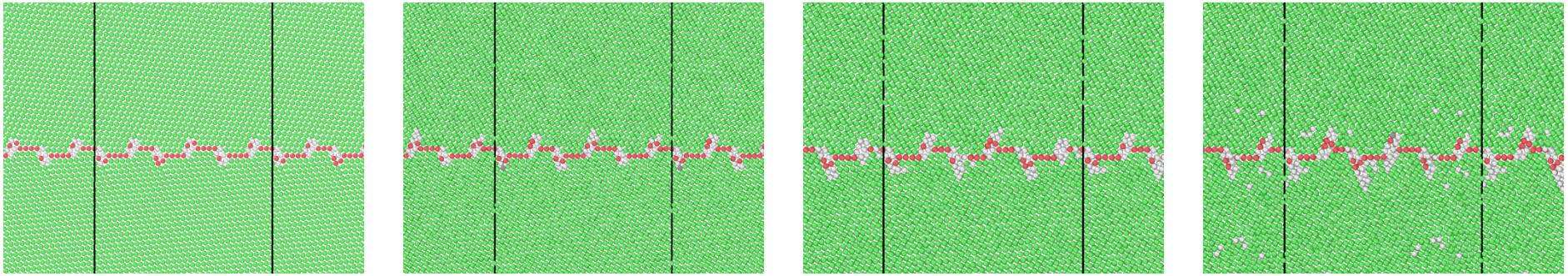
Interior (θ = +4.49°)

0K 300K 500K 700K



Exterior (θ = –5.05°)

0K 300K 500K 700K



Stability of Extended Stacking Faults in Interior GBs

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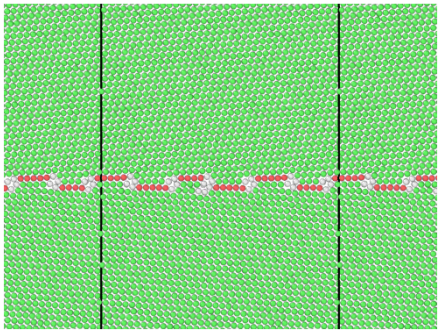
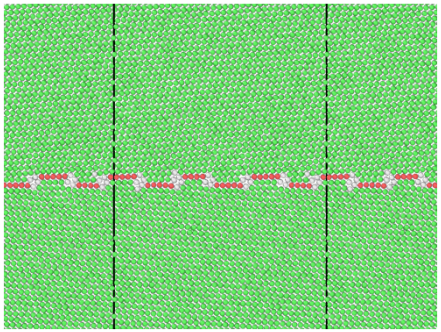
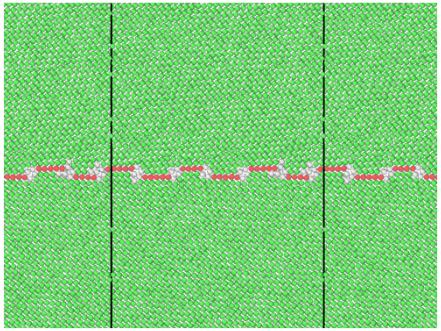
0K→100K



