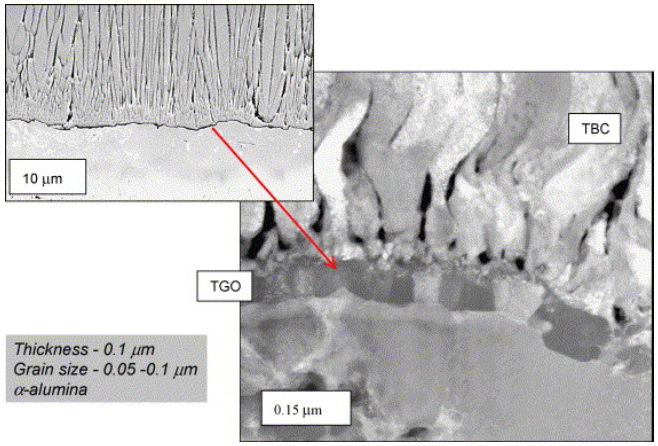
Interfacial Phases & Transport Kinetics

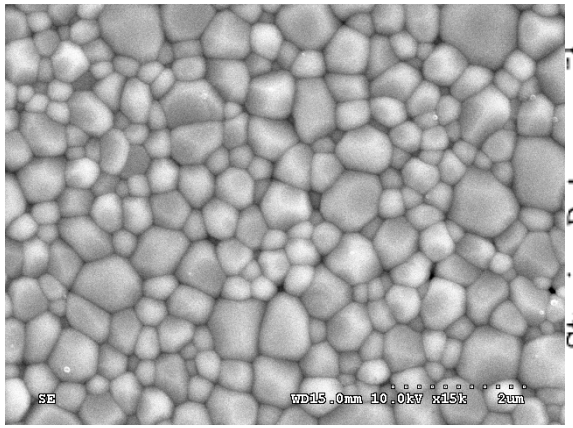
Shen J. Dillon

Interfacial Kinetic Engineering

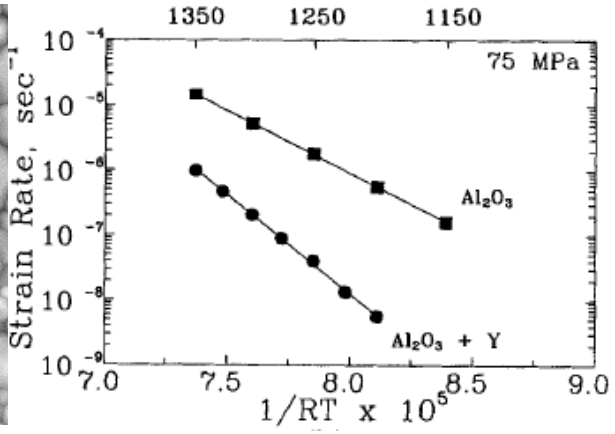
Slow Boundaries



I. Spitsberg, K. More, *Mat. sci, & Eng. A* 2006

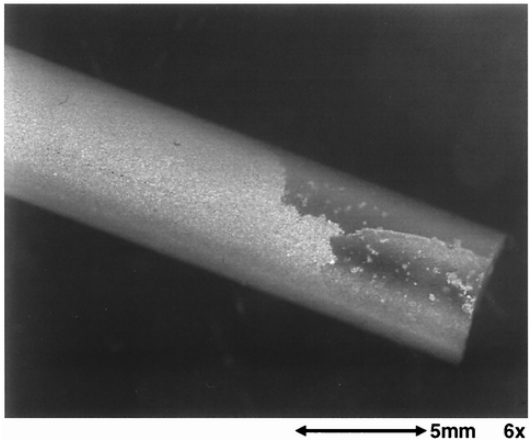


S. Ma

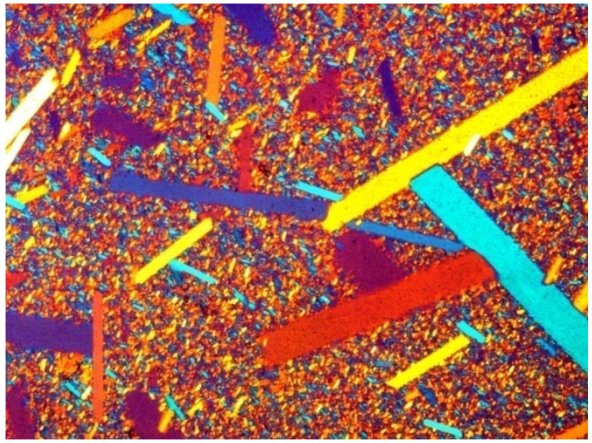


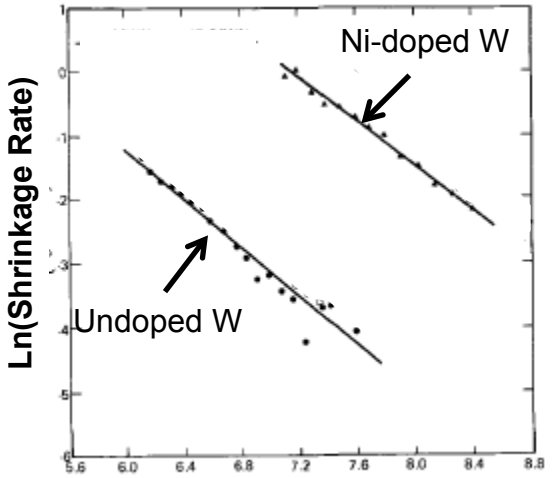
J.D. French, et al.*JACerS* (1994)

Fast Boundaries



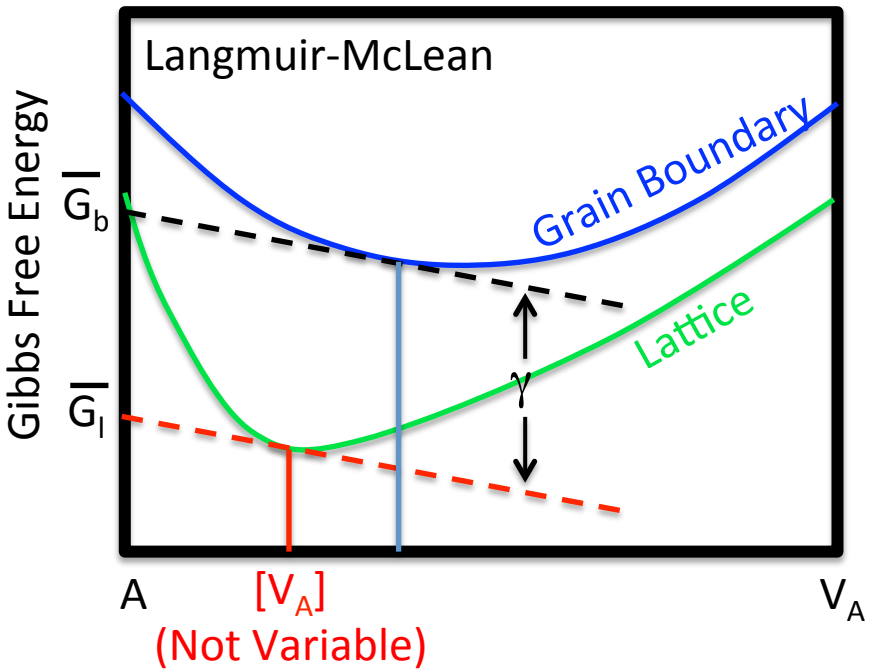
Curtis Scott, et al., *JACerS*, 2002

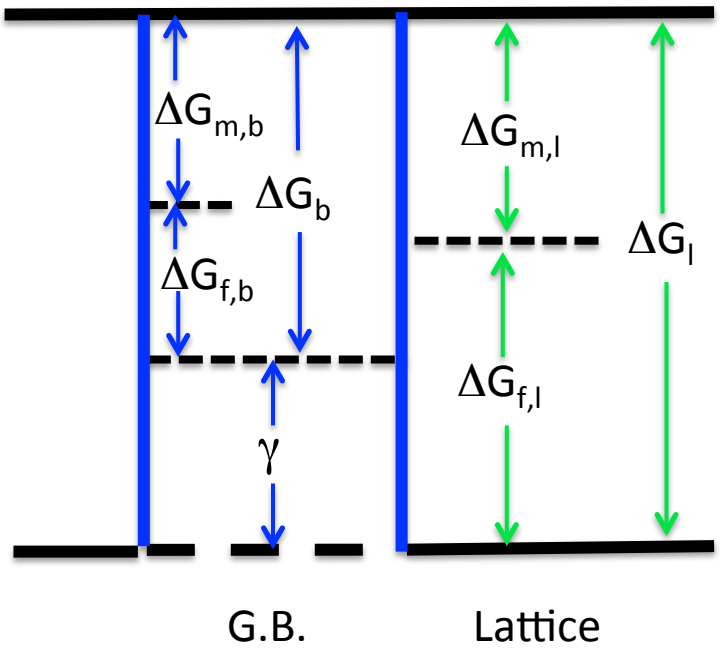




German, Munir, *Met. Trans. A,* (1974)

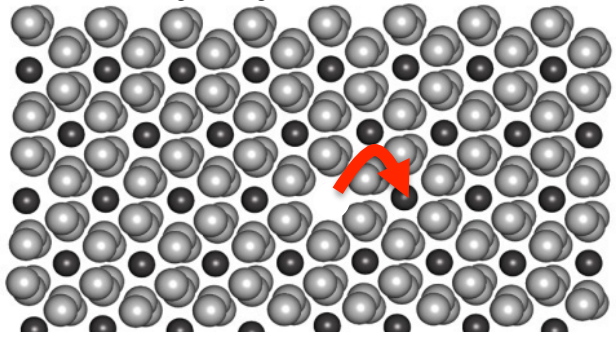
Linking Thermodynamics & Kinetics

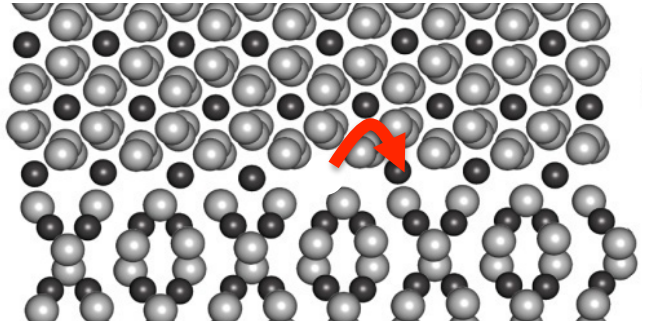




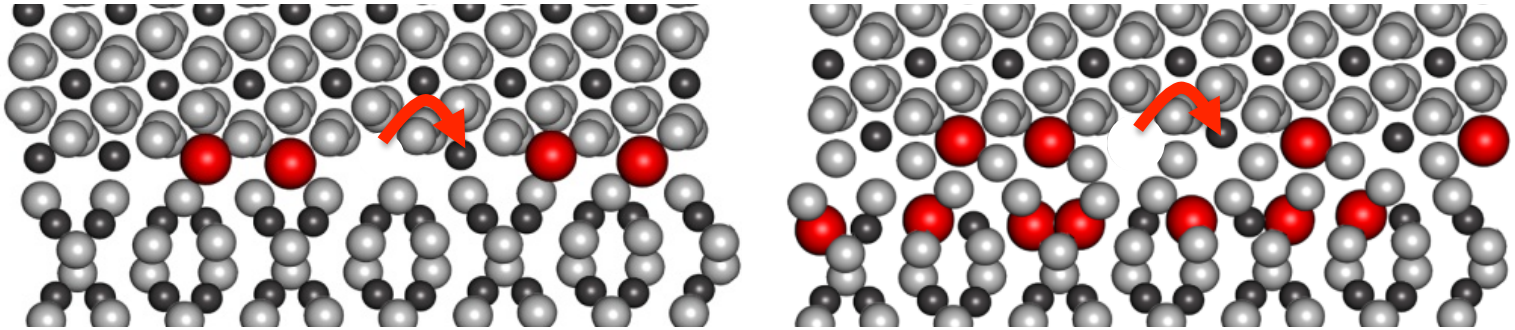
$$D=ga^2C_v\Gamma \qquad C_v=\exp(\Delta S_f/k)(-\Delta H_f/kT) \qquad \Gamma=\nu^*\exp(-\Delta H_m/kT)$$

$$\gamma=\rho[RT\ln(ga_b^2\nu_b^*/g\kappa_l a_l^2\nu_l^*)-T(\Delta S_{f,l}-\Delta S_{f,b})+(\Delta H_{f,l}-\Delta H_{f,b})+(\Delta H_{m,l}-\Delta H_{m,b})]$$





