Entropy and Enthalpy Effects on the Diffusivity of Different Grain Boundary Complexions

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Acknowledgements

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Revolutionary Research . . . Relevant Results

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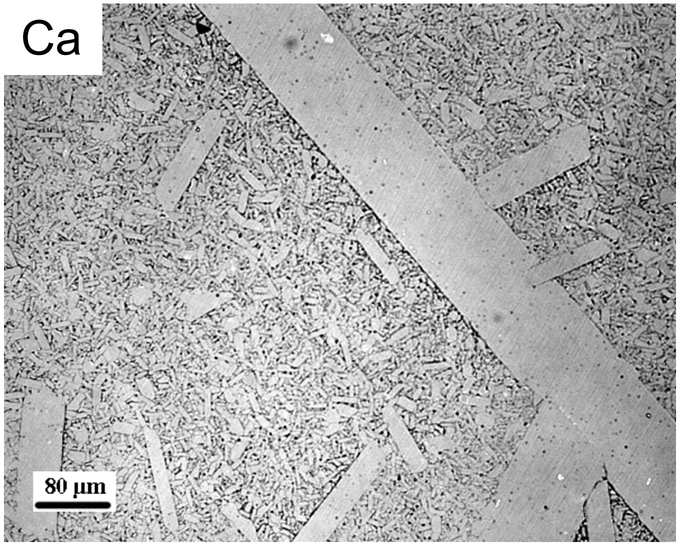
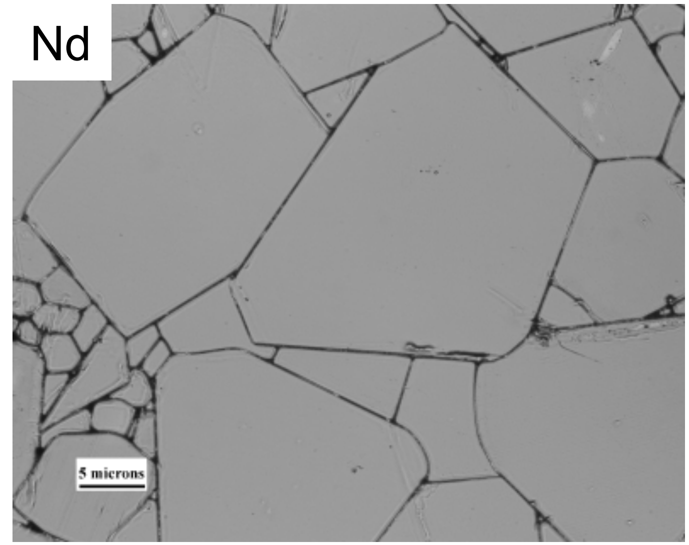
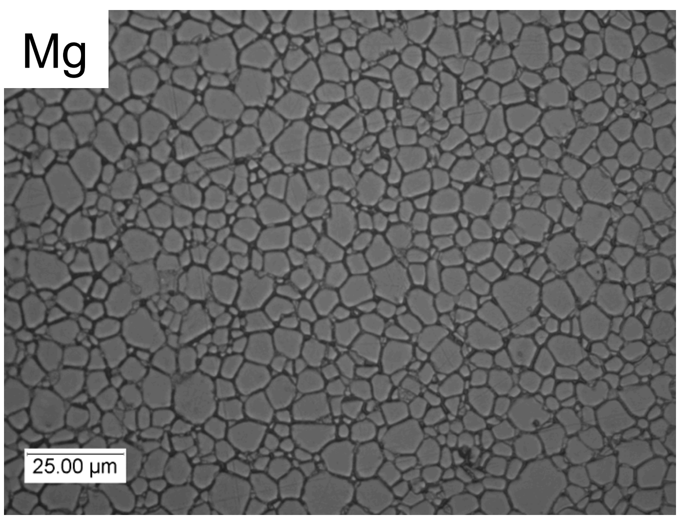
Overview

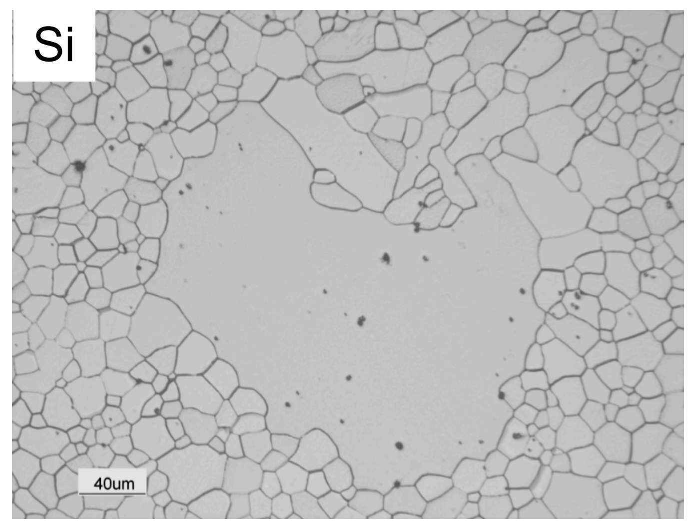
- Grain boundary complexions
- Approach to approximating S and H for G.B.
  - Measurements in Ni-Bi and Cu-Bi
- Diffusivity of nanograined samples
  - Is it different?
  - Does processing matter?