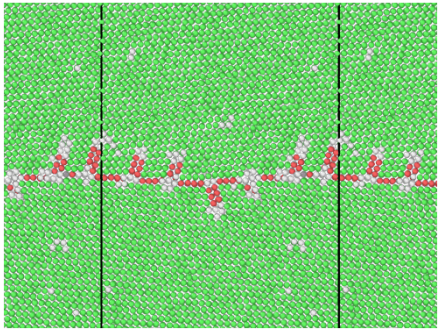
0K→300K



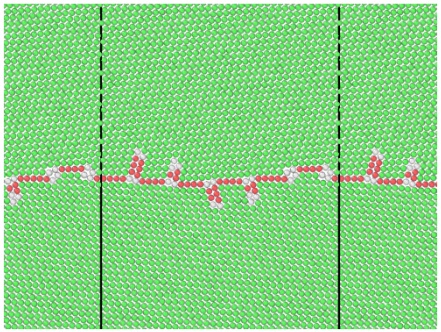
0K→500K



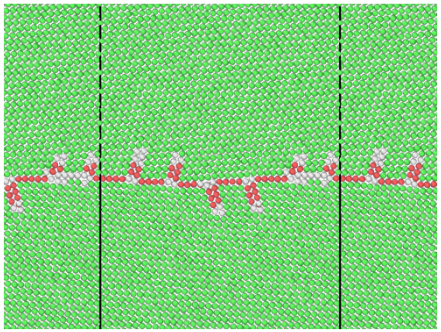
0K→700K



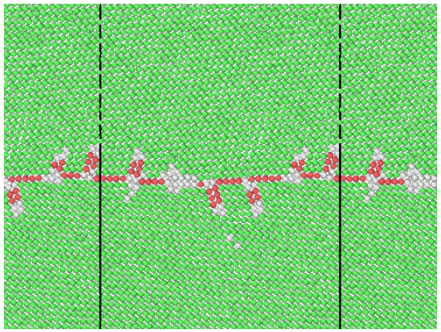
700K→100K



700K→300K



700K→500K



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

Helmholtz Free Energy Calculation

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- Calculated at and below Debye temperature using Frenkel-Ladd† technique with Einstein crystal as a reference state as implemented‡ in LAMMPS
  - FL technique calculates the Free Energy difference between two states described by a Hamiltonian with a switching function

$$\Delta F = -\int_0^{\lambda} \left\langle \frac{\partial \mathcal{H}(\lambda')}{\partial \lambda'} \right\rangle \mathrm{d}\lambda'.$$

  - Hamiltonian switches between Einstein crystal and crystal described by EAM potential
    - Since the Einstein crystal free energy is known analytically, the EAM free energy can be calculated
    - Einstein crystal is modeled by attaching a spring to each atom's equilibrium position and turning off interatomic interactions

$$\mathcal{H}(0 \leq \lambda \leq 1) = \lambda \cdot H_{\mathrm{EAM}} + (1-\lambda) H_{\mathrm{Ein}}$$

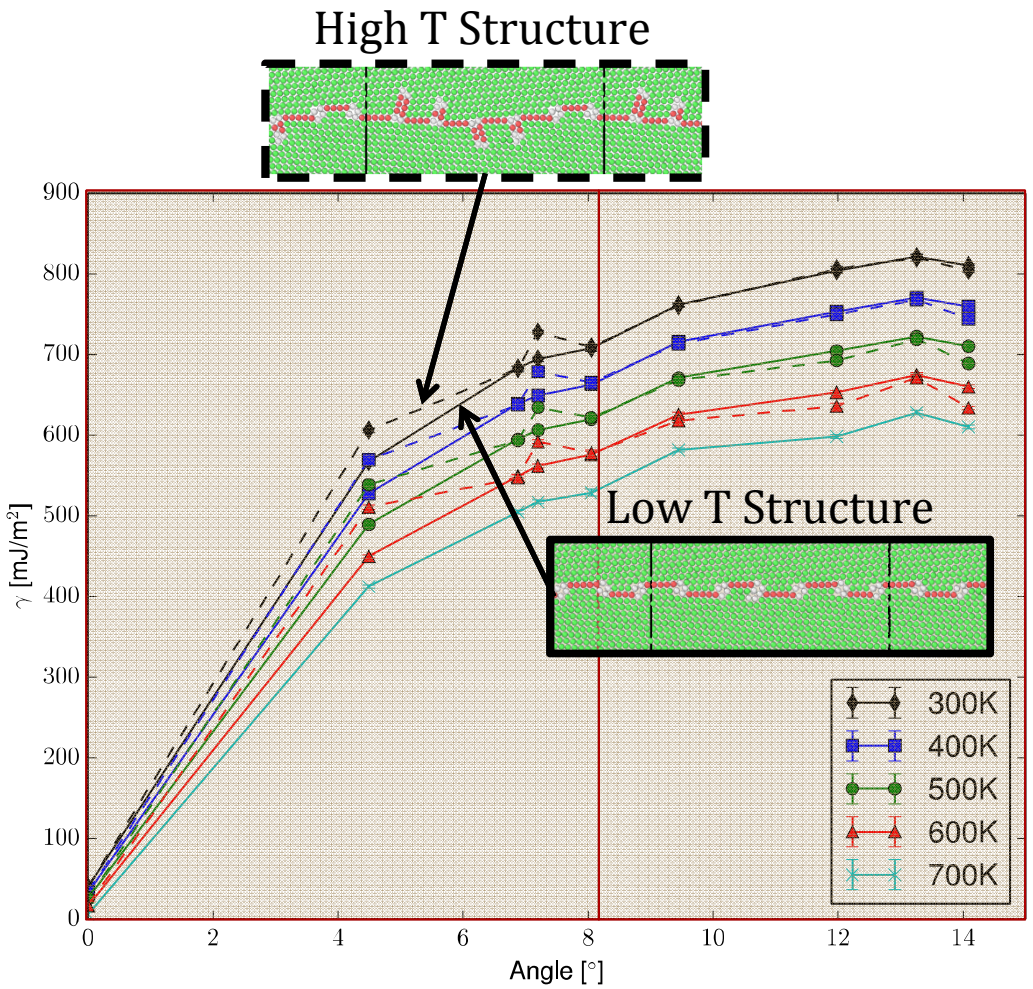
  - Calculated at higher temperature by thermodynamic integration of the Enthalpy according to formalism of Frolov & Mishin*

