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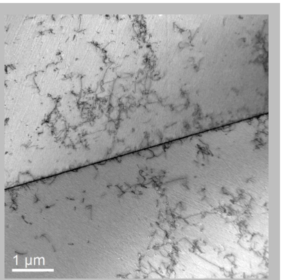


# Investigating the Structure and Segregation of Hydrogen to (nearly) Σ3 Grain Boundaries

**C. J. O’Brien**
D. L. Medlin
S. M. Foiles

*MMM ’14, Symposium E*

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# H in GB Engineered Materials

**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

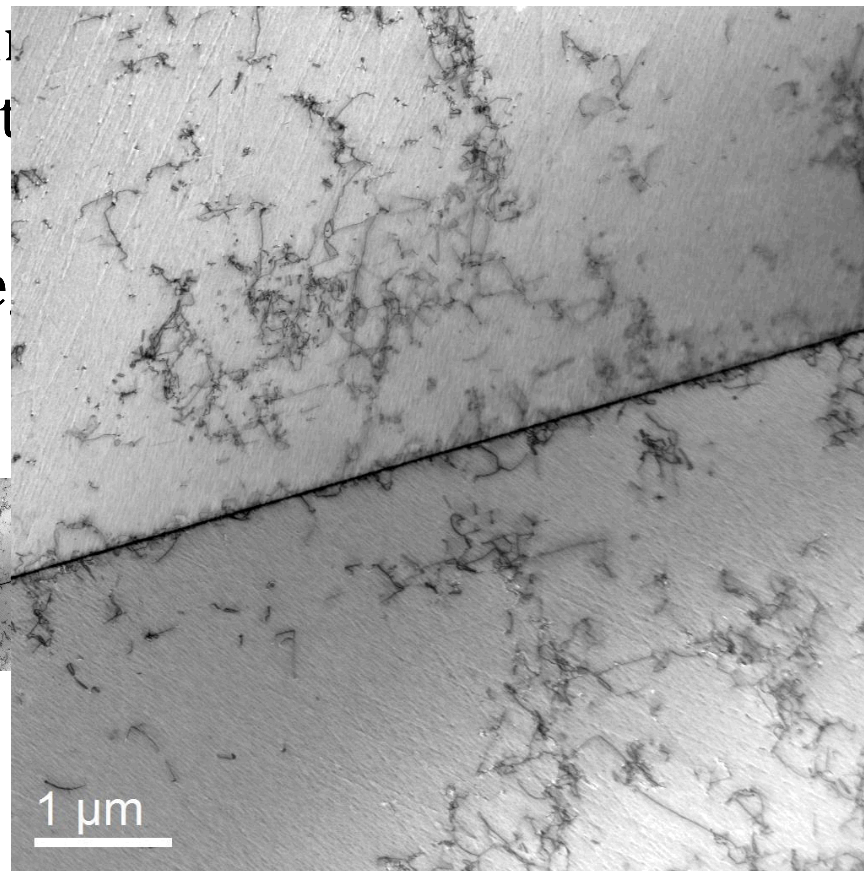


Image provided by D. Medlin

# Atomistic Models Support Higher Length Scale Modeling Efforts

## 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 ($0^\circ \le \Phi \le 90^\circ$)

- Enthalpies calculated via LAMMPS molecular dynamics code using Angelo, Moody, and Baskes† Ni-Al-H EAM potential
- Segregation of hydrogen
  - Investigated from 100–700K
  - Monte Carlo Model used to calculate hydrogen concentration and enthalpies
  - Fixed bulk concentration of $2.9 \times 10^{-4}$ atoms of H per Ni atom (290 appm)