Grain Growth in Aluminum Oxide

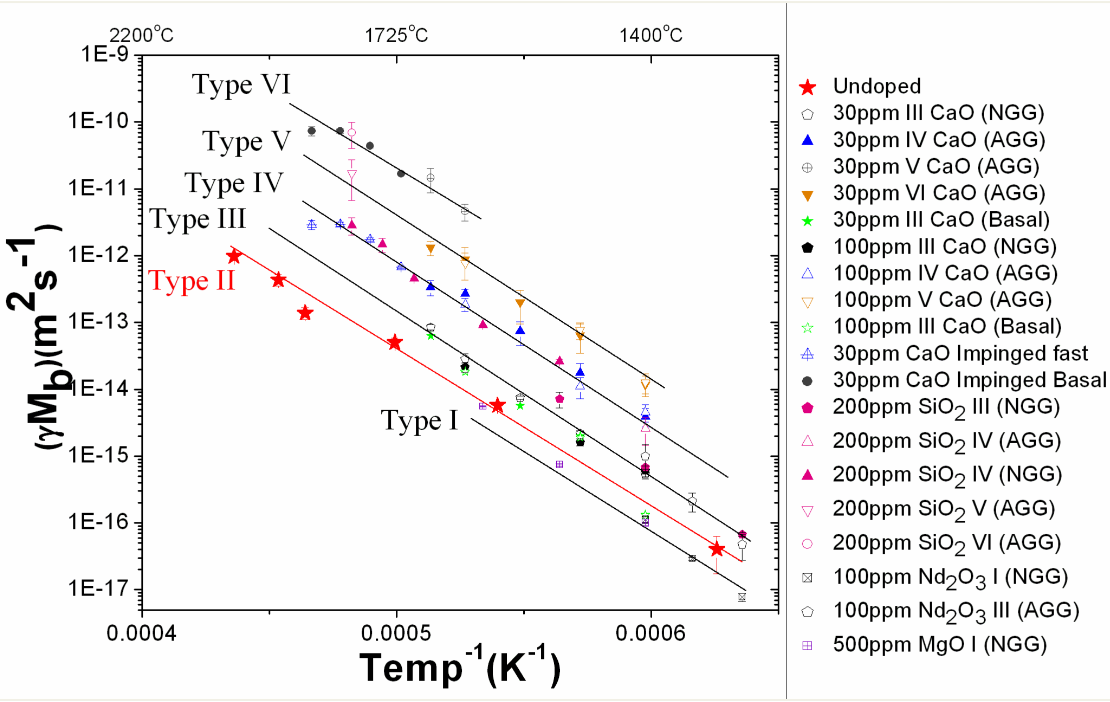


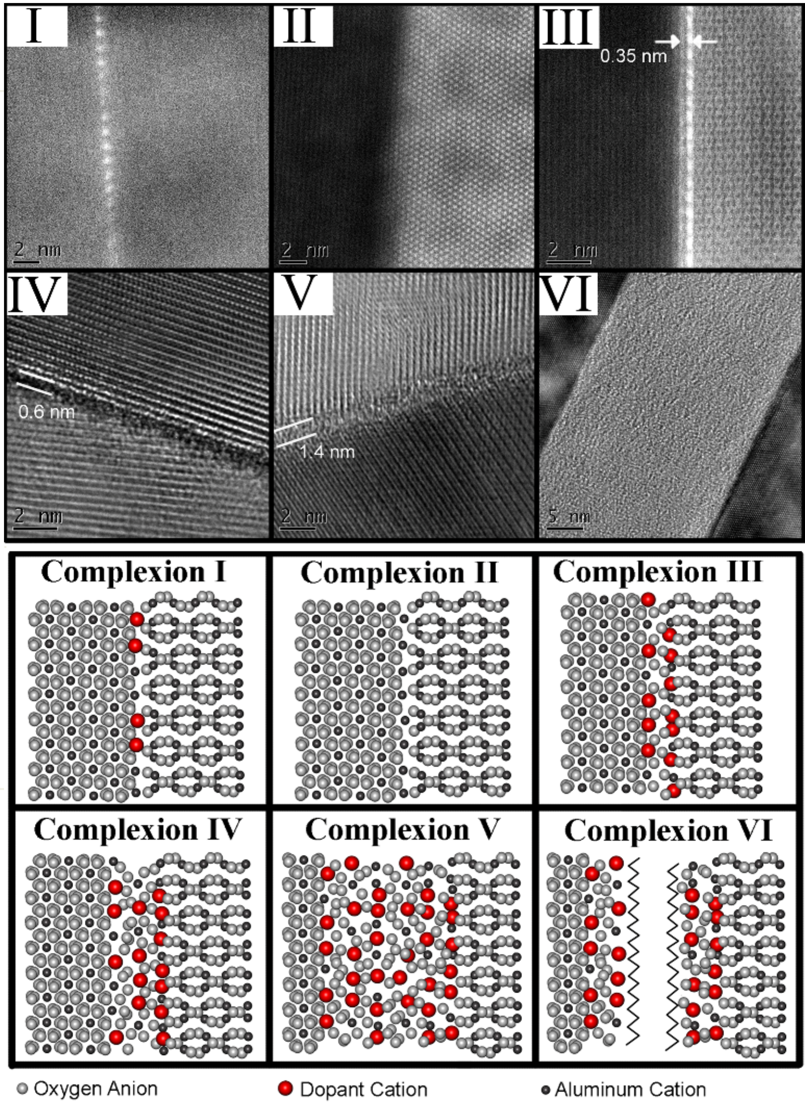






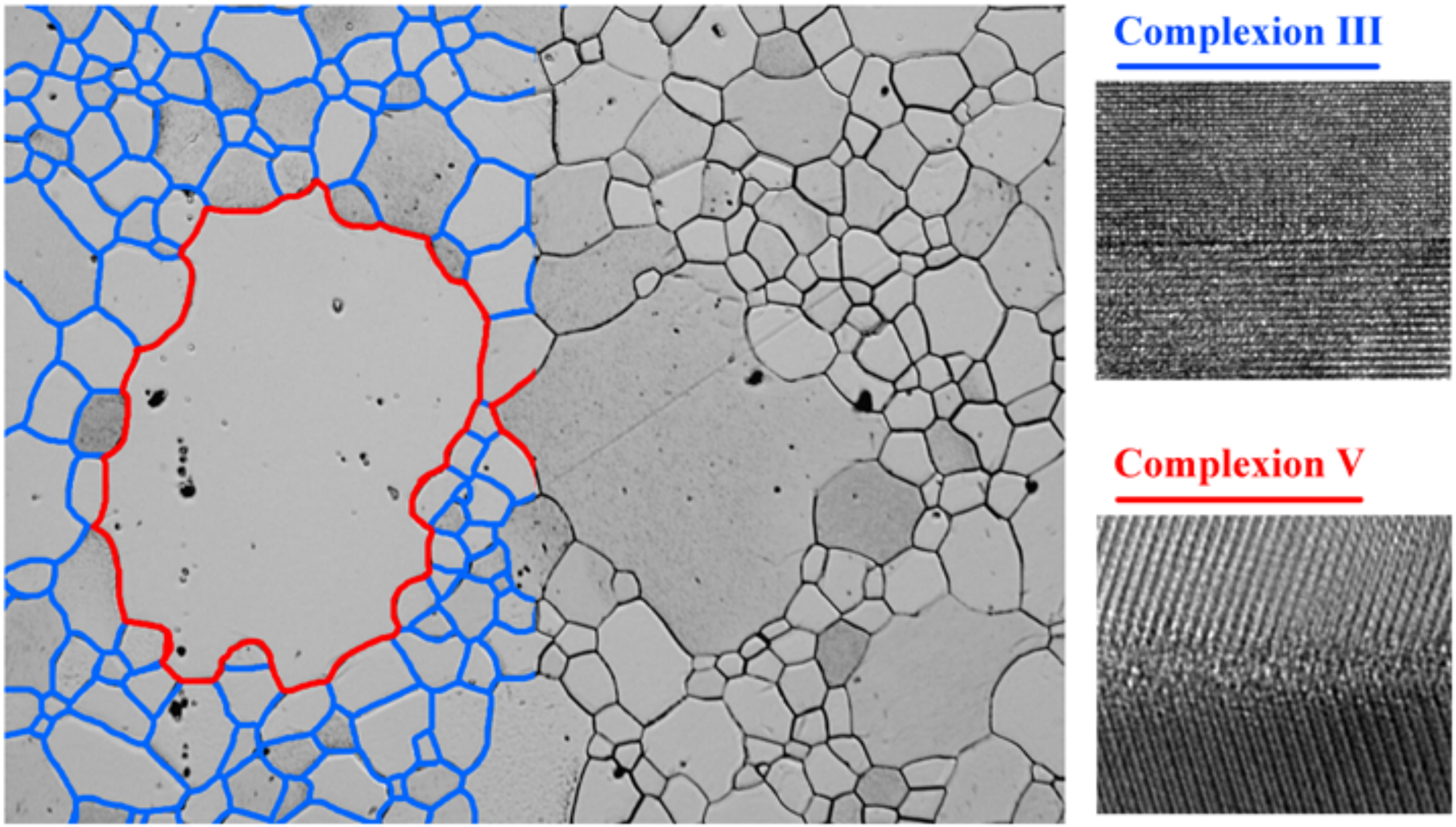
Grain Growth Kinetic Types



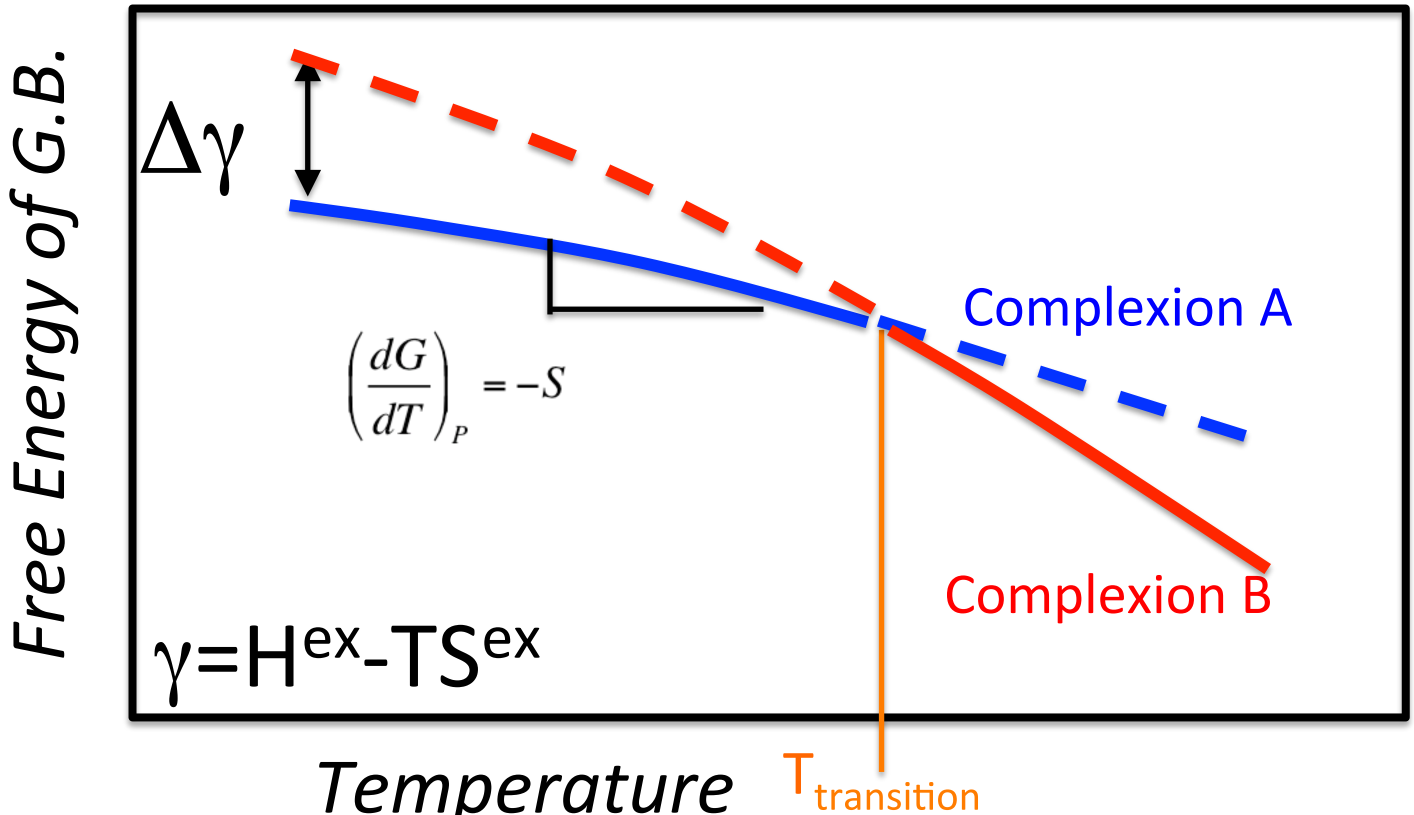


S.J. Dillon, M. Tang, W.C. Carter, M.P. Harmer, *Acta Mater.* (2007)