$$\gamma A(T) = (\gamma A)_0 \frac{T}{T_0} + T \int_{T_0}^{T} \left[-\frac{U^{ex}}{T'^2} + \frac{2\alpha(T')\tau(T')A}{T'} \right] \mathrm{d}T'$$

† D. Frenkel and A.J.C. Ladd, J. Chem. Phys. 81, 3188 (1984)
‡ M. de Koning & A. Antonelli, Phys. Rev. E 53, 465 (1996); Phys. Rev. B 55, 735 (1997)
*T. Frolov and Y. Mishin, Phys. Rev. B 79, 045430 (2009)

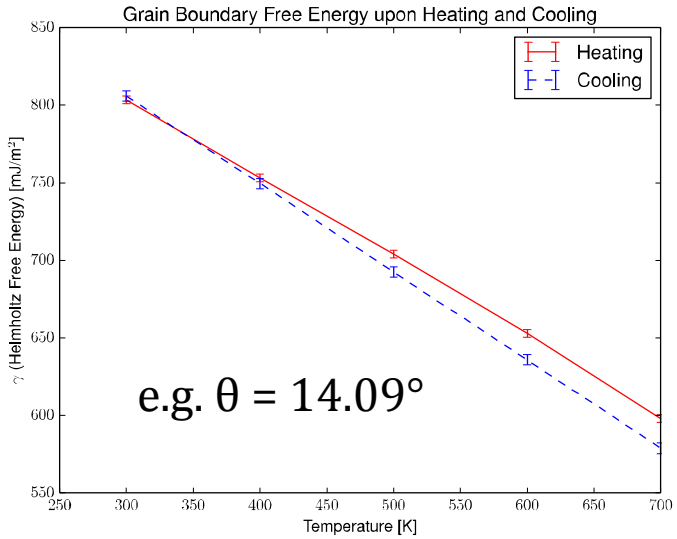
Compact Core Structure of Interior Disclinations Favored At Low Misorientation Angles