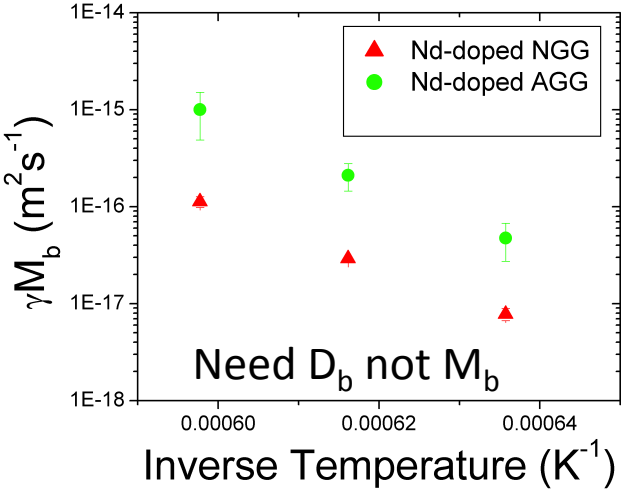
Comparing Complexions (ΔH & ΔS)

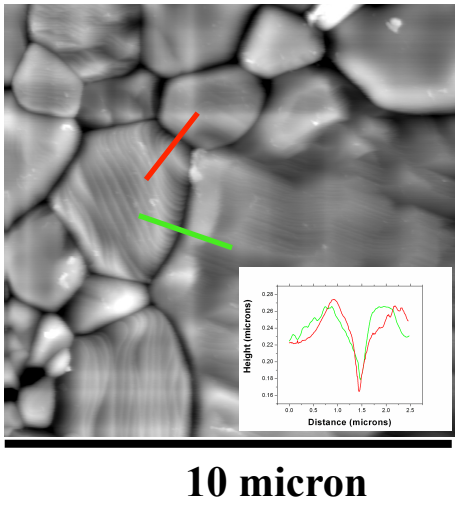


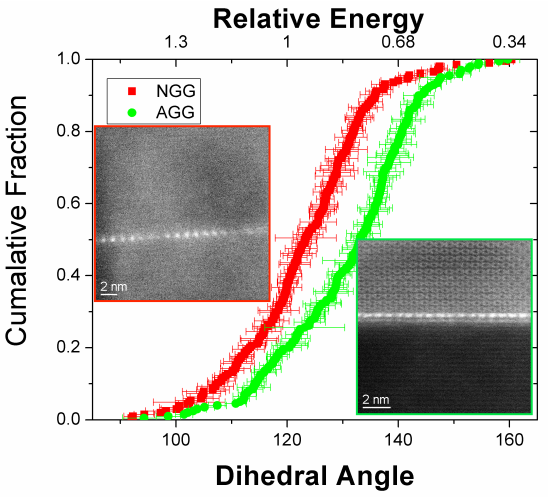
$$\Delta\gamma=\Delta\rho[RT\ln(g a_I^2 \nu_I^*/g\kappa_{II} a_{II}^2 \nu_{II}^*)-T(\Delta S_{f,I}-\Delta S_{f,II})+(\Delta H_{f,I}-\Delta H_{f,II})+(\Delta H_{m,I}-\Delta H_{m,II})]$$

Simplifying Assumptions: $\Delta\gamma=\Delta\rho[-T(\Delta S_I-\Delta S_{II})+(\Delta H_I-\Delta H_{II})]$

Approach:

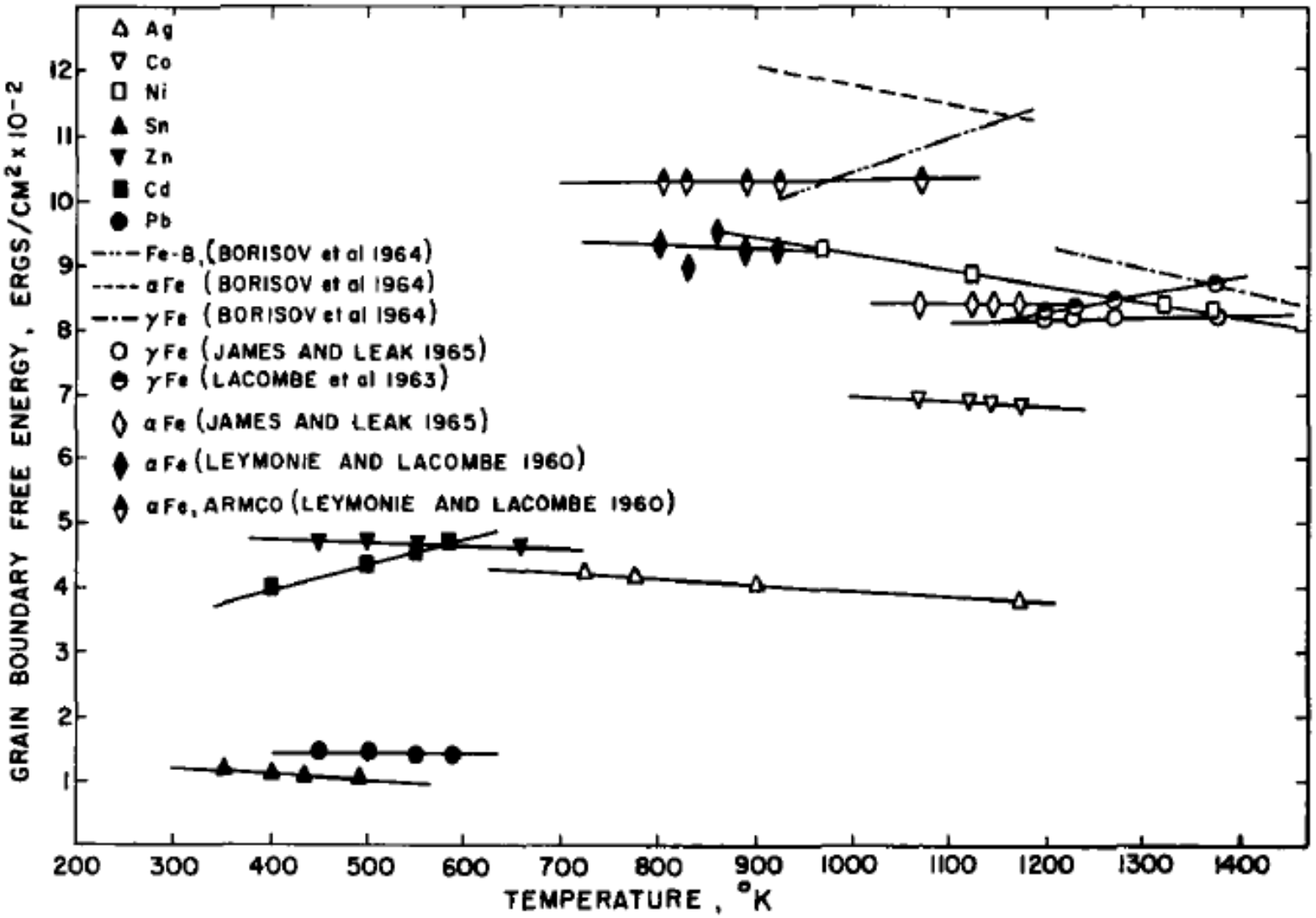






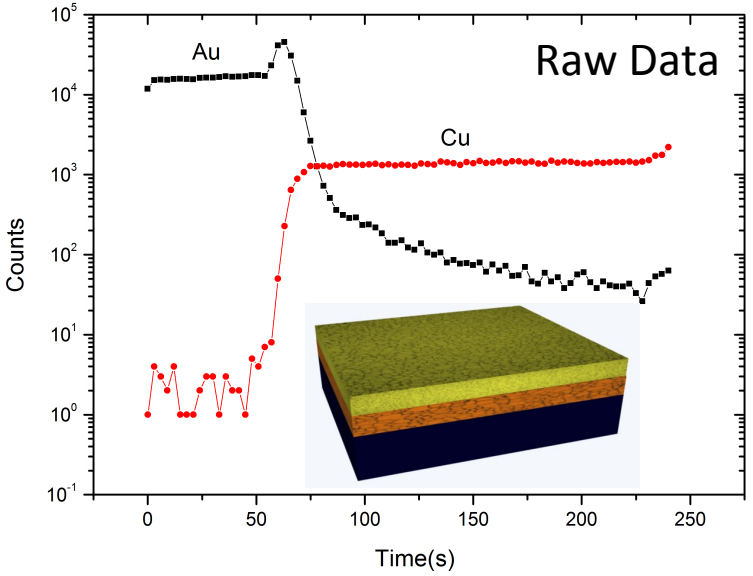
Check: $\gamma=\rho[RT\ln(g a_b^2 \nu_b^*/g\kappa_I a_I^2 \nu_I^*)-T(\Delta S_I-\Delta S_b)+(\Delta H_I-\Delta H_b)+(P\Delta V_I-P\Delta V_b)]$

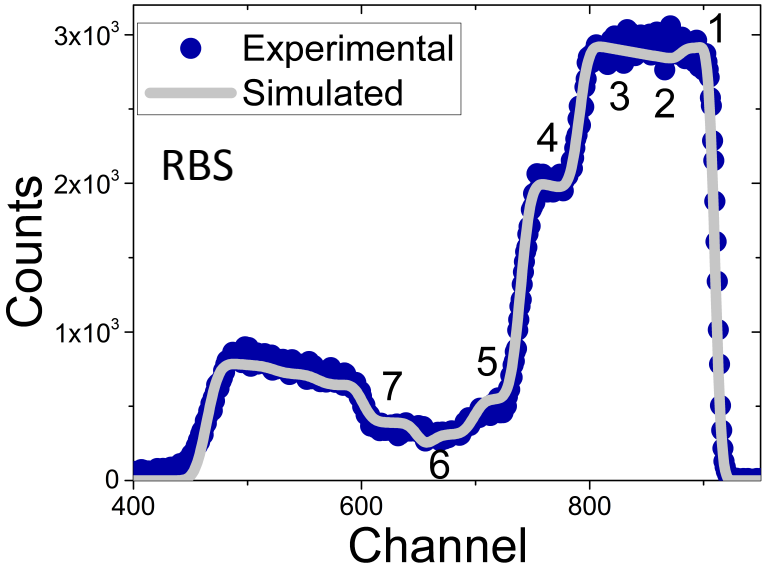
Early Tests of Borisov Model

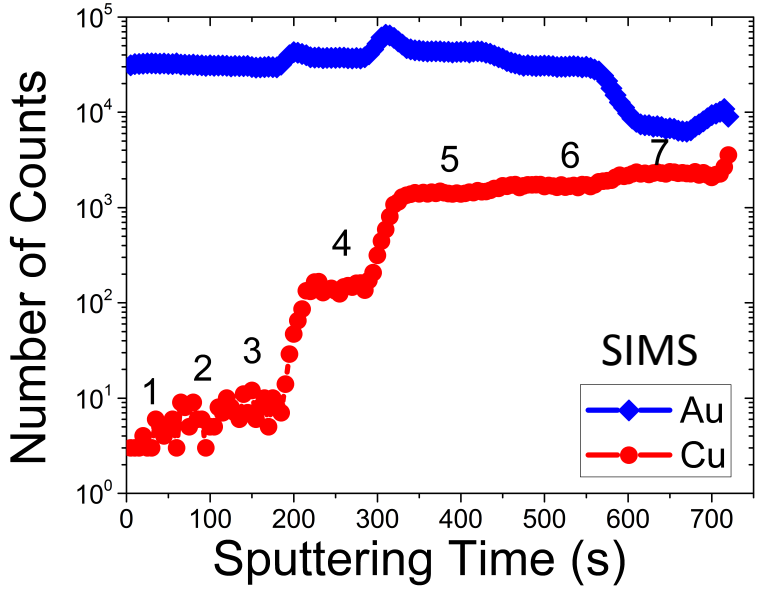


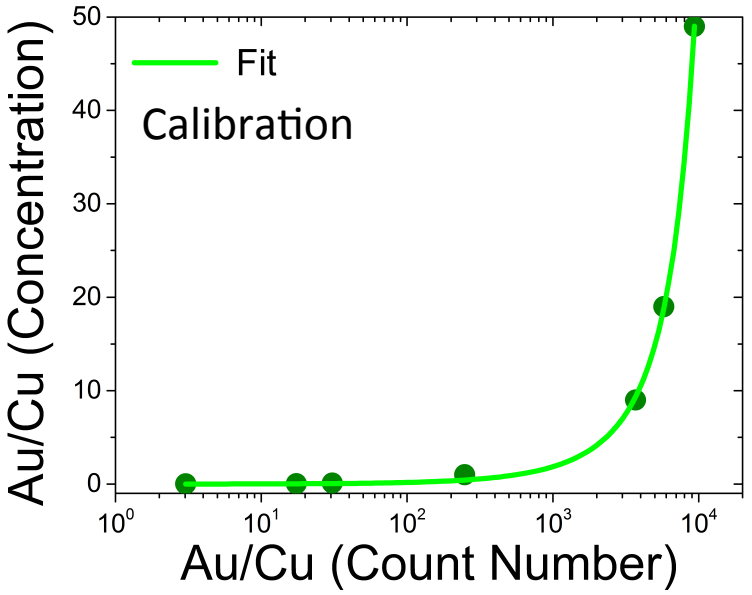
Pelleg *Phil. Mag. (*1966)