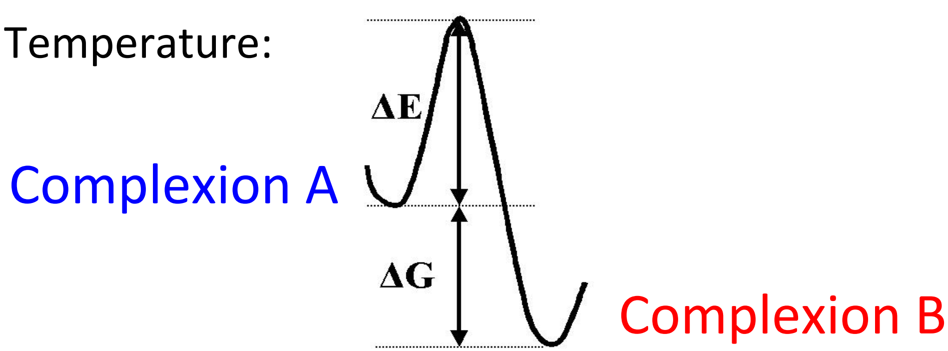
Simple Interpretation of AGG Mechanism



Simple Thermodynamic Model



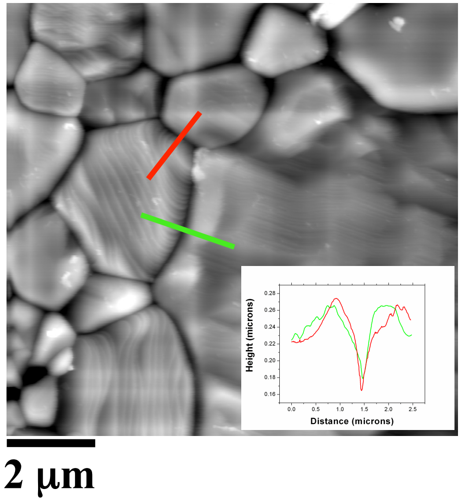
High Temperature:

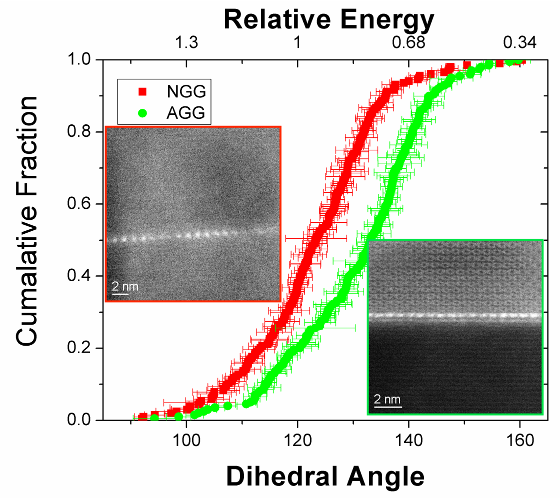


Transition Driven by Energy Minimization

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	
30 ppm-CaO	1400	III (NGG)	1.02	0.1
	1400	IV+ (AGG)	1.02	
	1400	III (Basal plane)	0.77	
200 ppm-SiO_2	1400	III (NGG)	0.65	9.5
	1400	IV (AGG)	0.71	
200 ppm-SiO_2	1750	IV (NGG)	0.98	−1.7
	1750	V+ (AGG)	0.96	