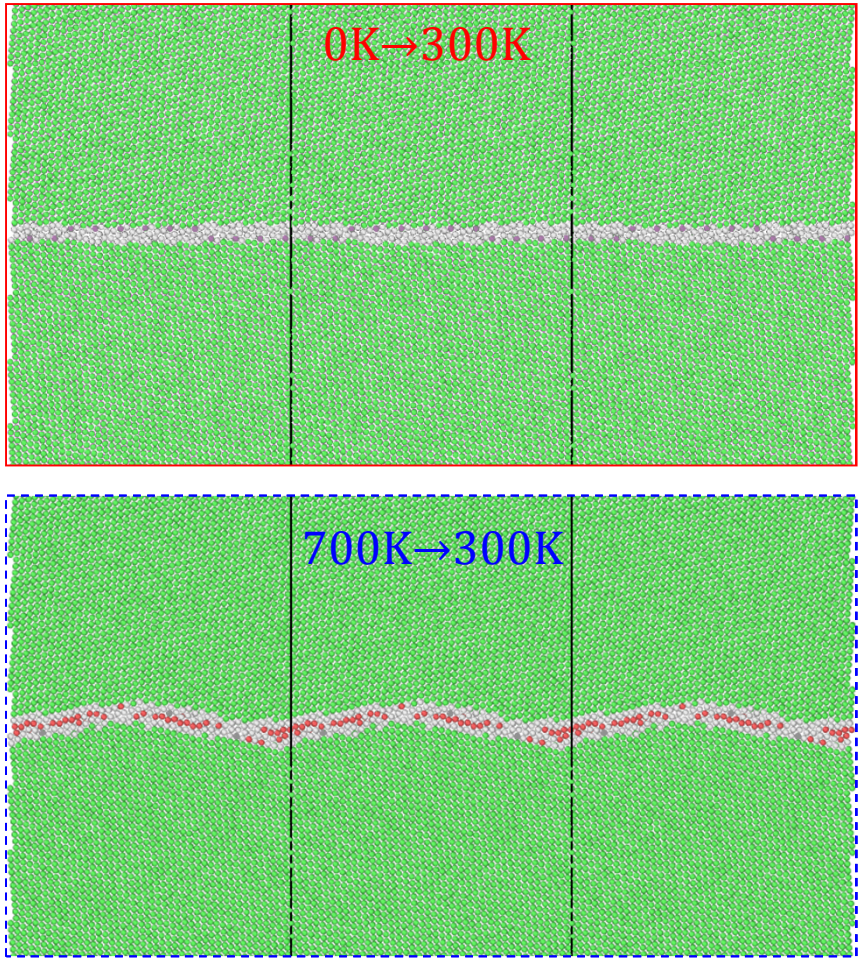
- $\theta \leq 8^\circ$
  - Low temperature structure of interior disconnections (compact cores) favored
- $\theta > 8^\circ$
  - High temperature structure favored
  - Change in character of boundaries
- Transition temperature for favorability of high temperature structures is unknown
  - Thermodynamic integration is used to calculate free energies above 300K
  - Change from low to high temperature form occurs occu at 500–600K in MD simulatior
  - 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





Summary: Temperature Dependent Structure

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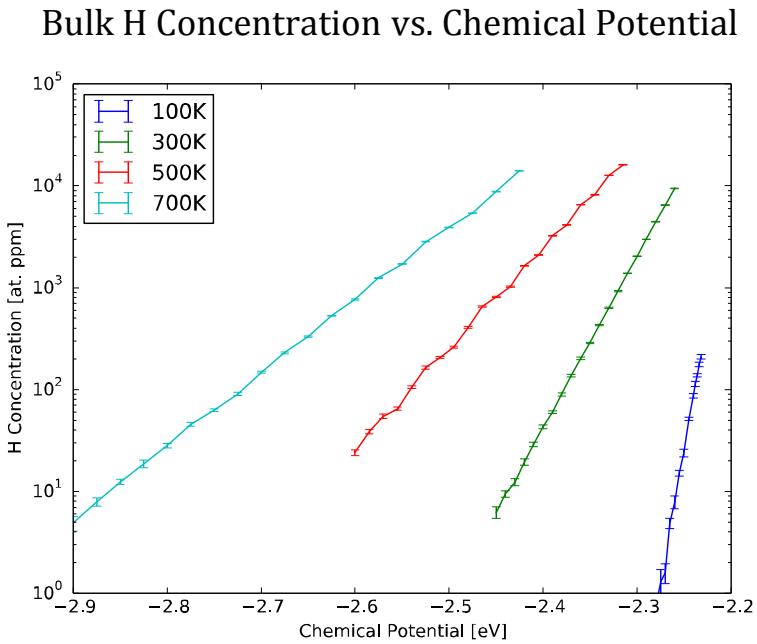
Small deviations from perfect twin boundaries result in substantial changes to thermodynamics