Sample Preparation and Testing



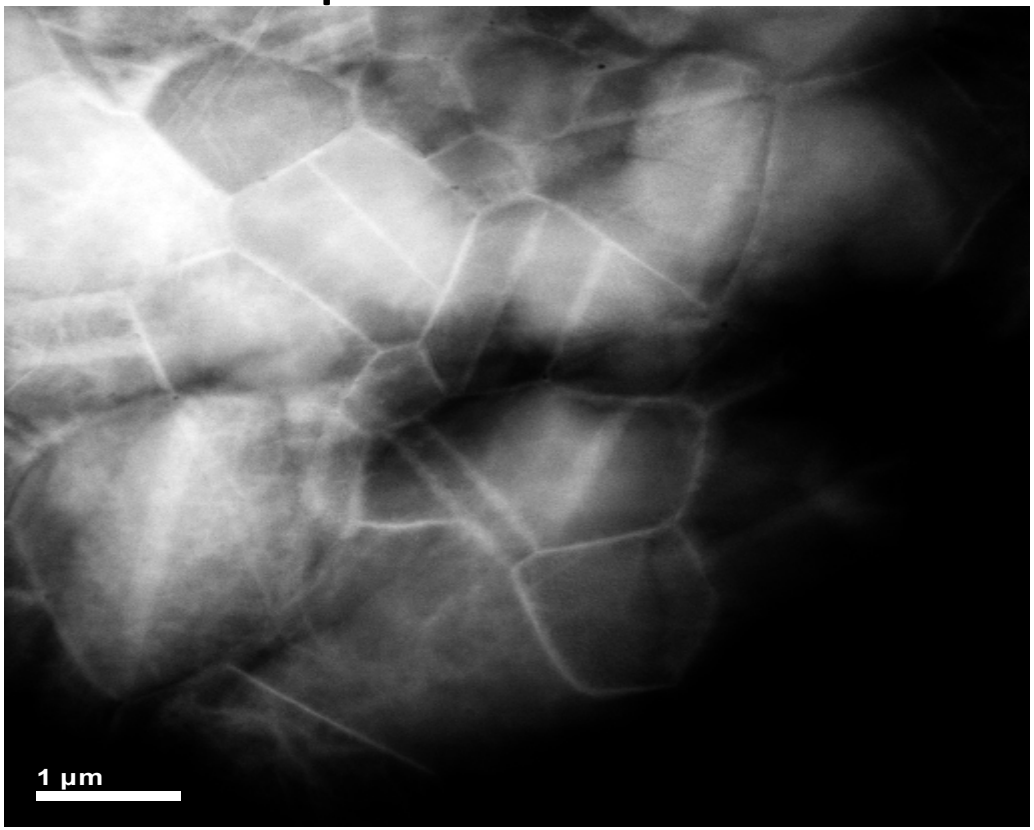




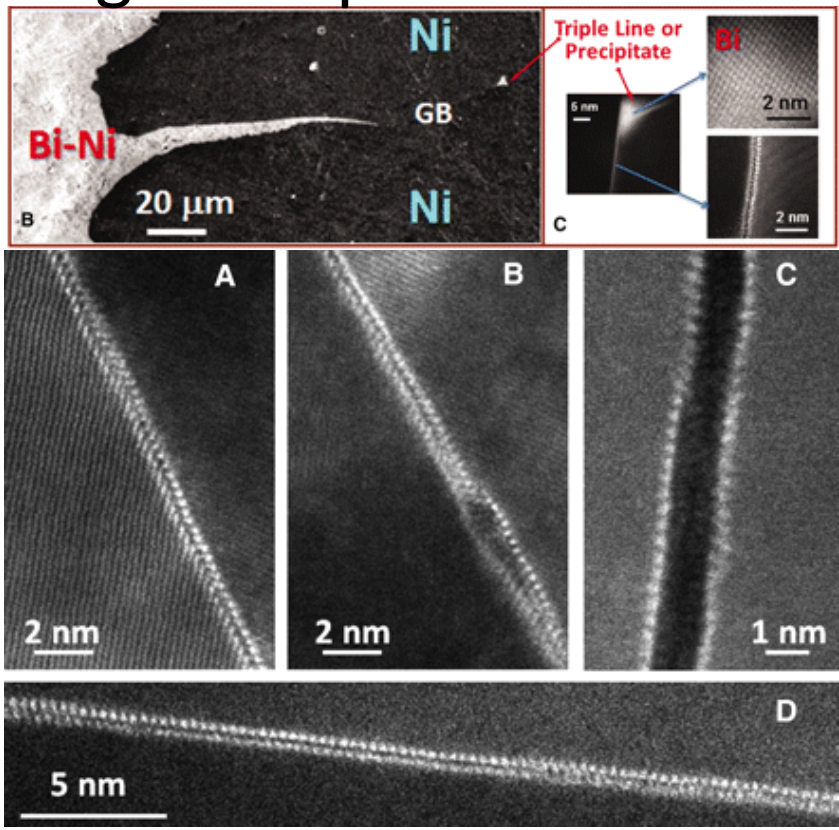


Bi-doped Ni

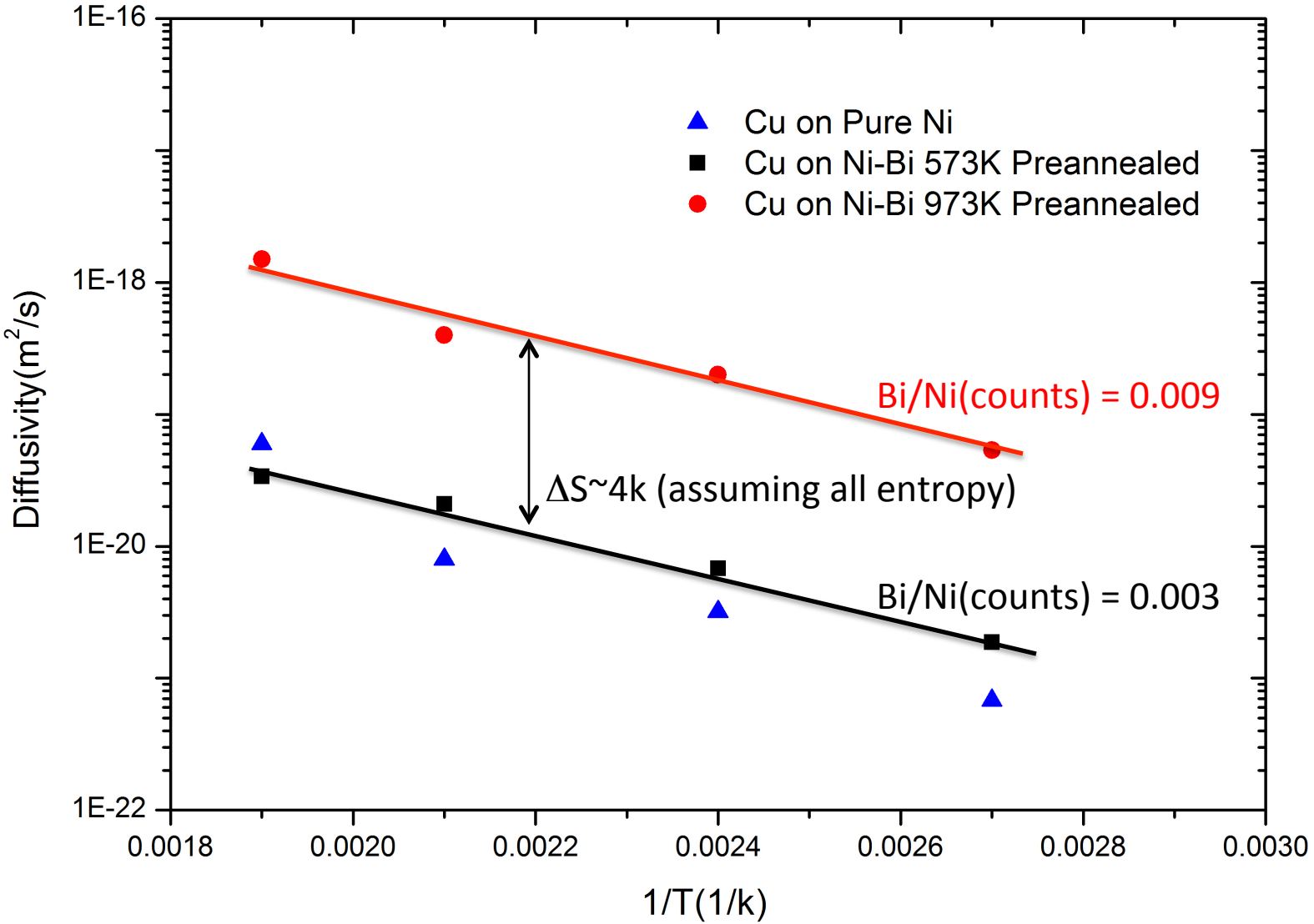
Low Temperature 300°C



High Temperature 700°C

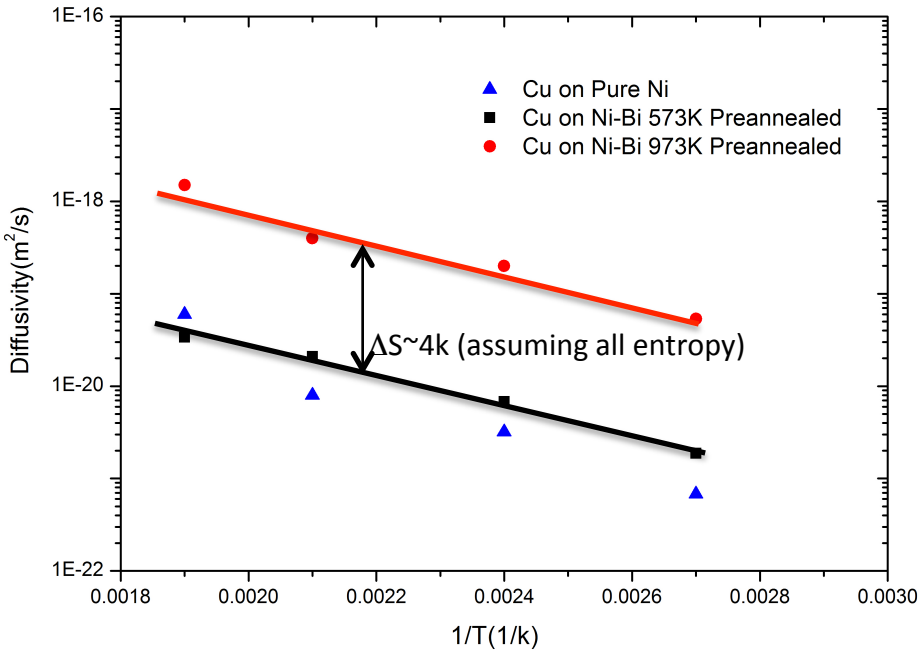


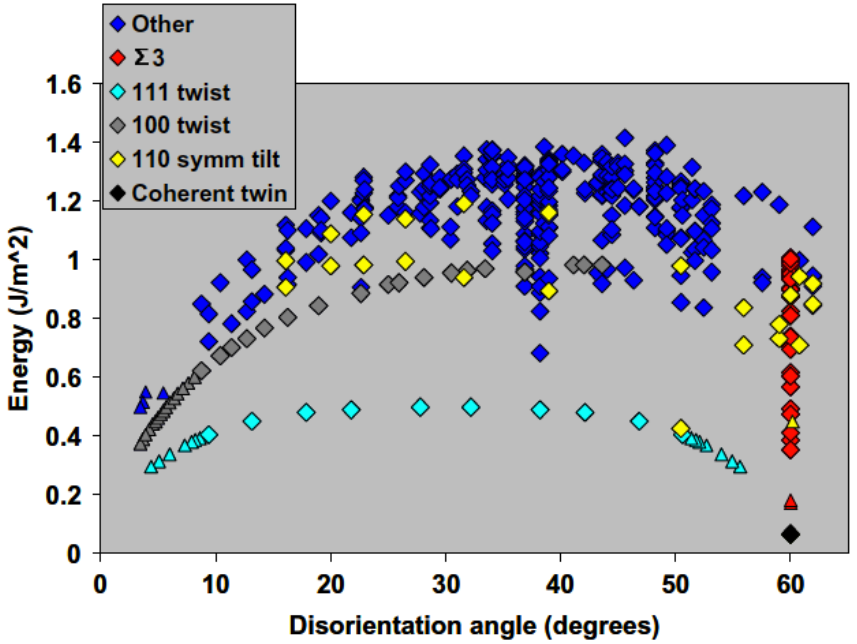
Cu diffusion into Bi doped Ni Matrix



Cu diffusion into Ni and Ni-Bi (GB doped) samples

Cu diffusion into Bi doped Ni Matrix





Olmstead et al. *Acta Mater.* (2009)

ΔS~4k (assuming entropy only)