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

# Misoriented Twin Grain Boundaries

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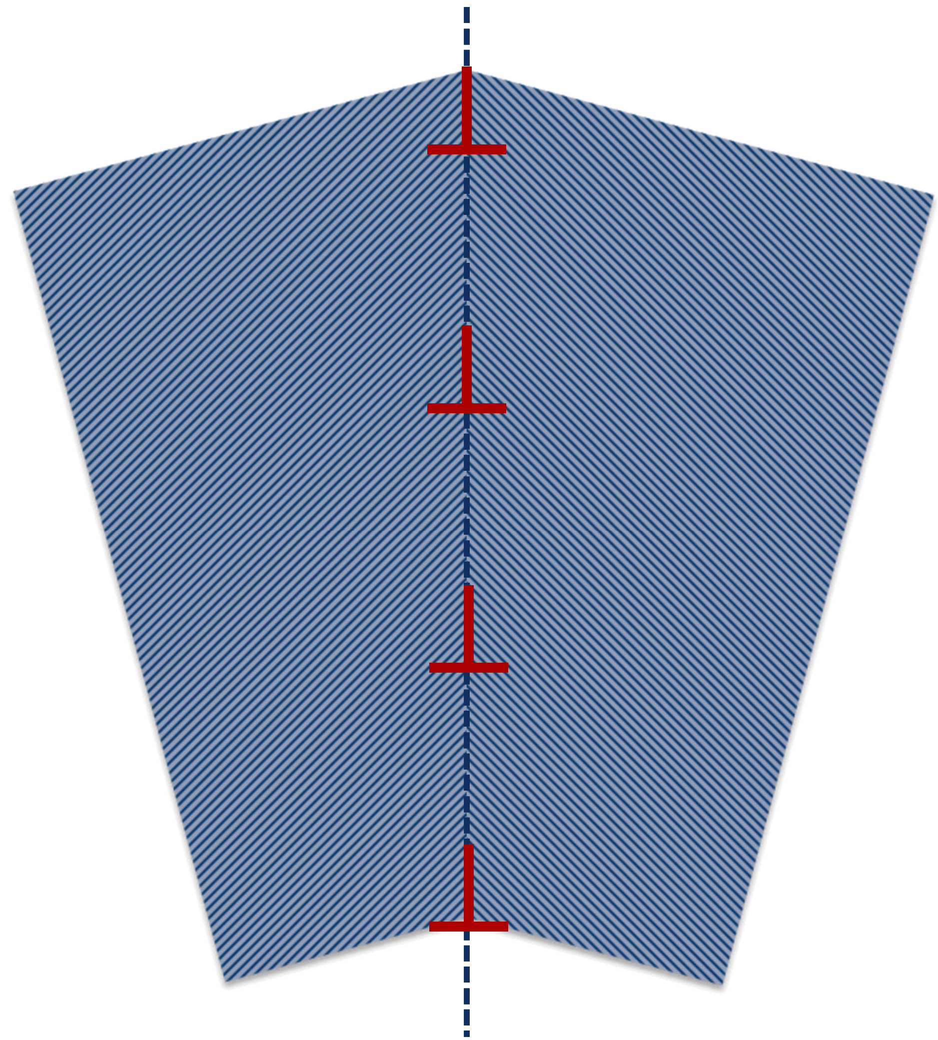