- Misoriented boundaries may be constructed of two types of disconnections

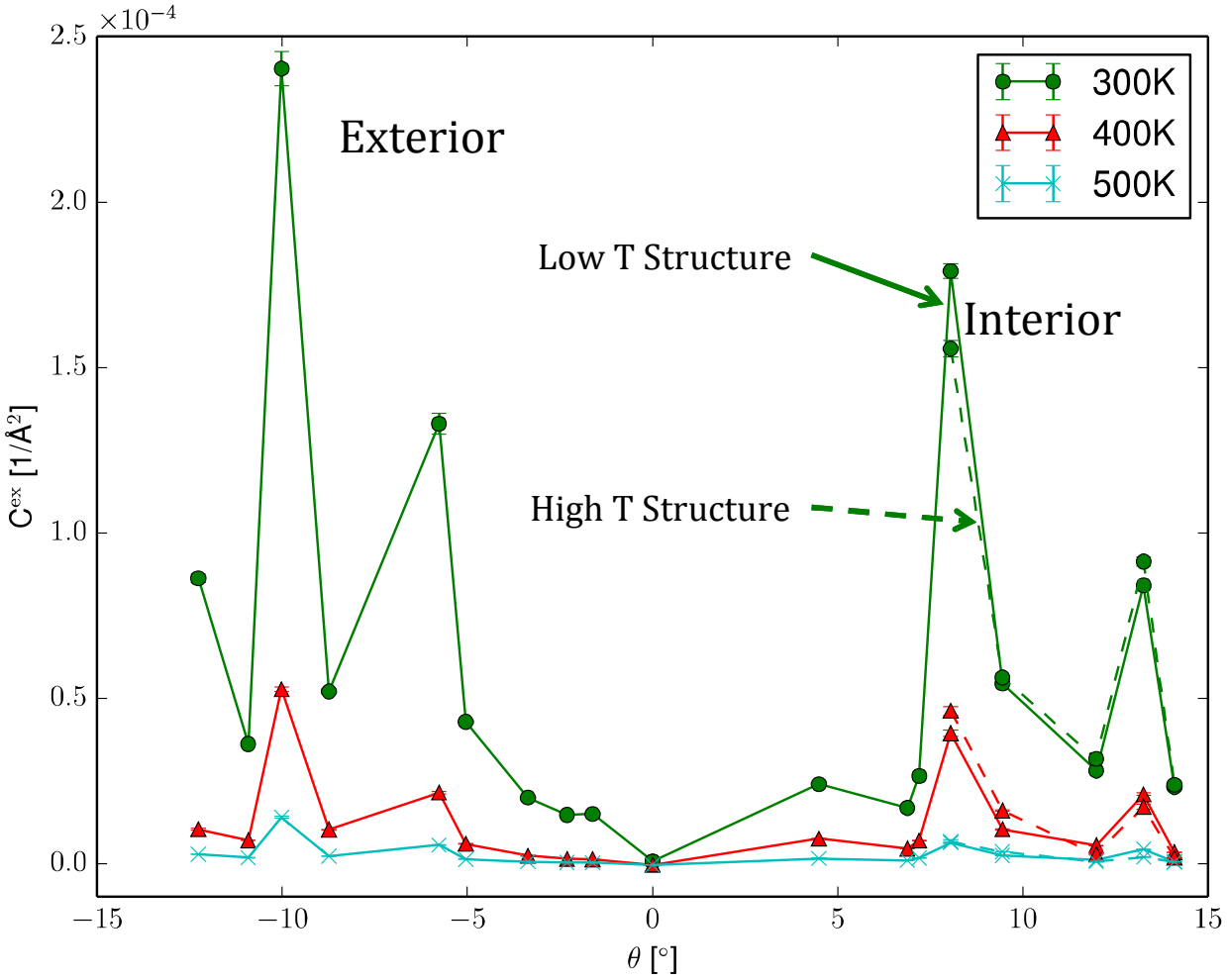
1. Boundaries consisting of interior disconnections
   - May change structure at high temperature ($T \geq 600K$ for Ni)
   - Boundaries misoriented by $\theta \geq 8^\circ$ facet along (111) planes
2. Boundaries consisting of exterior dislocations
   - Retain structure at all temperatures