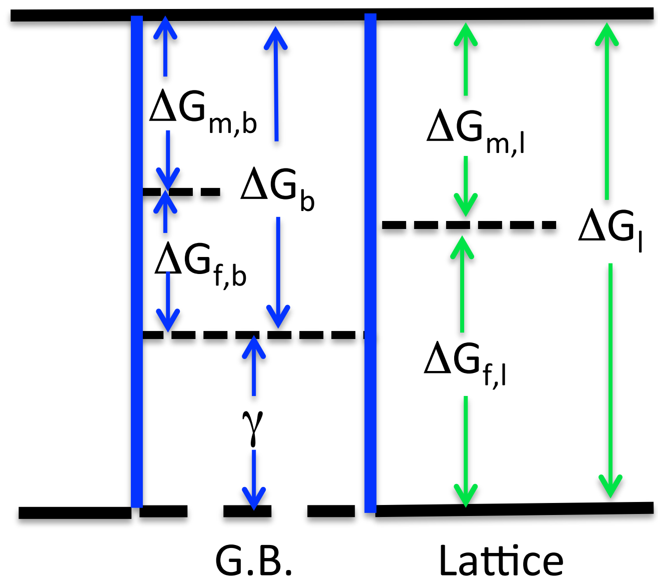
Relative Contributions?

$$\gamma = H^{ex} - TS^{ex}$$

Borisov Model: Linking Thermos & Kinetics

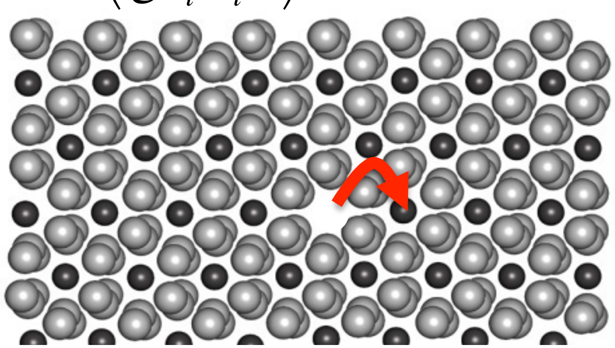
$D=ga^2C_v\Gamma$ $C_v=\exp(\Delta S_f/k)(-\Delta H_f/kT)$ $\Gamma=\nu^*\exp(-\Delta H_m/kT)$

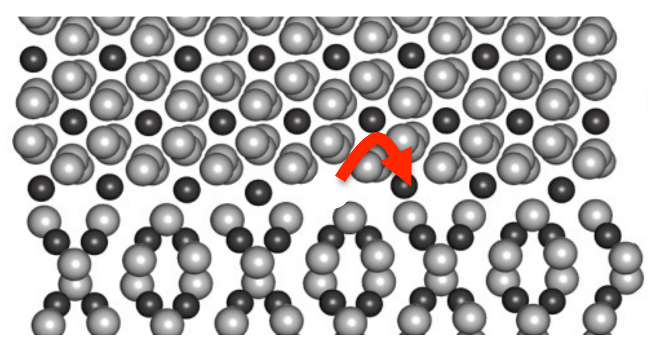
Assumption: $D_b = ga_o^2\nu^*\exp[-(\Delta G_l-\rho\gamma')/kT]$ Remember $\rho\gamma'=\Delta\bar{G}_b-\Delta\bar{G}_l$



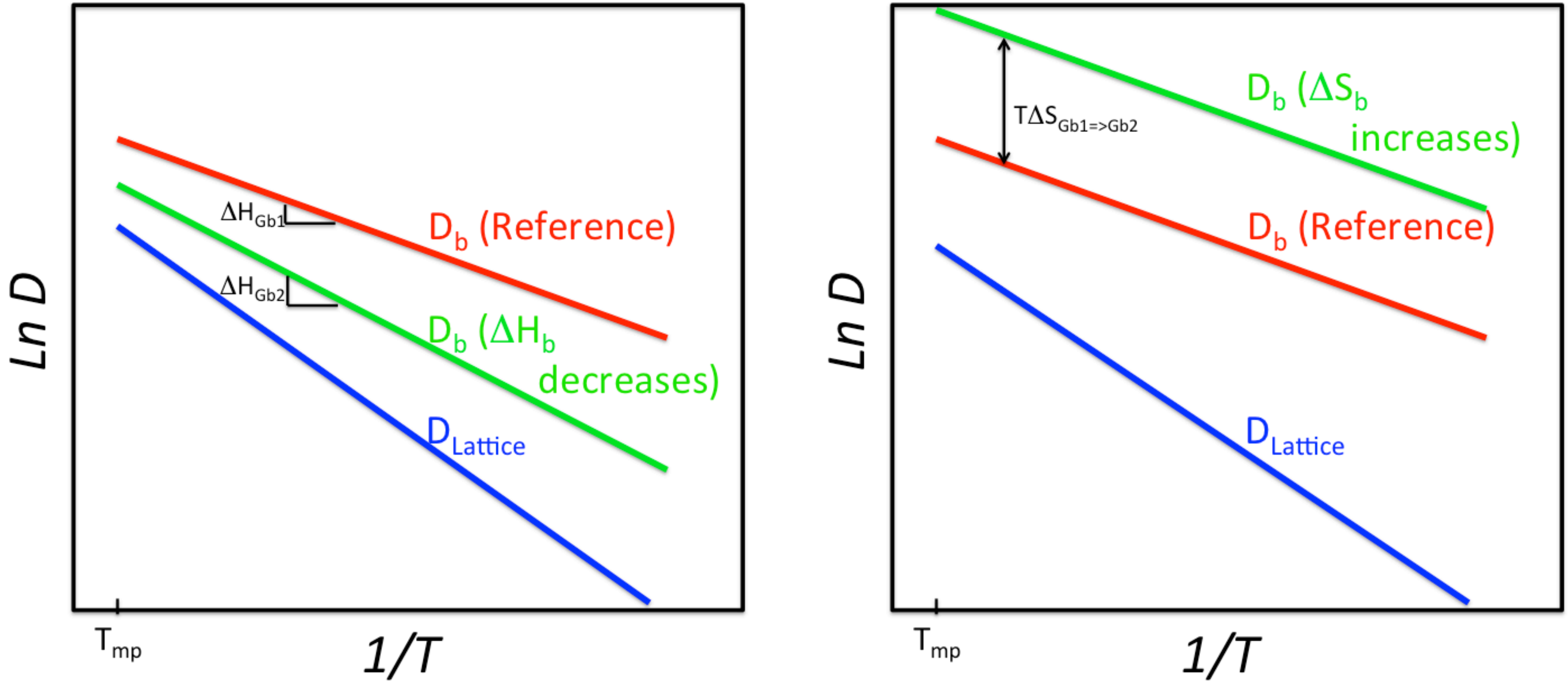
Adapted from Gupta *Met Trans.* (1977)