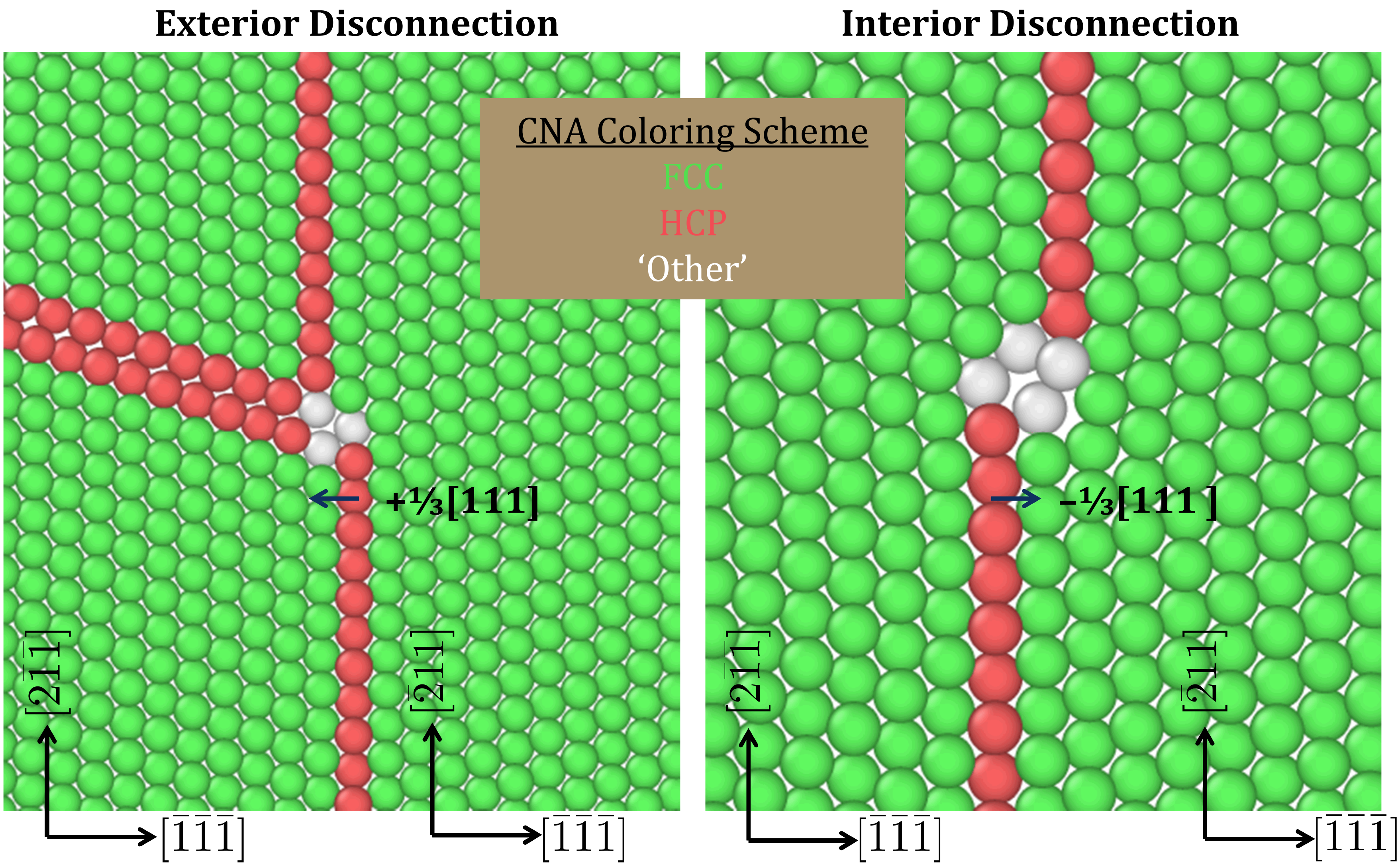
<u>Definition:</u> Misoriented GBs are produced by a symmetric rotation of grains about $(111)\langle 110\rangle$ (coherent) twin $(-15^\circ < \theta < +15^\circ)$