Calculating H Segregation

- H concentration and location of adsorption sites are determined by Grand-Canonical Monte Carlo
  - Chemical potential set to value that yields desired concentration in bulk
- Details
  - 100,000 MC steps per atom
  - 50% of steps attempt to add/remove H



Hydrogen Segregation is Highly Sensitive to Misorientation



Bulk Concentration of 290appm (2.9×10^{-4} H/Ni)

Hydrogen Segregates to Disconnection Cores in Hydrogenated GBs

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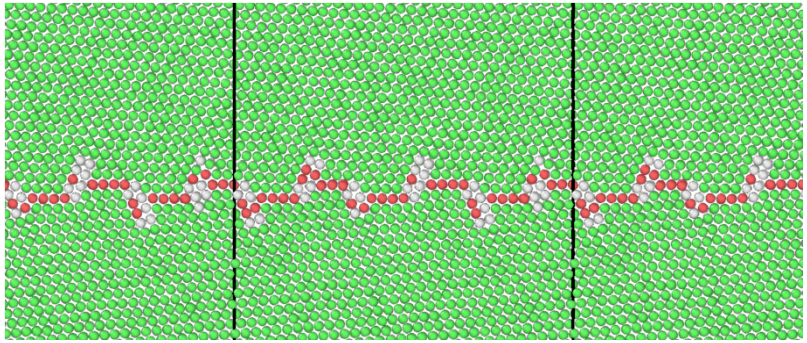
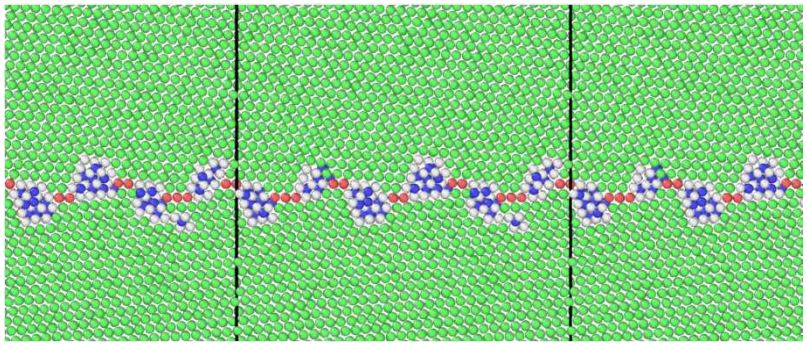
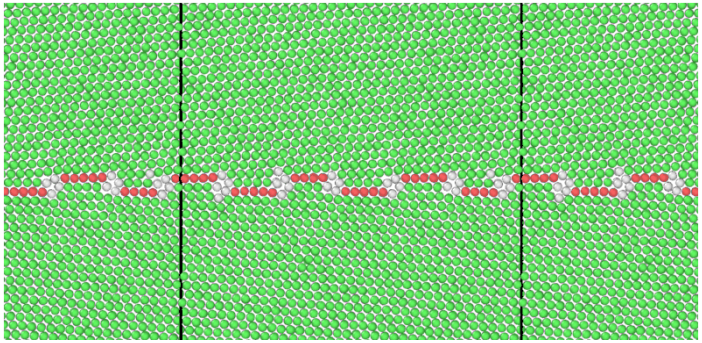
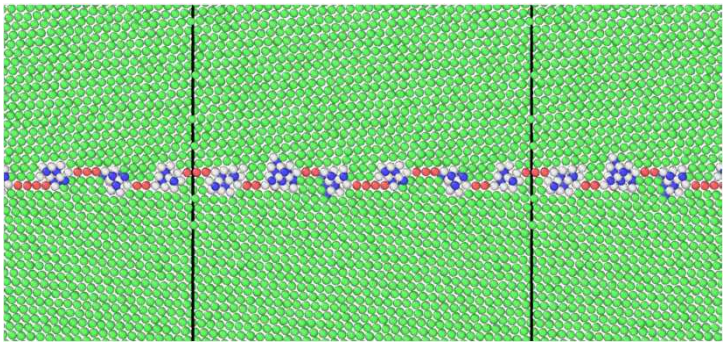
$\theta = -5.05°$





$\theta = 4.49°$





Summary of Hydrogen Segregation To Vicinal Twins

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Temperature dependent structures have little impact on H segregation excess to vicinal twins

- H segregation
  - The coherent twin has a very weak affinity for H adsorption consistent with experimental findings
  - Segregation behavior and energetics of boundaries are asymmetric with respect to misorientation
  - At low concentrations (≈290 appm), nearly all H segregates to disconnection cores
- Ongoing investigations
  - Structure and Segregation of Hydrogen to inclined twins
  - Generation of H adsorption isotherms for Σ3-like grain boundaries

Thank you for your attention

cjobrie@sandia.gov

QUESTIONS?