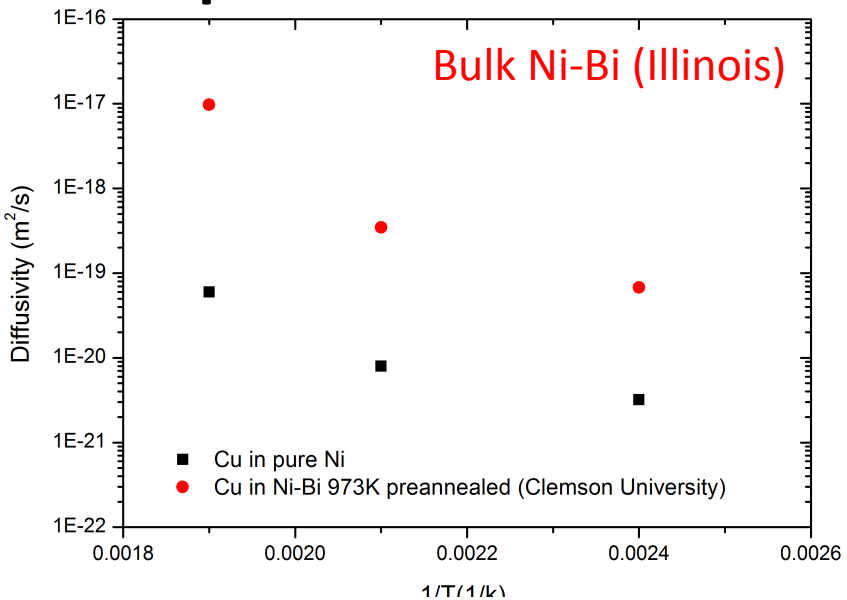
$\Delta\gamma$~0.3-0.5 J/m^2

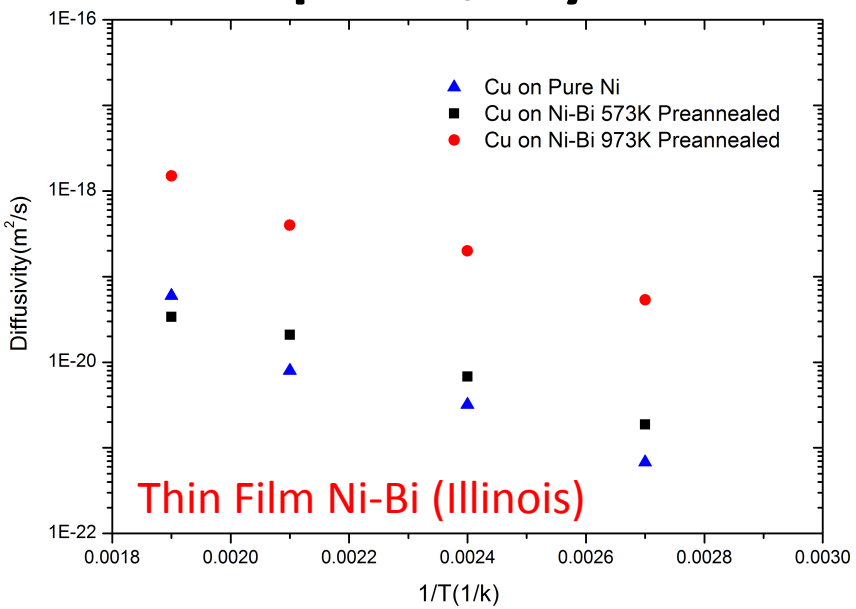
Table I. The Mean Relative Energies of Different Grain-Boundary Complexions Occurring as Normal and Abnormal Grains in Doped and Undoped Alumina Annealed at Different Temperatures

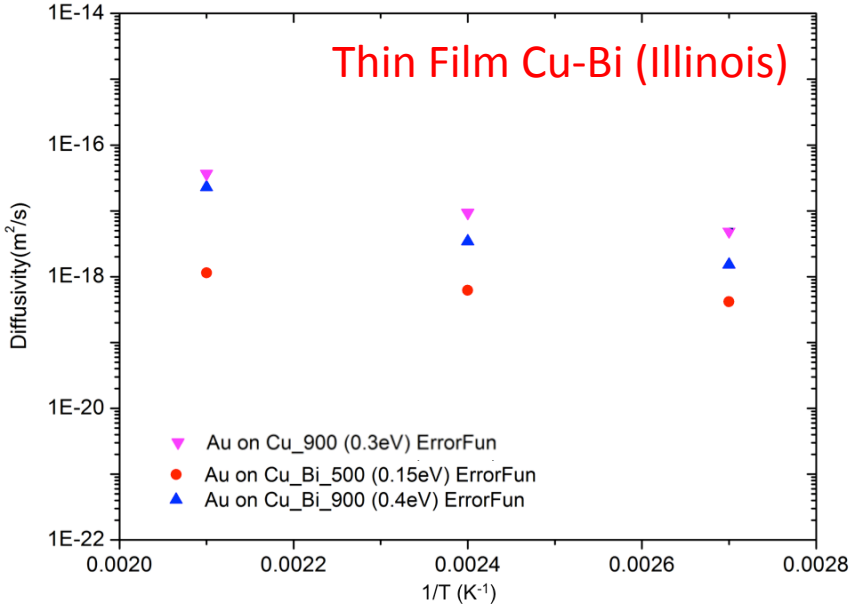
Chemistry	Temperature (°C)	Complexion	Relative energy	% energy change (complexion transition)
Undoped	1400	II (NGG)	1.11	
	2020	II (NGG)	1.08	
100 ppm-Nd_2O_3	1400	I (NGG)	0.95	−16
	1400	III (AGG)	0.8	
100 ppm-Y_2O_3	1400	I (NGG)	0.57	−46
	1400	III (AGG)	0.31	
500 ppm-MgO	1400	I (NGG)	1.07	−26
	1700	III (NGG)	0.79	
30 ppm-CaO	1200	I (NGG)	0.82	−20
	1200	III (AGG)	0.69	
200 ppm-SiO_2	1200	I (NGG)	0.68	−10
	1200	III (AGG)	0.61	

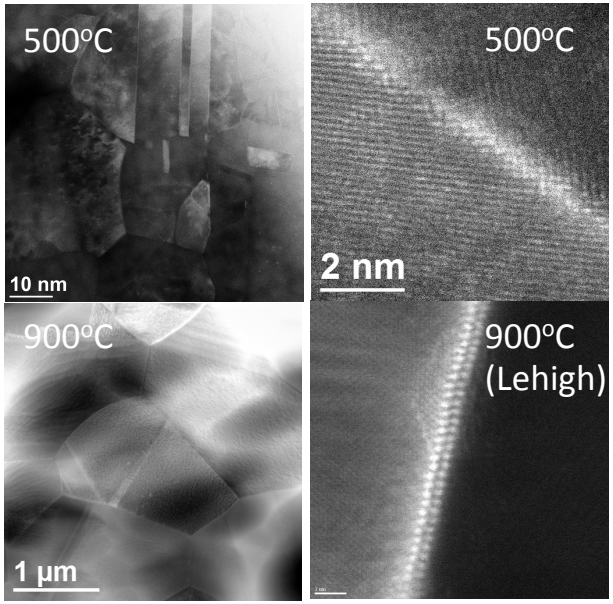
Dillon et al. *JACerS* 2010

Comparison with Other Samples/Systems

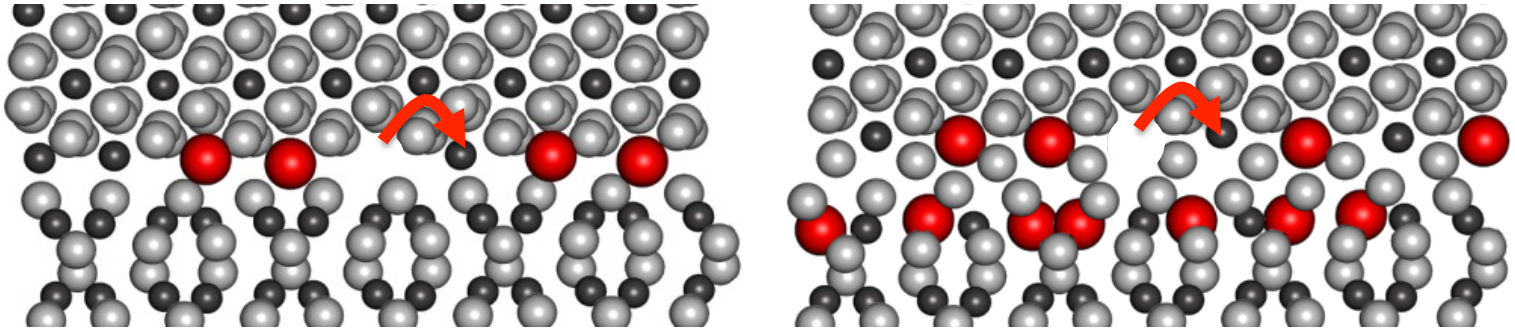








Experimental Approach

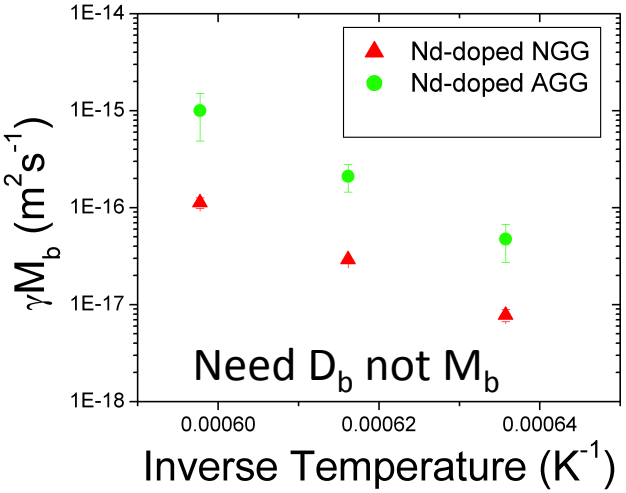


$$\Delta\gamma=\Delta\rho[RT\ln(ga_I^2\nu_I^*/g\kappa_{II}a_{II}^2\nu_{II}^*)-T(\Delta S_{f,I}-\Delta S_{f,II})+(\Delta H_{f,I}-\Delta H_{f,II})+(\Delta H_{m,I}-\Delta H_{m,II})]$$

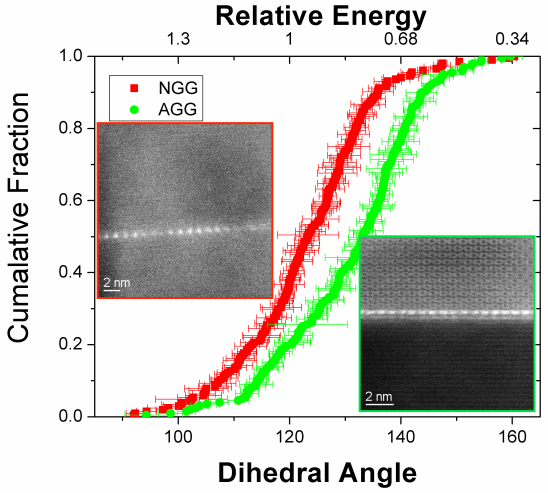
Simplifying Assumptions: $\Delta\gamma=\Delta\rho[-T(\Delta S_I-\Delta S_{II})+(\Delta H_I-\Delta H_{II})]$

Approach:

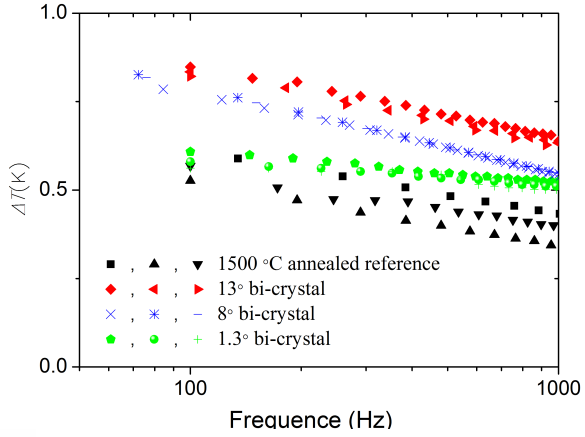
Measure Diffusivity



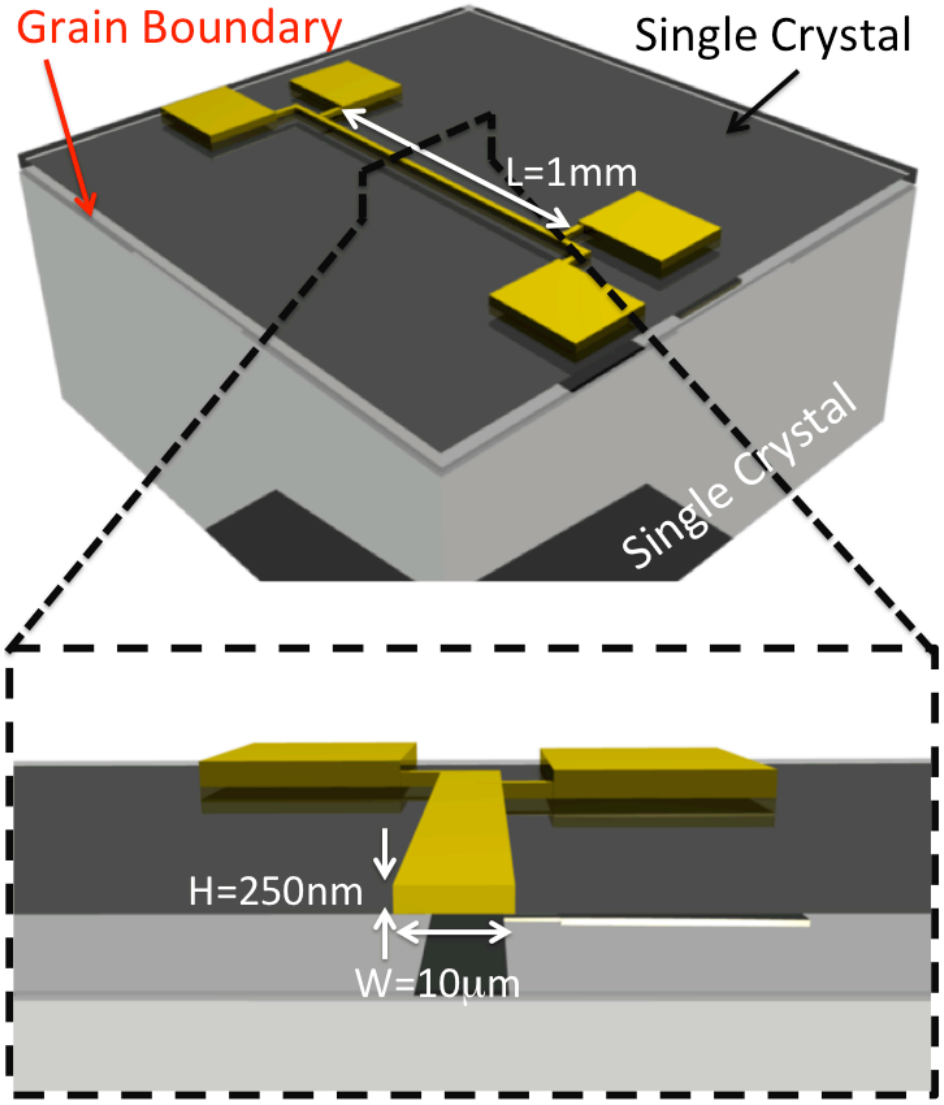
Measure Relative Energy

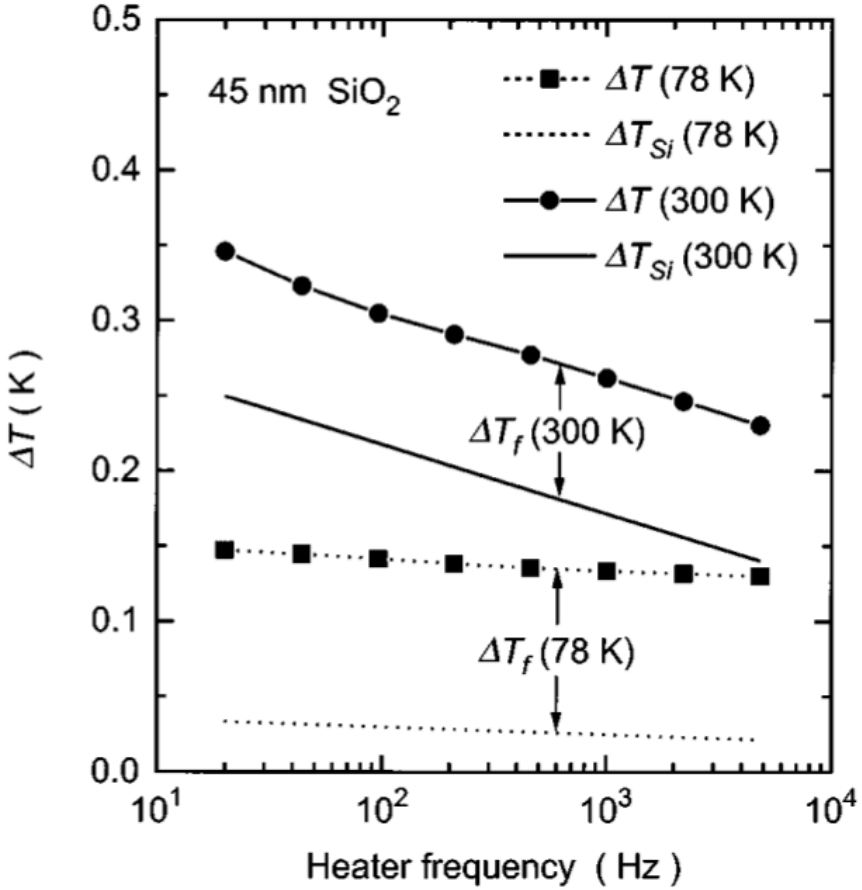


Measure Therm. Cond.



Interfacial Thermal Conductance - Approach



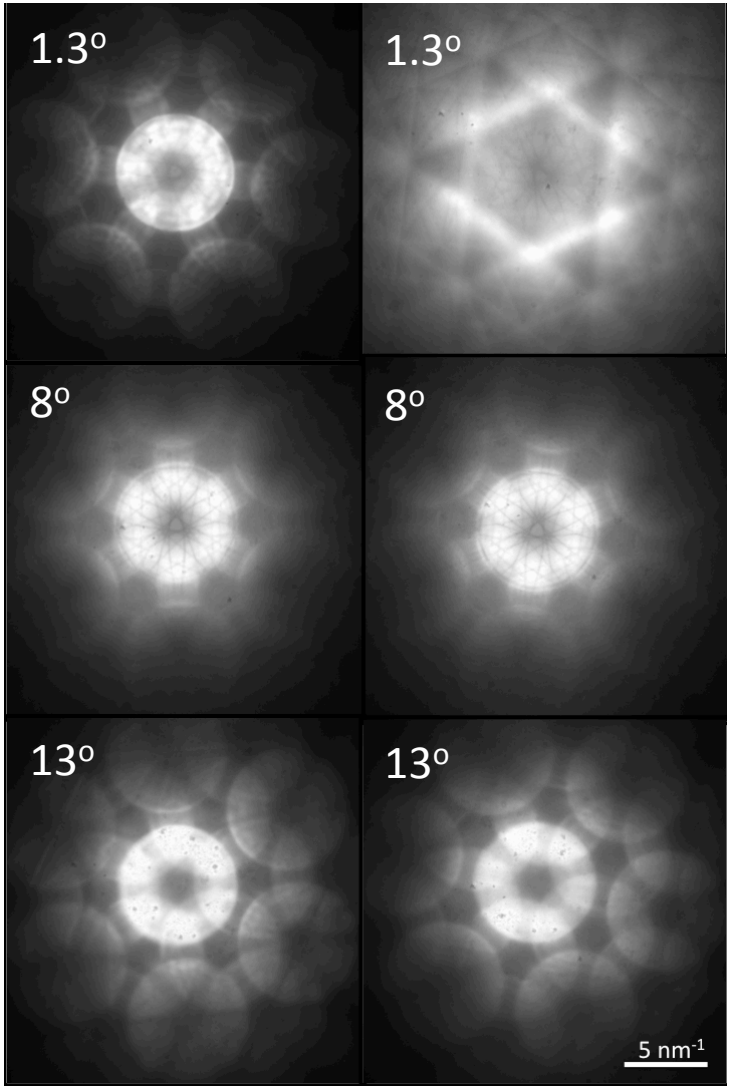


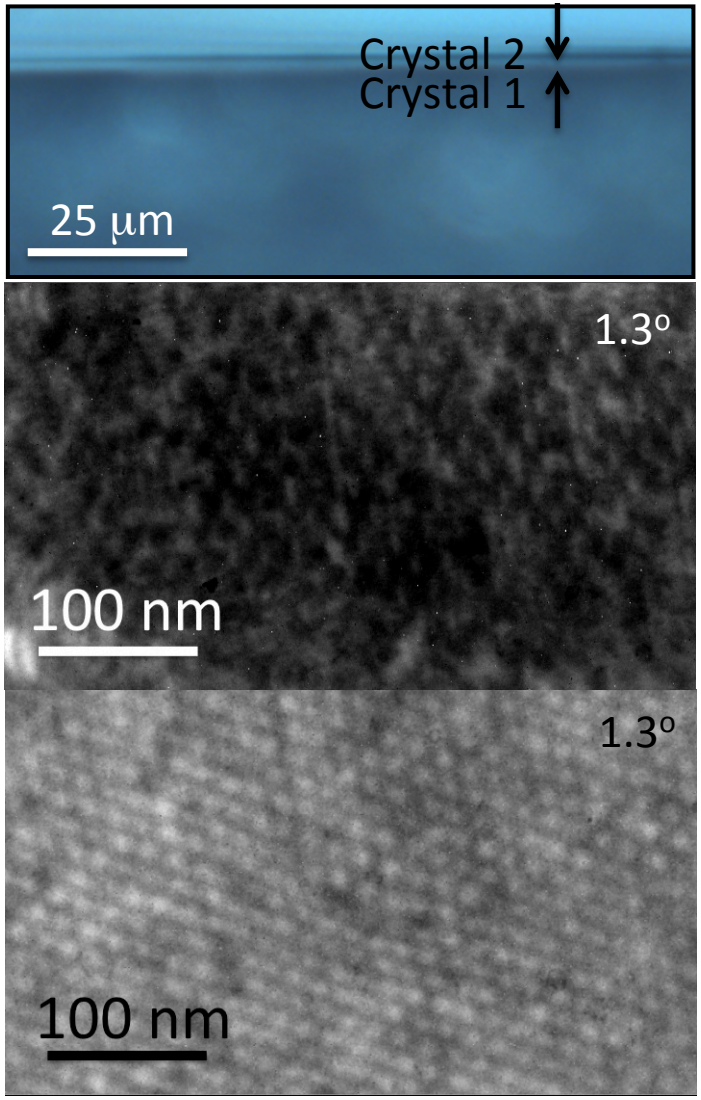
$$\Lambda = \frac{V^{\circ} \ln f_2 / f_1}{4\pi l R^2 (V_{3,1} - V_{3,2})} \frac{dR}{dT}$$

$$\Delta T_f = \frac{P}{\Lambda_a} \frac{t}{w} \qquad \Lambda_a = \frac{\Lambda_i}{1 + R_I \Lambda_i / t}$$

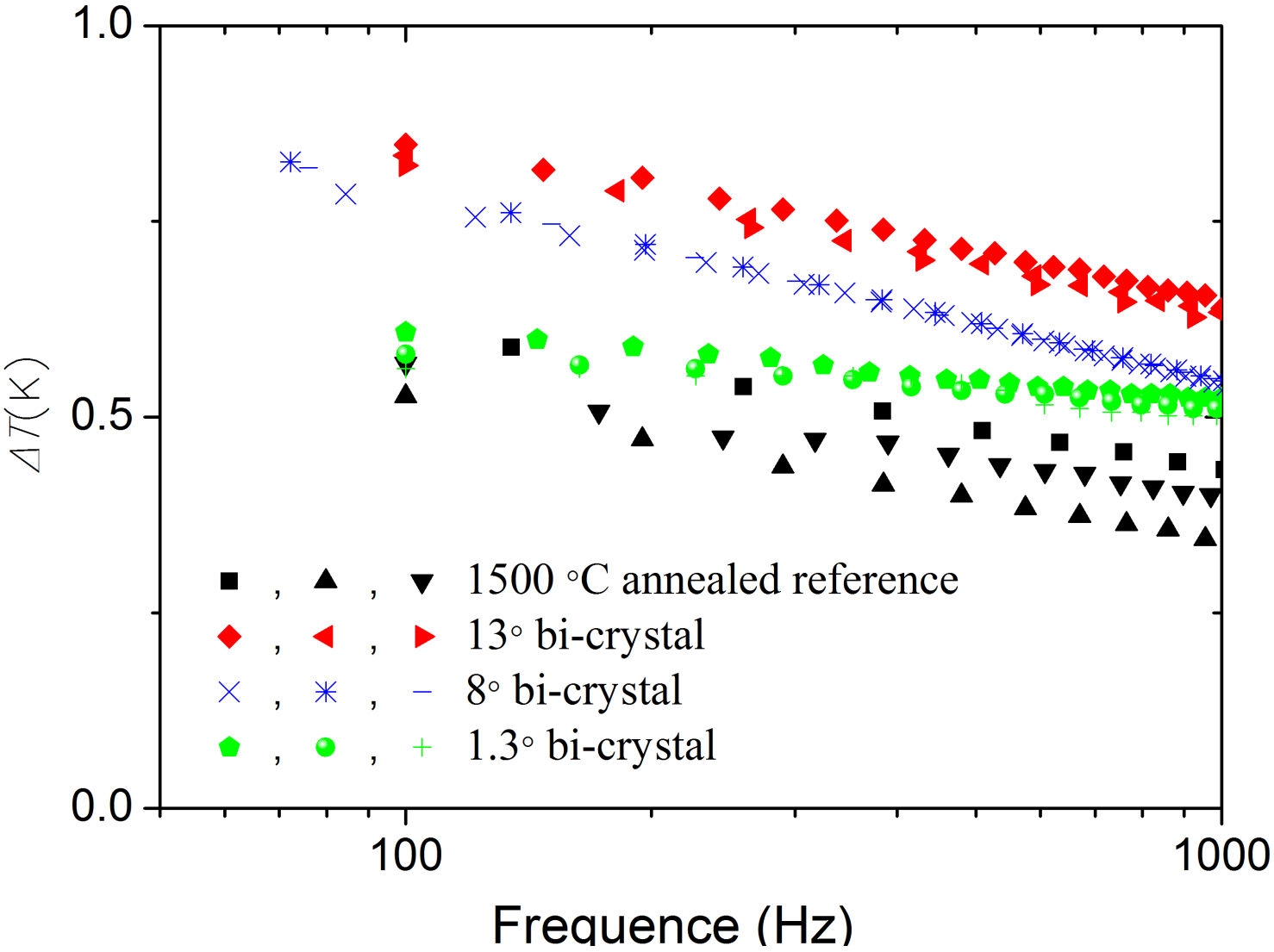
Cahill, *JAP* (2002)