- 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



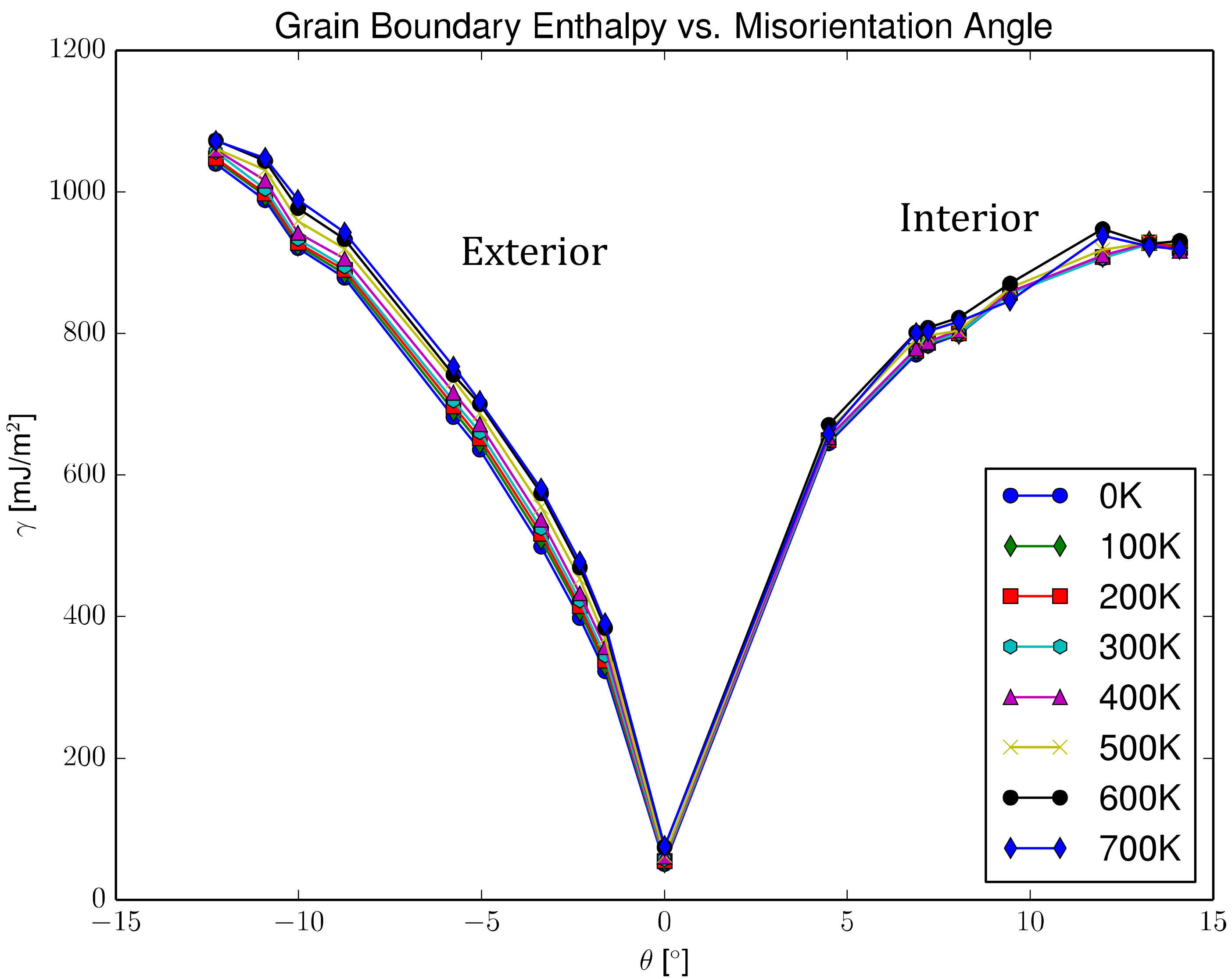
†Phil. Mag. Lett. 85 (8), 387–394, 2005

# Fundamental Structural Difference Between ±⅓⟨111⟩ Disconnections




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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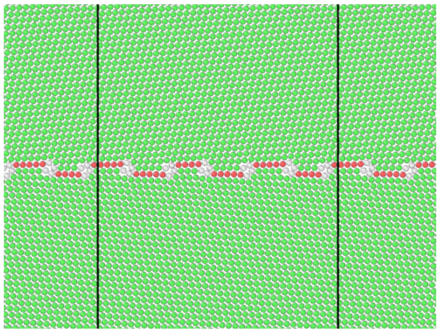