$$\gamma'=\rho^{-1}[kT\ln\left(\frac{ga_b^2\nu_b^*}{ga_l^2\nu_l^*}\right)-T(\Delta S_{f,b}-\Delta S_{f,l})+(\Delta H_{f,b}-\Delta H_{f,l})+(\Delta H_{m,b}-\Delta H_{m,l})]=\rho^{-1}[kT\ln\left(\frac{D_b}{D_l}\right)]$$

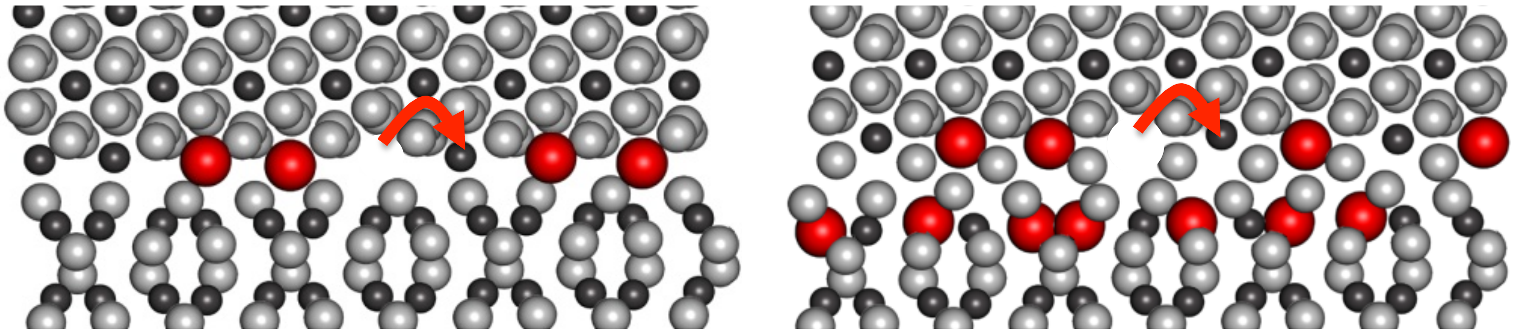




General Predictions of Borisov Model

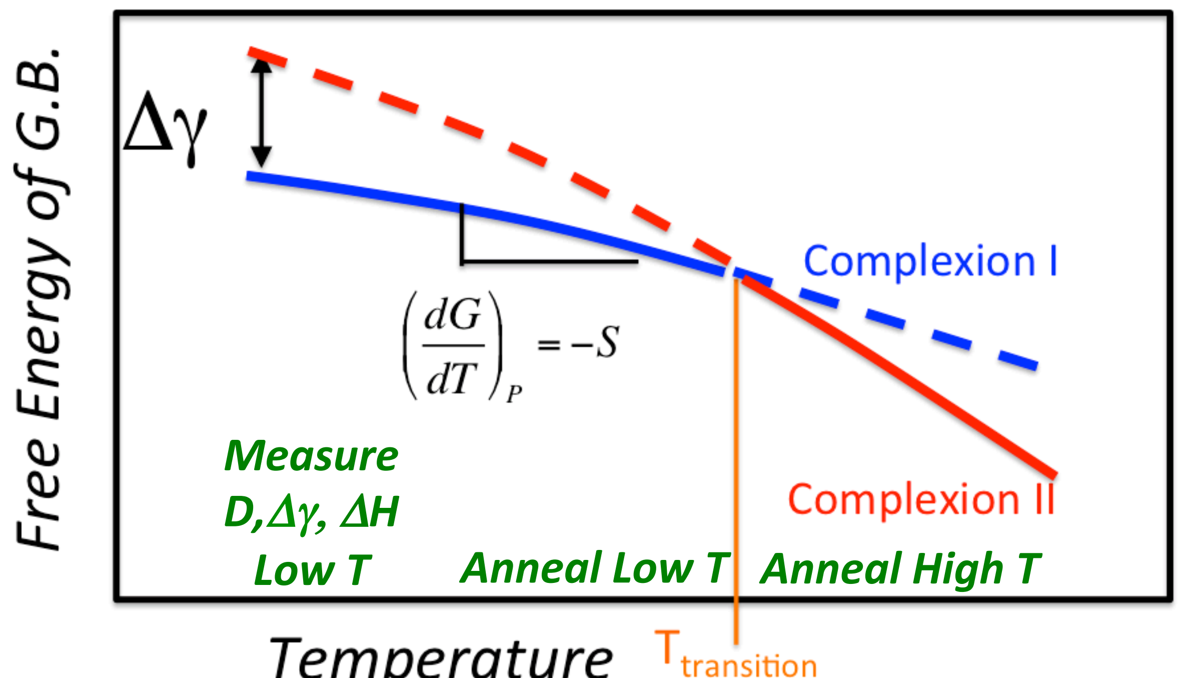


Comparing Complexions (ΔH & ΔS)