Potential Validation

- Validation of Angelo, Moody & Baskes† Ni-Al-H EAM Potential
  - Only empirical potential available for Ni-H
- Effect of H Inclusion on Thermodynamics of Boundaries
  - ∑3 (Coherent and Lateral) Twin Boundaries
    - Coherent (111):
      - Adsorption favored by 45.0 meV (oct. site) or 47.9 meV (tet. Site)
    - Lateral (112):
      - Adsorption favored by -0.4eV, but varies greatly.
  - Stacking Faults
    - Presence of H decreases SFE from 88.8 mJ/m^2 to 35.74 (oct. site) or 45.48 (tet. site)
    - H prefers octahedral site on SF by 82.4 meV and tetrahedral site by 74.3 meV when compared to the bulk

† Mod. Simul. Mater. Sci. Eng. 3 p. 289, 1995

Ni-H Potential Validation

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Property	VASP	LAMMPS	Reported	Experiment
A_0 [Å]	3.523	3.520	3.52	3.52
E_0 [eV]	-5.577	-4.450	-4.45	-4.45
B [GPa]	192.240	-	180.33	180
E_{sf} [mJ/m2]	124.201	88.800	89.000	125
E_{solv}(oct) [eV]	-2.170	-2.192	-1.865	-2.050
E_{solv}(tet) [eV]	-1.920	-1.783		
E_{vac} [eV]	0.911	-	1.59	1.6
∑3 (111)	83.622	50.340	-	-
∑3 (112)	-	806.93/1250.36	807/1165	
Edge Disc. [eV/Å]	-	1.005	1.03	-
Screw Disc. [eV/Å]	-	0.756	0.80	-
Lomer Disc. [eV/Å]	-	1.386	1.40	-

Multifaceted Faceting

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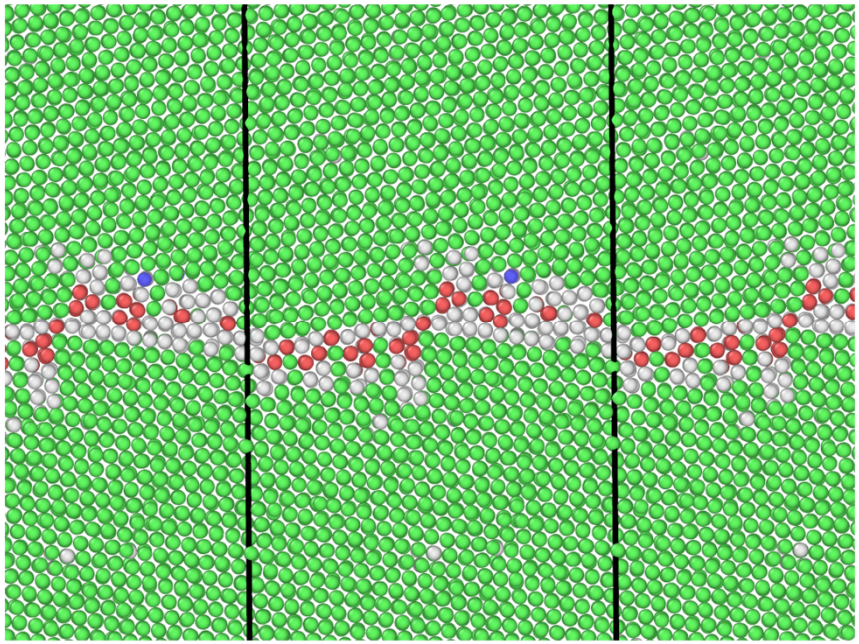
600K



700K