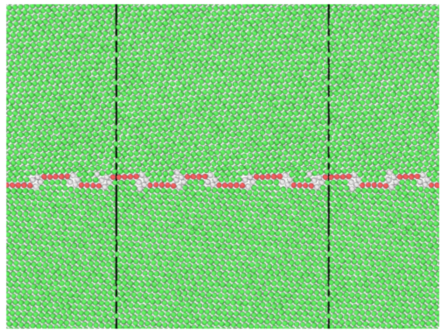
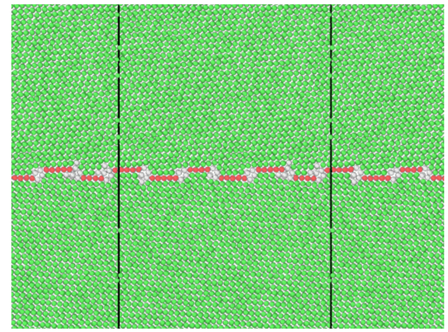
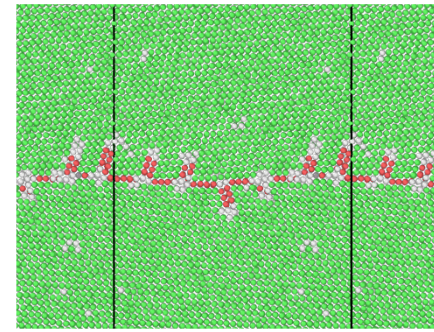
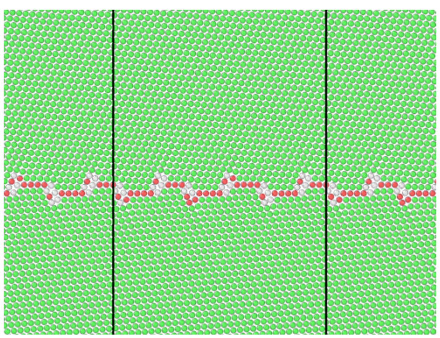
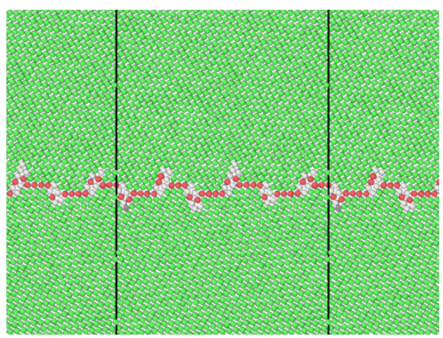
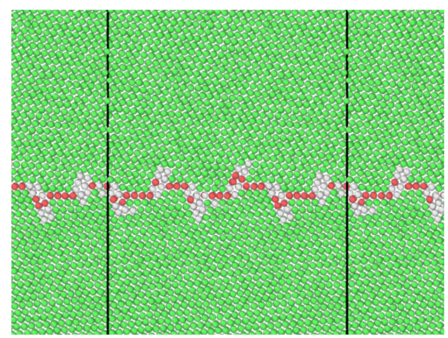
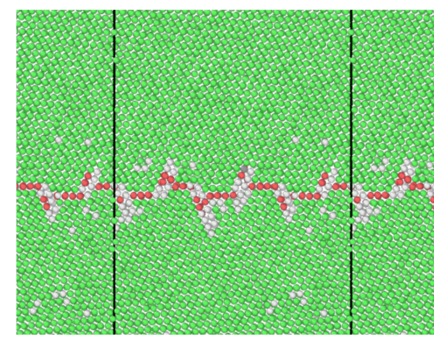
**Interior (θ = +4.49°)**