Bicrystal Samples

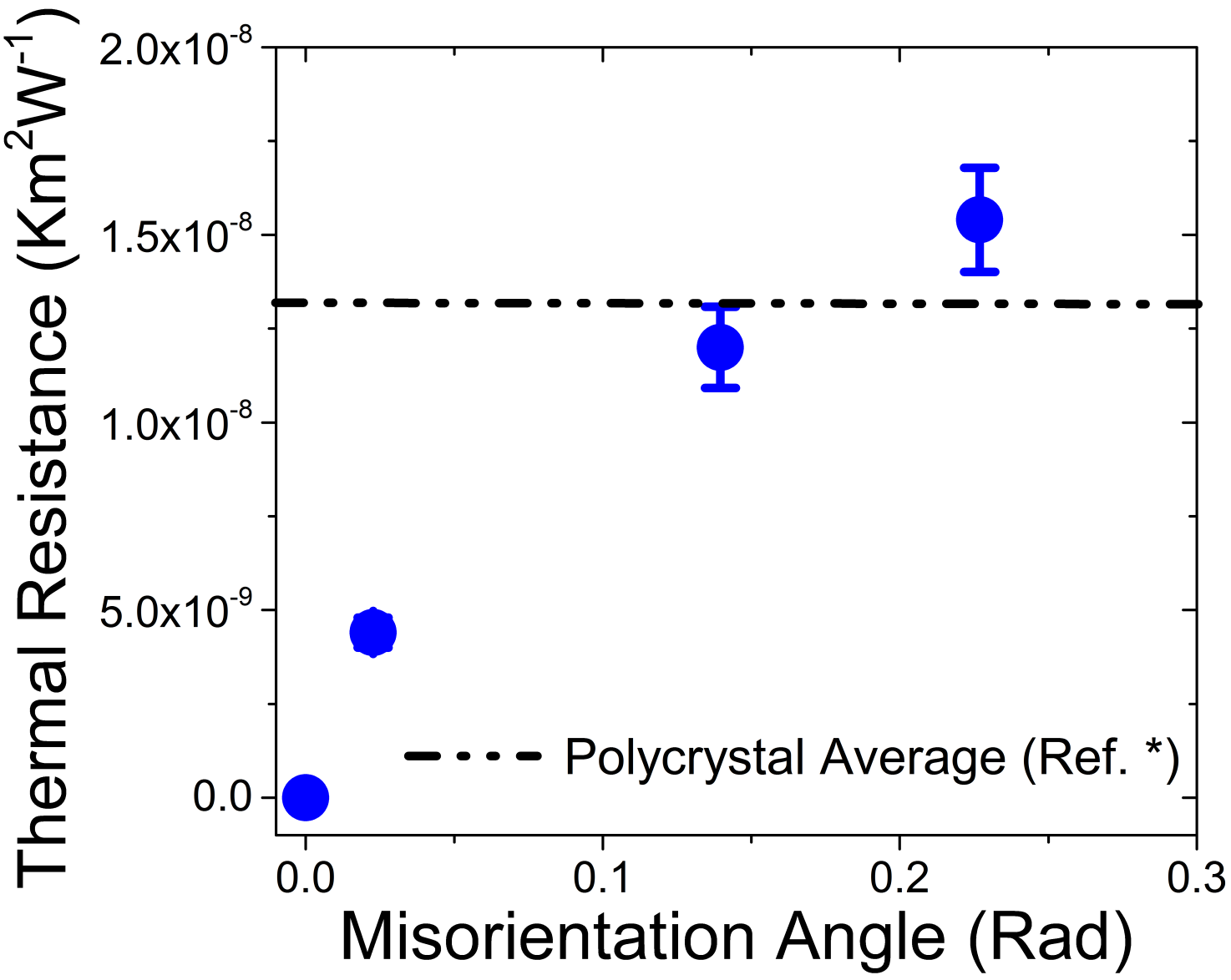




Interfacial Thermal Conductance

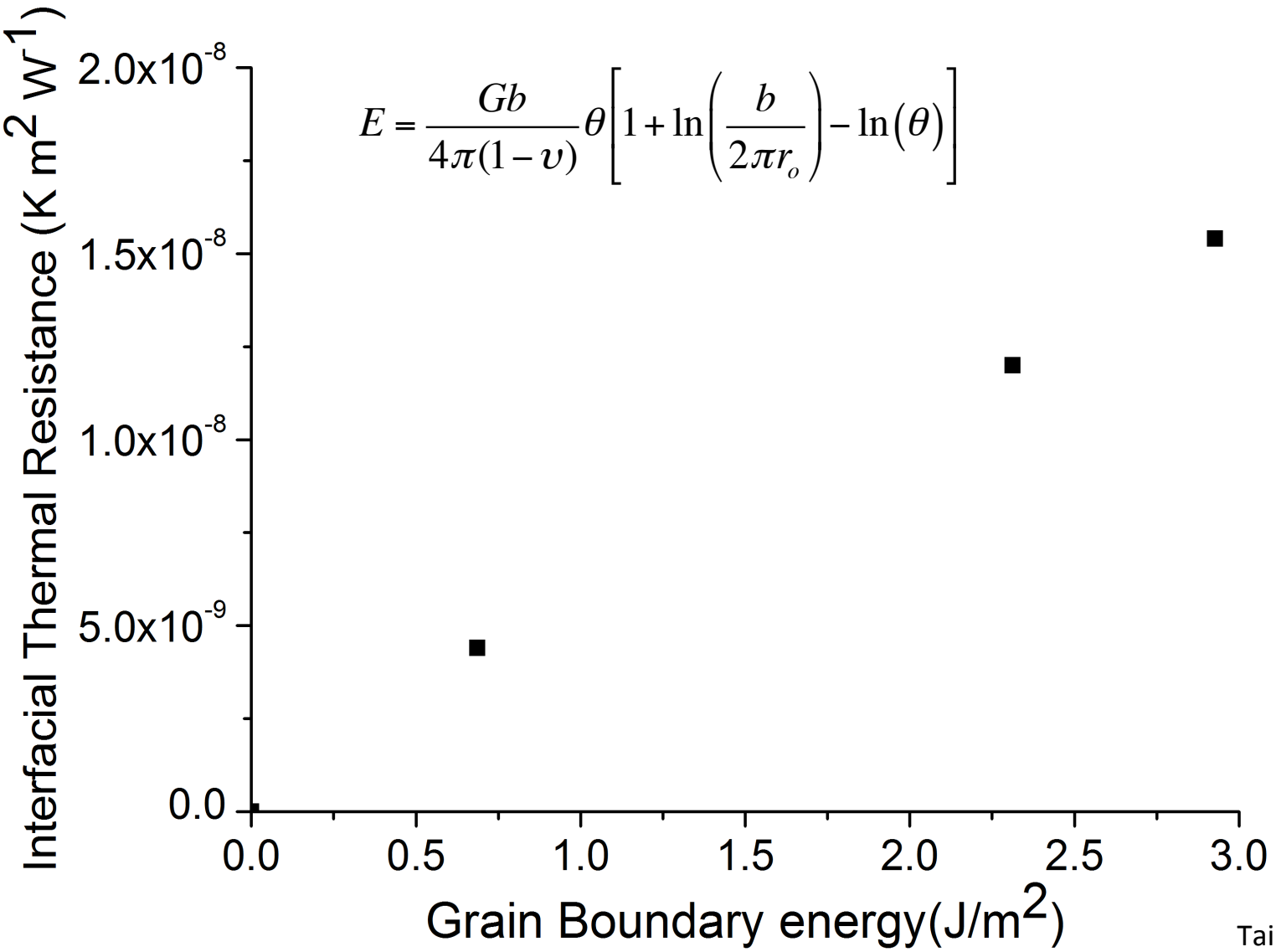


Misorientation Effect on Kapitza Resistance



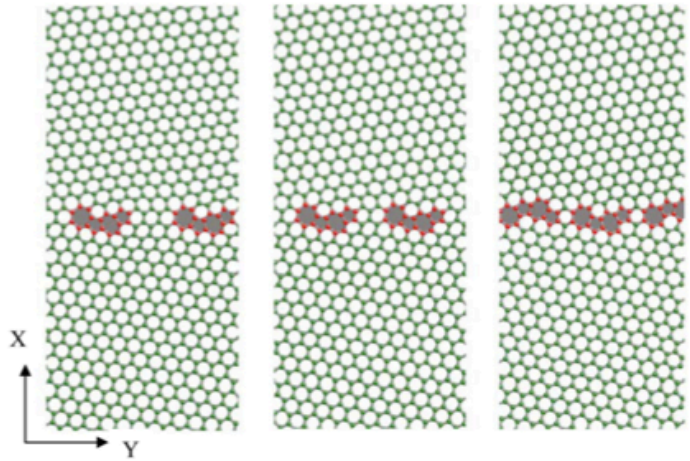
*Smith et al. *JACerS* (2003)

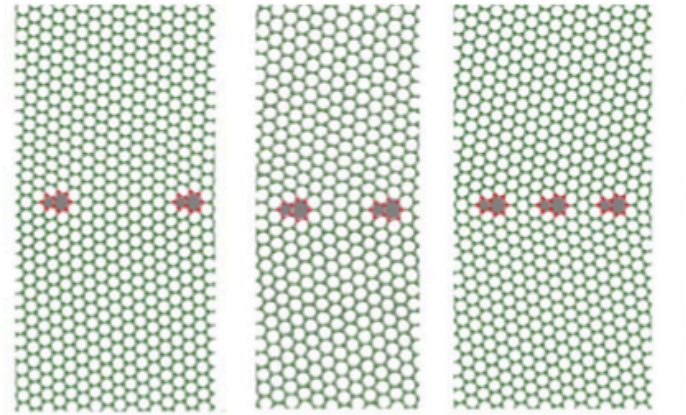
Comparison with Read-Shockley

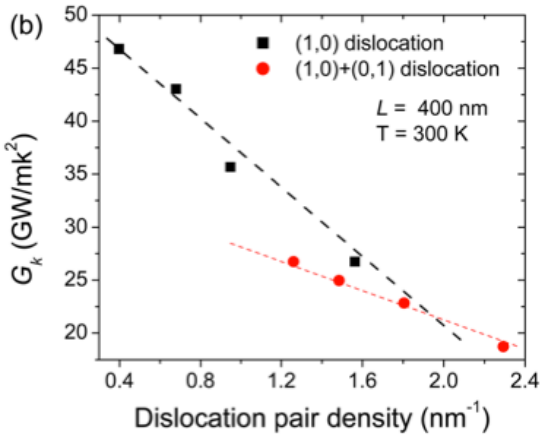


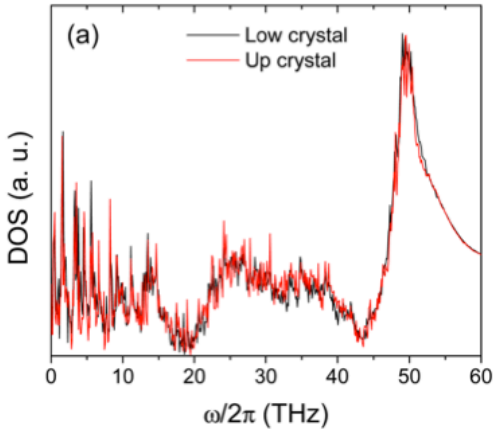
Tai & Dillon *Submitted*

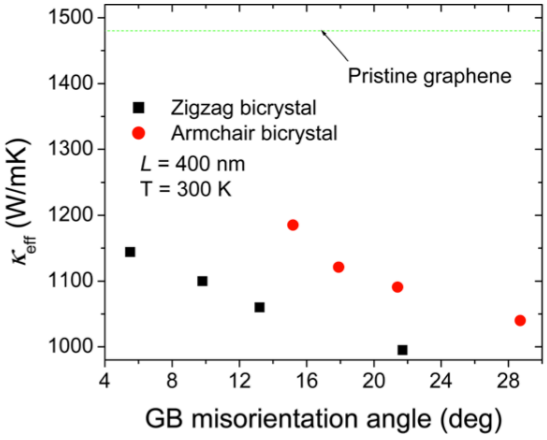
T.C. & Grain Boundary Defects (Graphene)

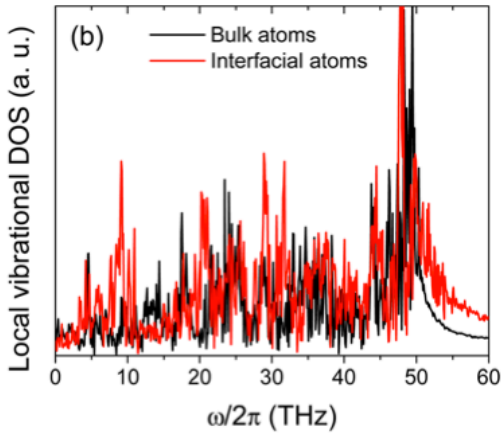






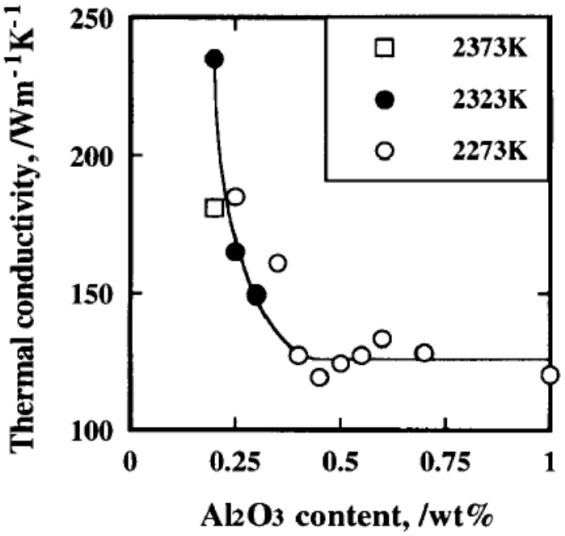


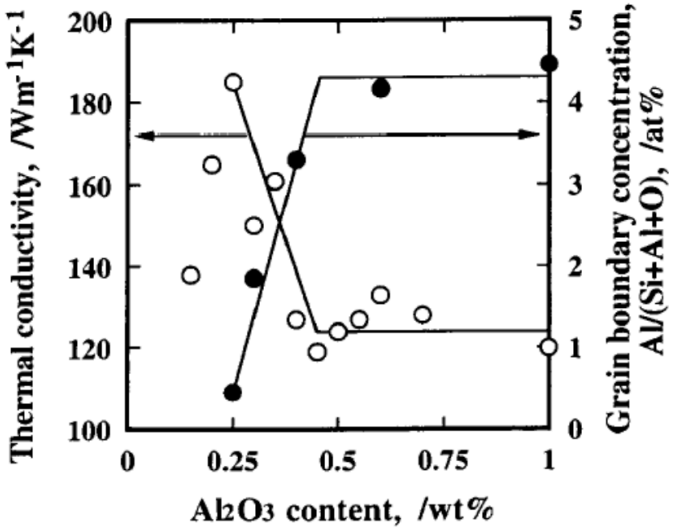




Cao, *JAP* (2012)

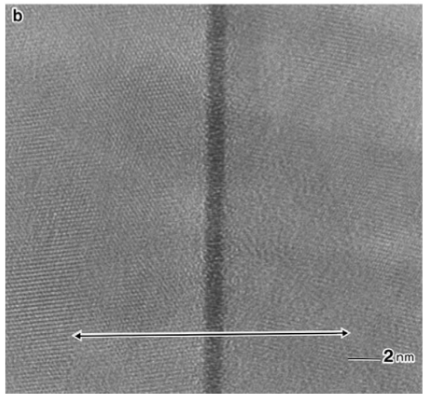
Future Work: Doped Bicystals & Complexions

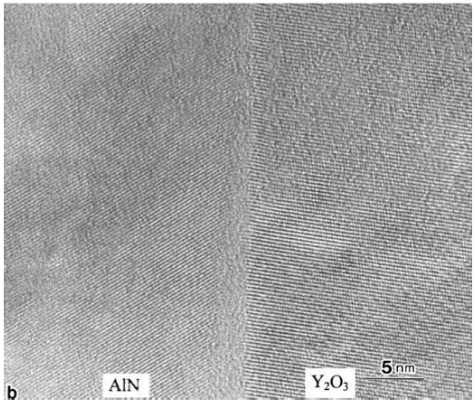


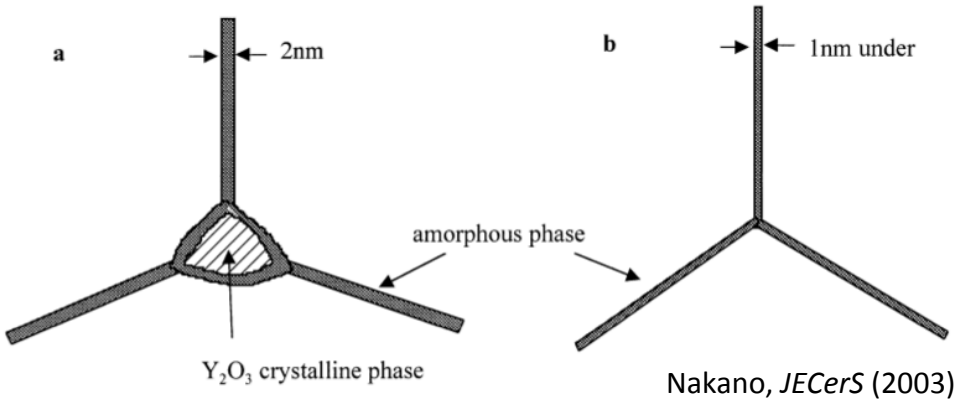


Kinoshita, *Acta Mater.* (1997)

Sintering conditions	Density (kg/m^3)	Chemical composition		Grain boundary phase	Thermal conductivity (W/m°C)
		Oxygen (mass%)	Yttrium (mass%)		
1900 °C, 20 h	3281	0.14	0.20	None	220
1900 °C, 100 h	3260	0.05	0.03	None	272



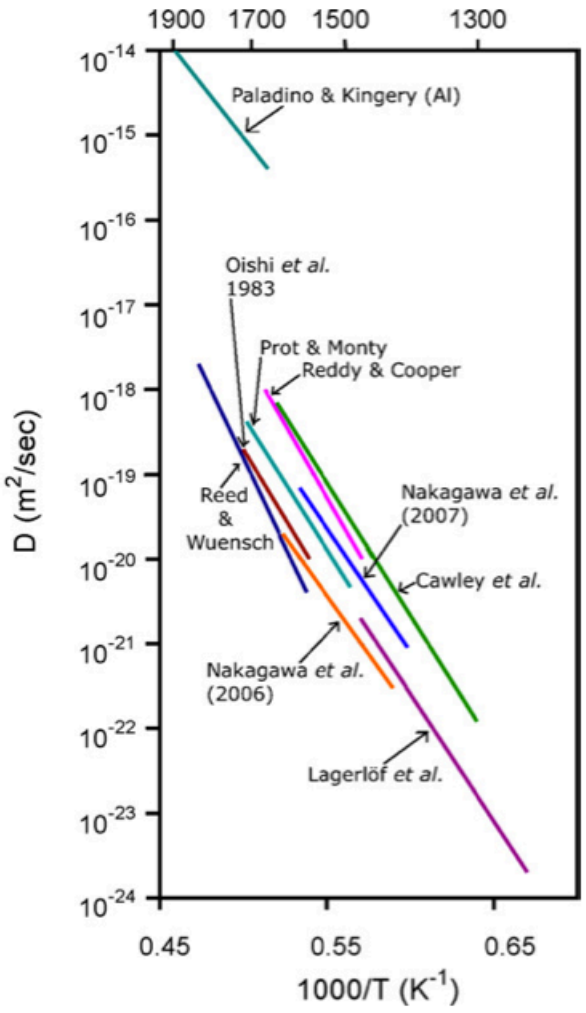




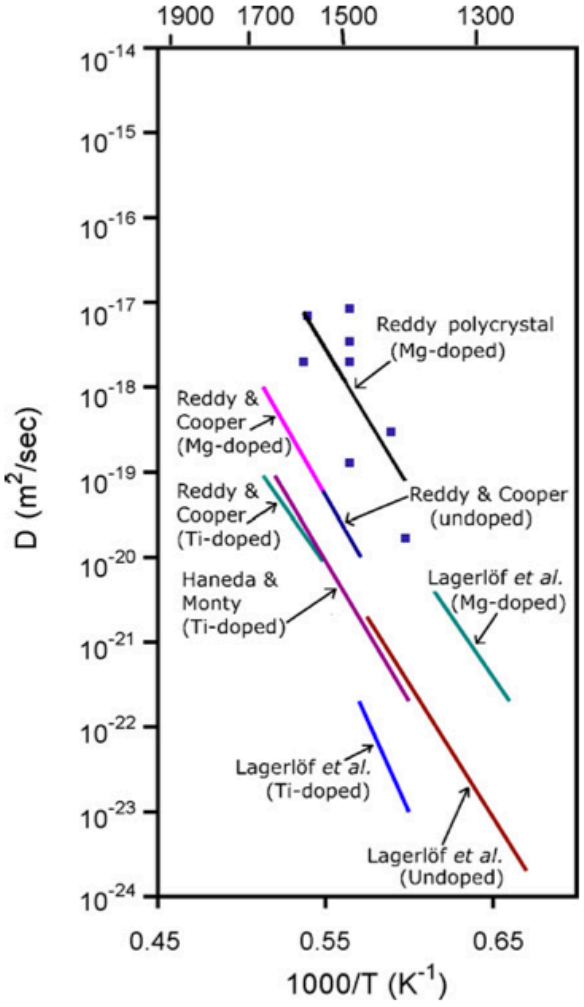
Nakano, *JECerS* (2003)