0K 300K 500K 700K

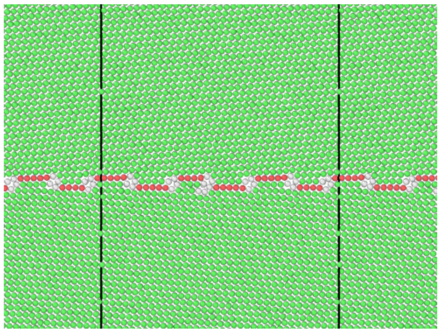
**Exterior (θ = –5.05°)**

0K 300K 500K 700K

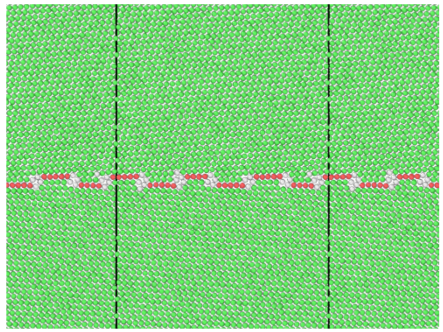
   

# Stability of Extended Stacking Faults in Interior GBs

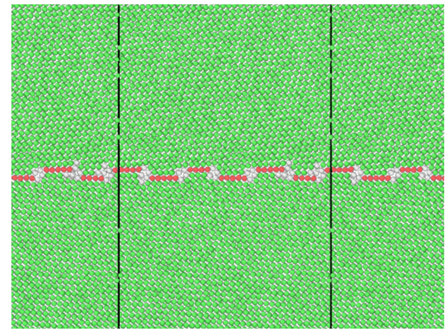
0K→100K



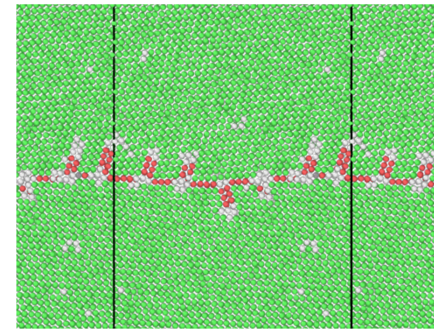
0K→300K



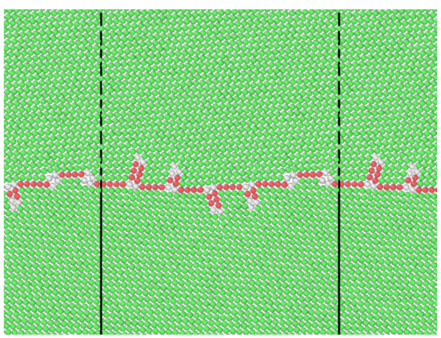
0K→500K



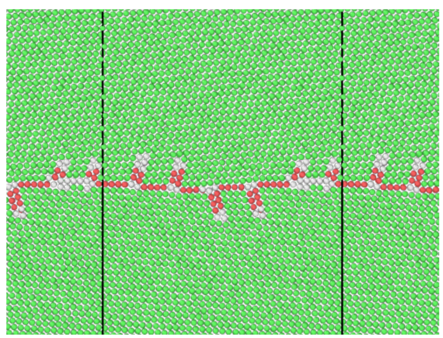
0K→700K



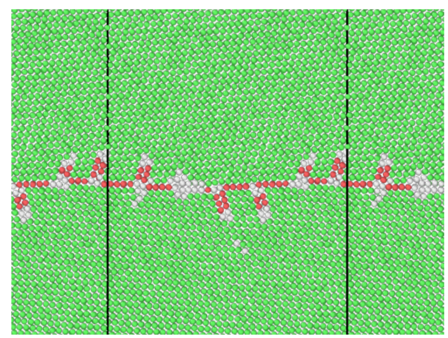
700K→100K



700K→300K



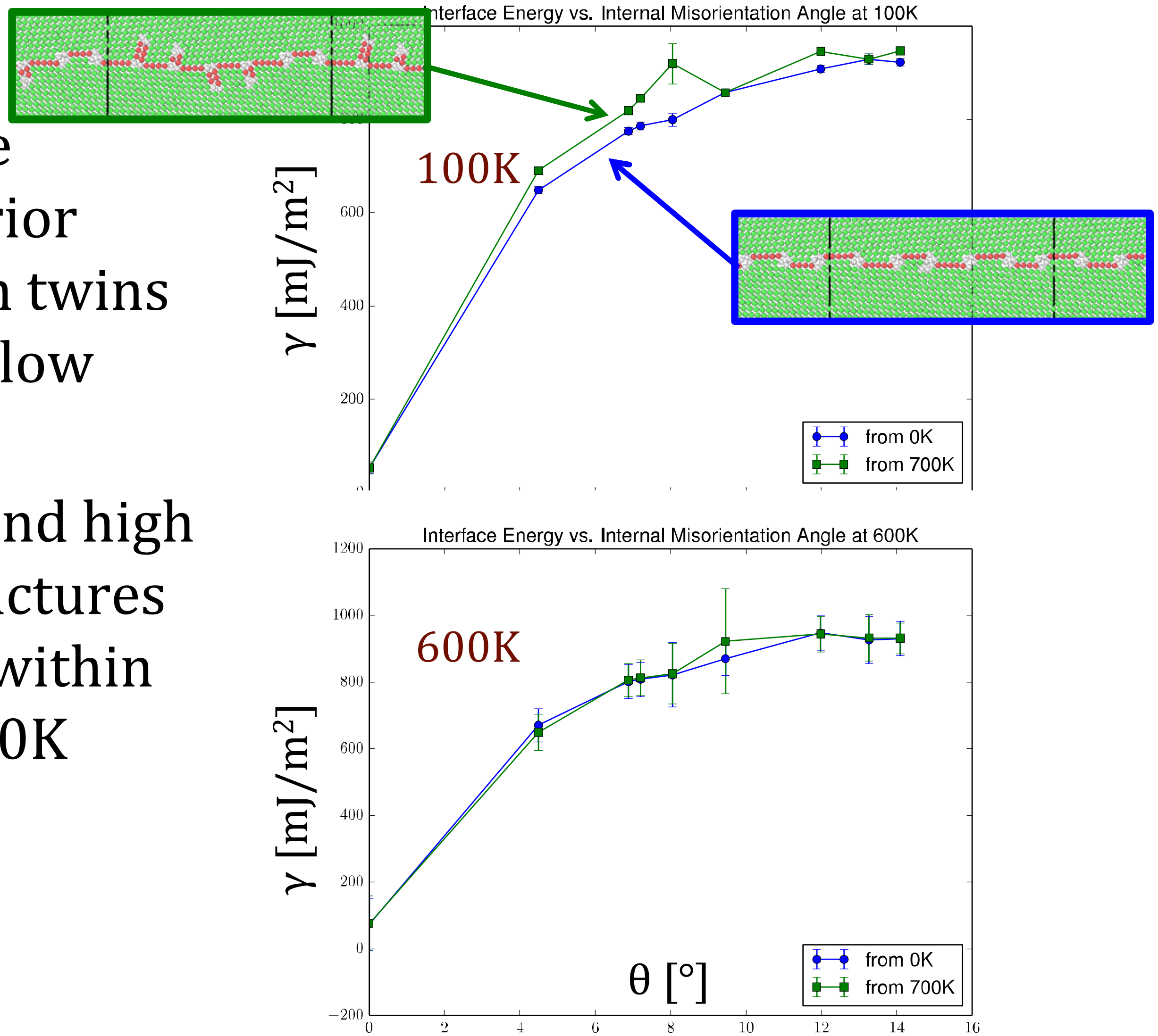
700K→500K



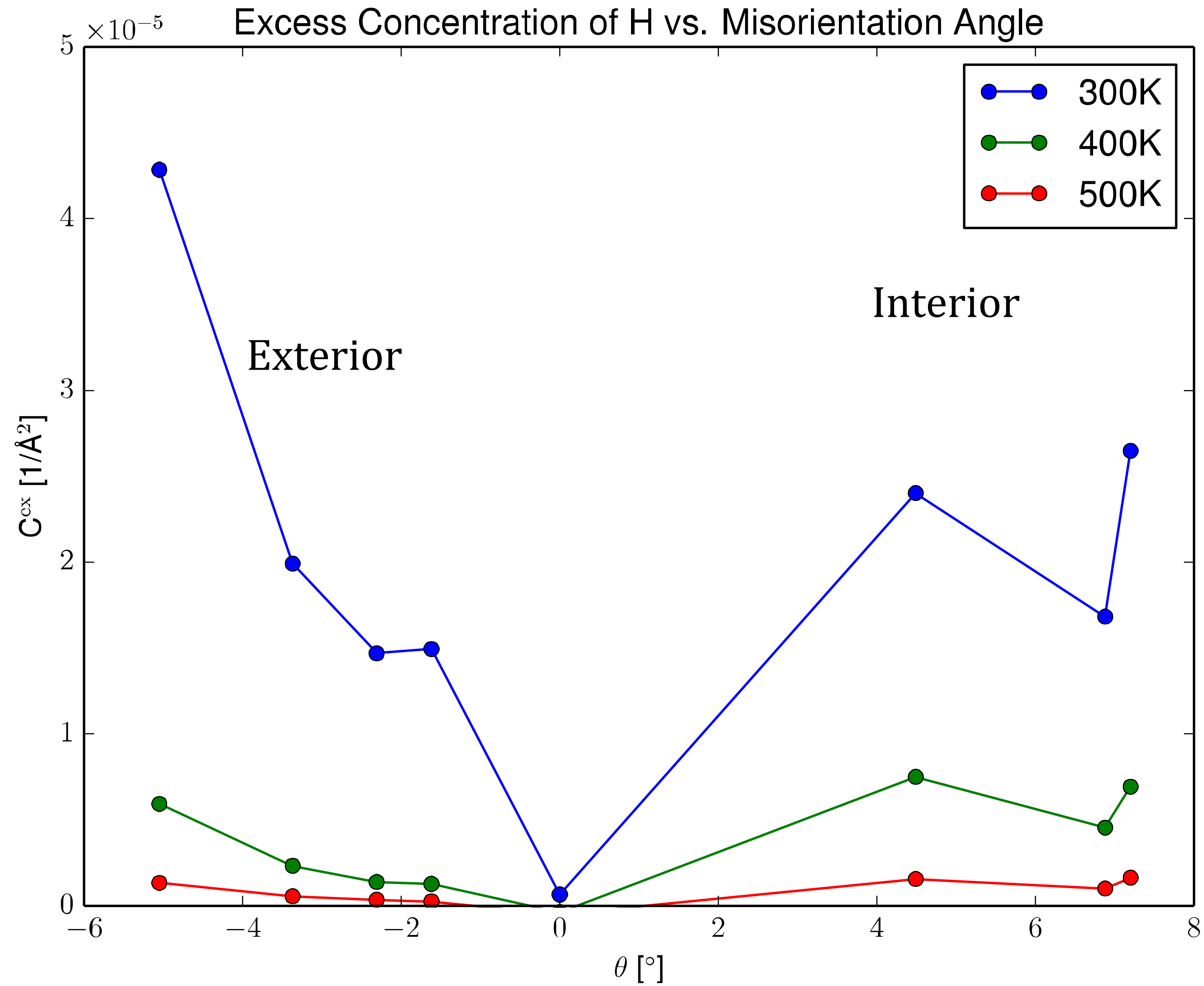
Faults are frozen in upon cooling, but are they stable?