Oxygen Diffusion in Al_2O_3

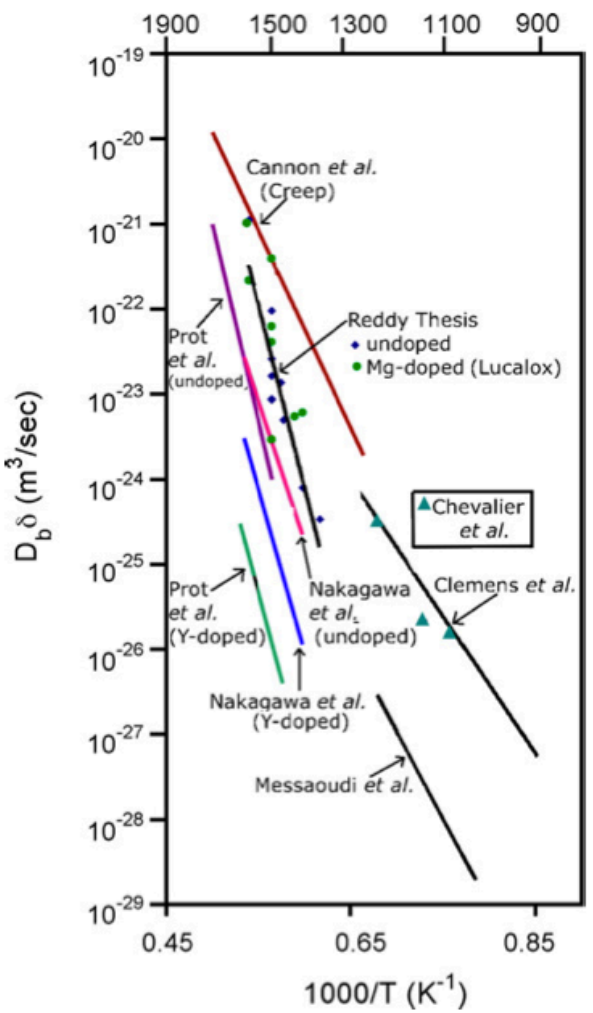
Oxygen Lattice



Doped Oxygen Lattice

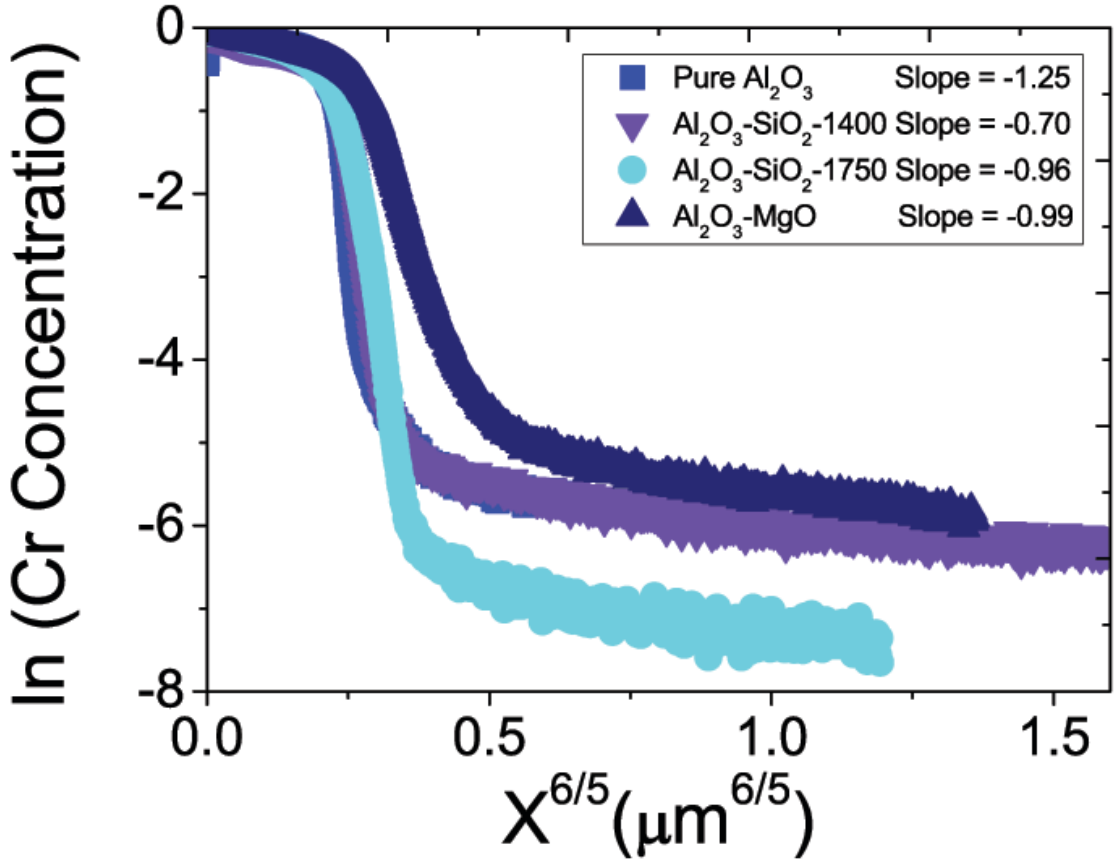


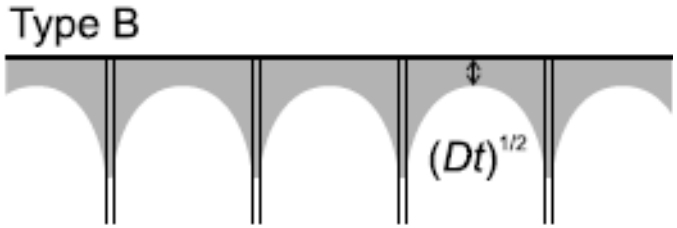
Oxygen Grain Boundary



Heuer, *JECerS* (2008)

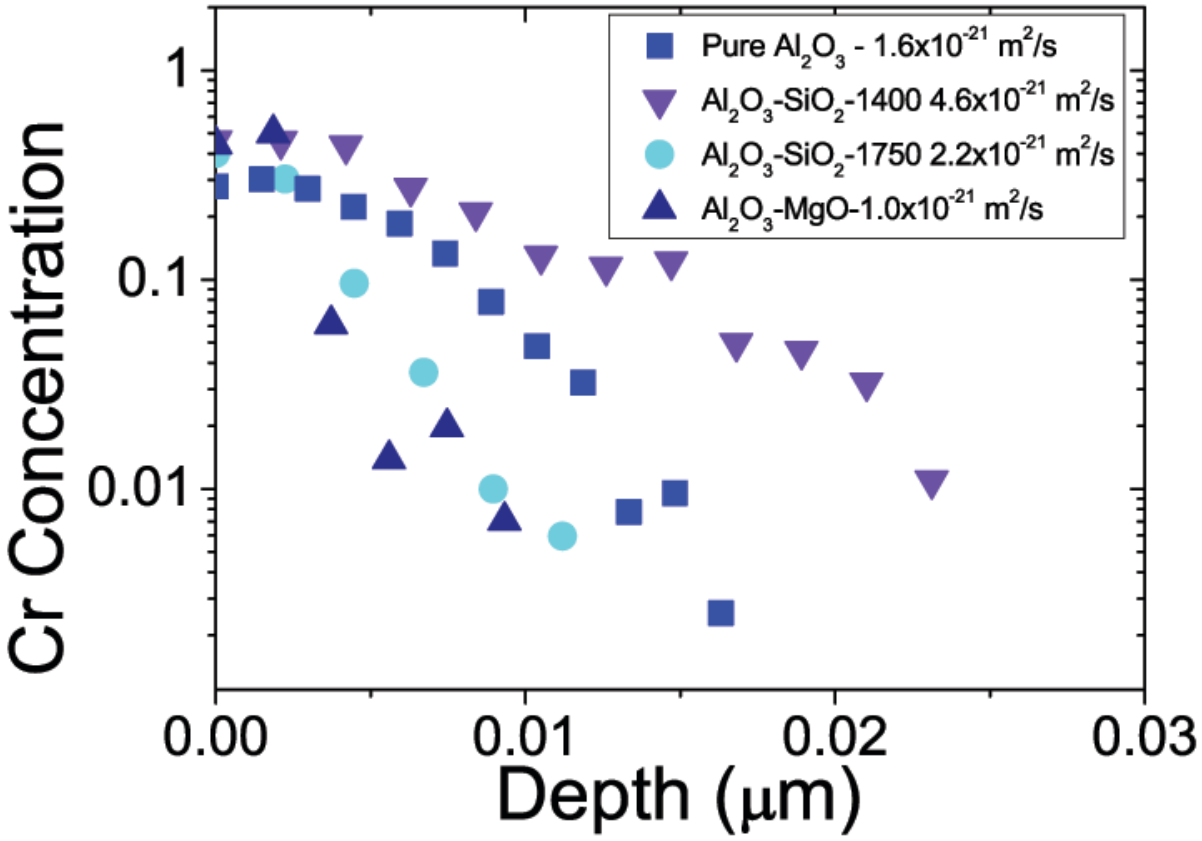
Preliminary Tracer Diffusion

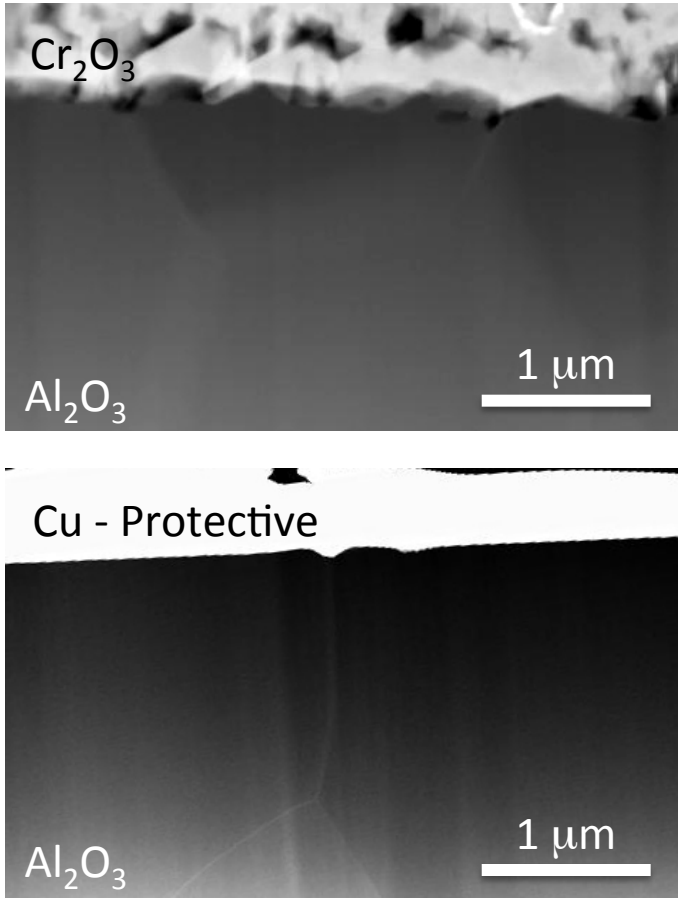




$$sD_{gb}\delta = 1.308\sqrt{\frac{D}{t}}(-\partial\bar{c}/\partial z^{6/5})^{-5/3}$$

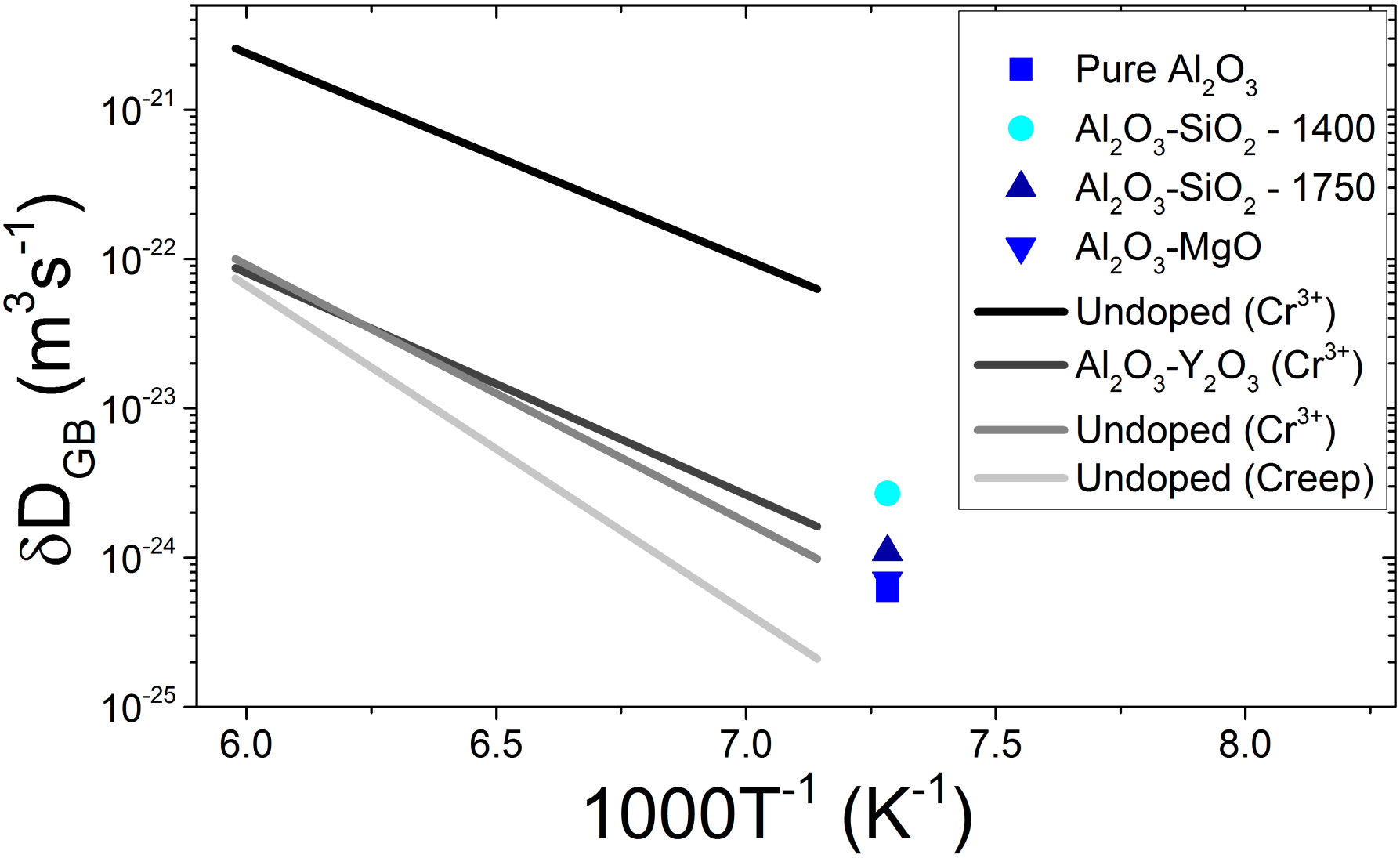
Preliminary Lattice Diffusion





Paladino Kingery (1962) => D_{al}=1.7x10^{-22} m^2/s at 1100°C (Extrapolated from 1670°C)
Moya et al. (1995) =>D_{Cr}=1.1x10^{-21} m^2/s at 1100°C

Preliminary Al_2O_3 Diffusivity Results



Conclusions

- Kinetics indicate G.B. complexion transition in Ni-Bi system (similar Cu-Bi)
  - Kinetics indicate significant entropy contribution
- Kapitza resistance scales with G.B. energy for low angle boundaries
- Preliminary results suggest cation diffusion (G.B. and lattice) not strongly sensitive to complexions/dopants