# Compact Core Structure of Interior Disclinations Favored At Moderate Temperatures

- Low temperature structure of interior disconnections in twins is more stable below T ≲ 500K
- Energies of low and high temperature structures are degenerate (within error) for T ≳ 500K

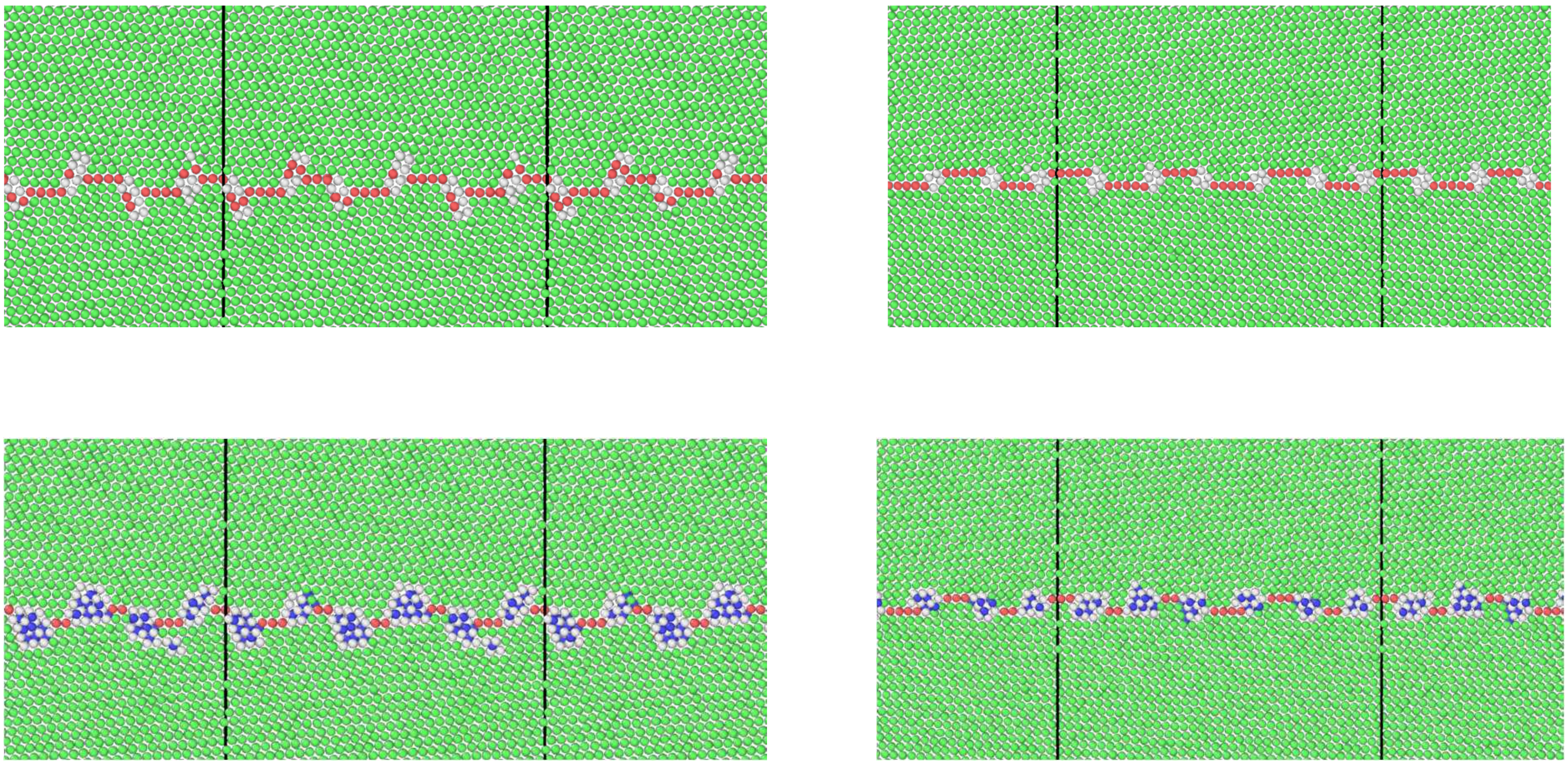


# Hydrogen Segregation is Highly Sensitive to Misorientation



# Hydrogen Segregates to Disconnection Cores in Hydrogenated GBs

$\theta = -5.05°$ $\theta = 4.49°$



# Results Summary

Small deviations from perfect twin boundaries result in substantial changes to thermodynamics and hydrogen segregation behavior.

- Boundary structure may change at high temperature ($T \geq 700K$ for Ni)
- 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
  - Even at low concentrations (≈290 appm), nearly all H segregates to disconnection cores

- Ongoing investigations
  - Thermodynamic stability of faceting in inclined twins
  - Hydrogen segregation to inclined twins
  - Thermodynamic stability of high and low temperature forms of misoriented boundaries
  - Generation of adsorption isotherms for $\Sigma 3$-like grain boundaries

Thank you for your attention

# QUESTIONS?