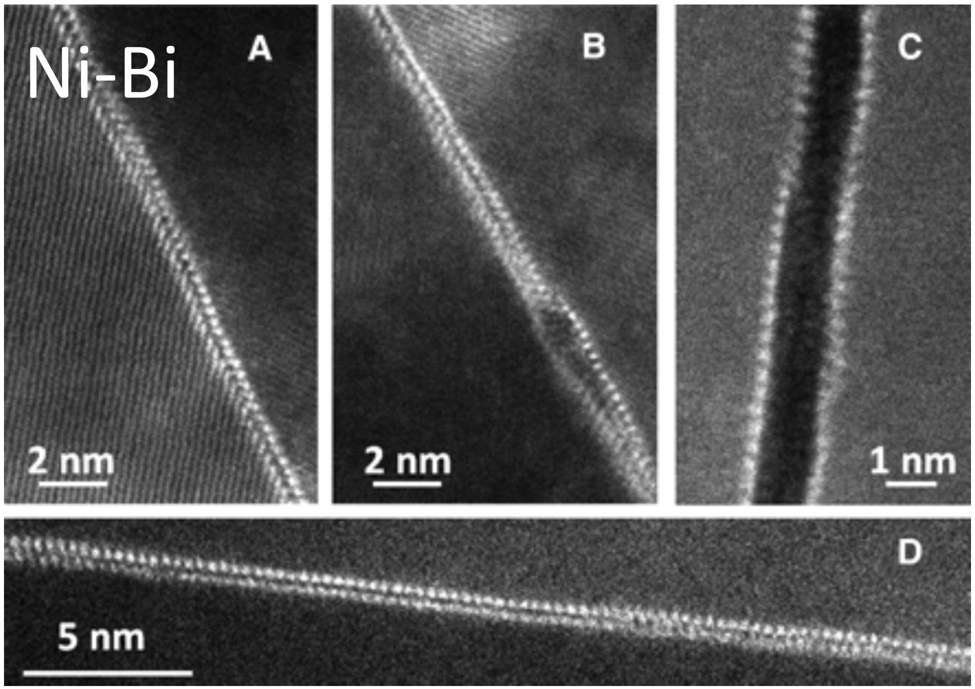


$$\Delta\gamma' = \rho^{-1}[kT\ln\left(\frac{ga_{II}^2 \nu_{II}^*}{ga_I^2 \nu_I^*}\right) - T(\Delta S_{f,I} - \Delta S_{f,II}) + (\Delta H_{f,I} - \Delta H_{f,II}) + (\Delta H_{m,I} - \Delta H_{m,II})] = \rho^{-1}[kT\ln\left(\frac{D_I}{D_{II}}\right)]$$

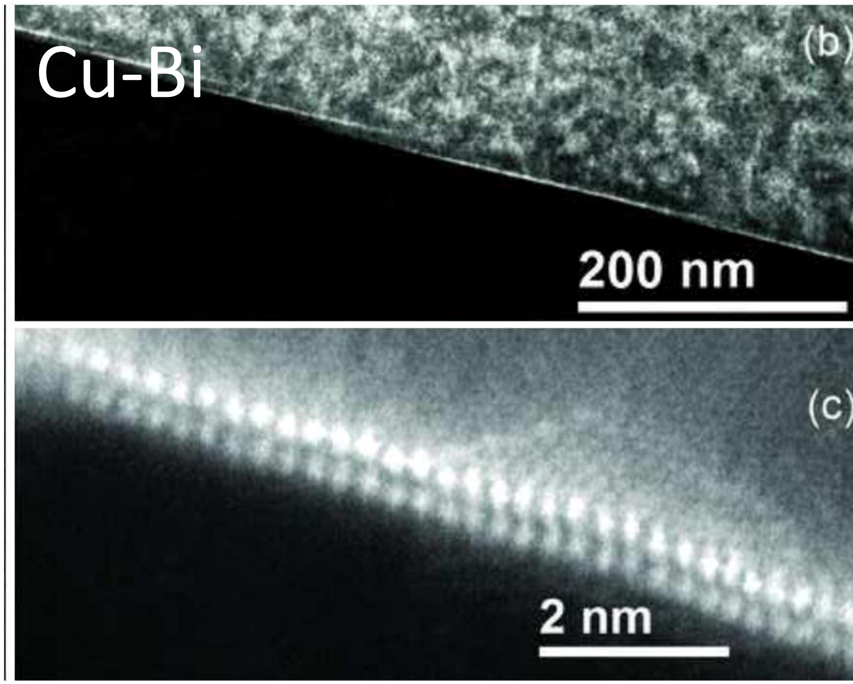
Approach:



2 Simple Model Systems

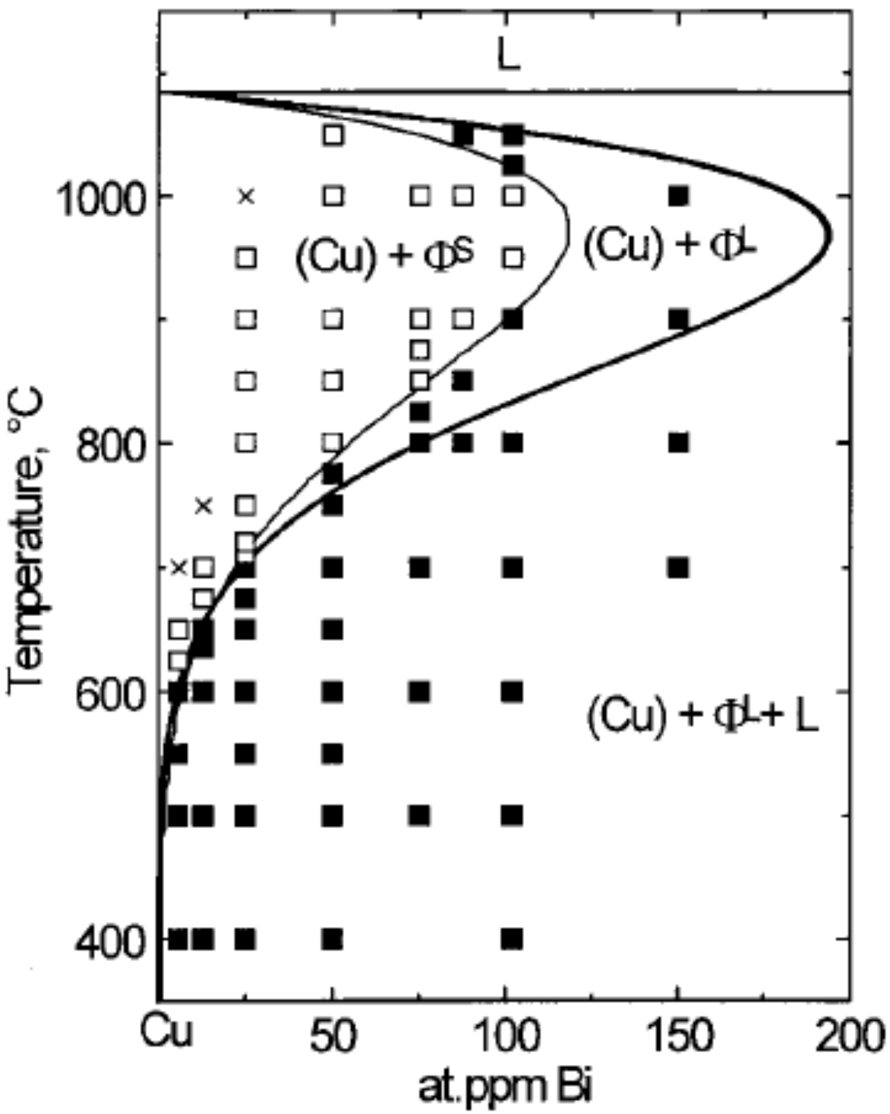


Luoet al. *Science* (2011)

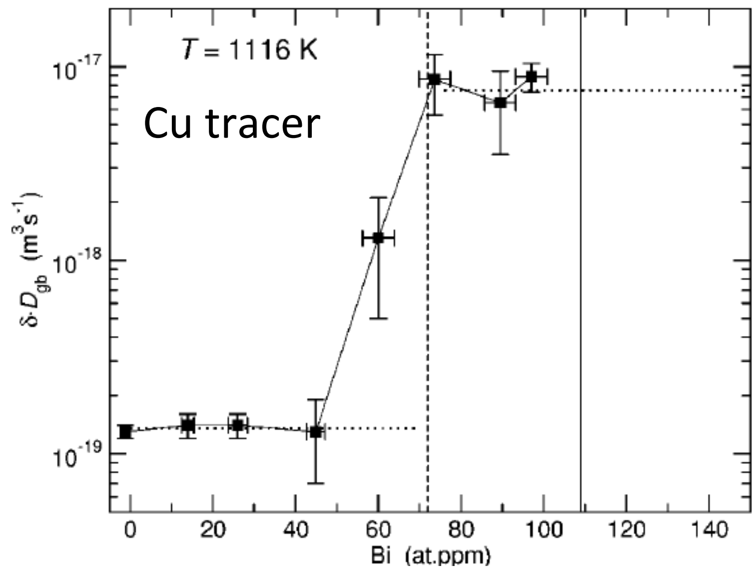


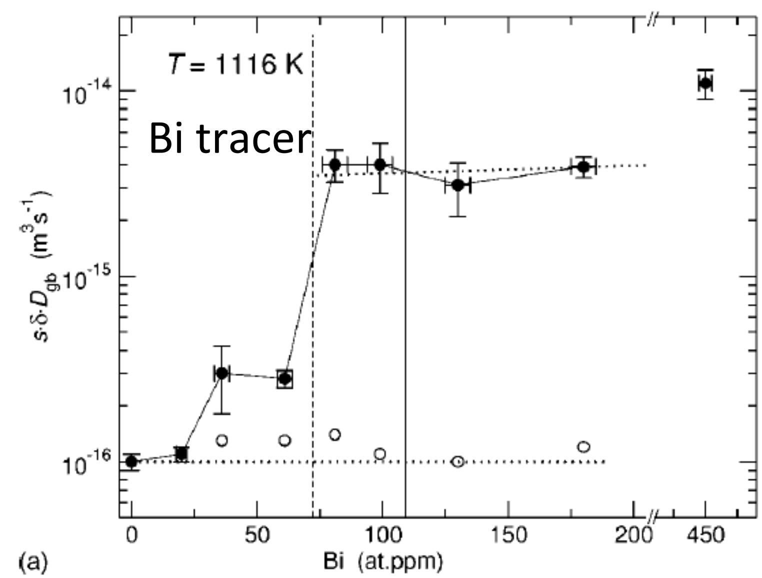
Kundu et al. *Scripta Mater*. (2012)

Prior Work on Cu-Bi



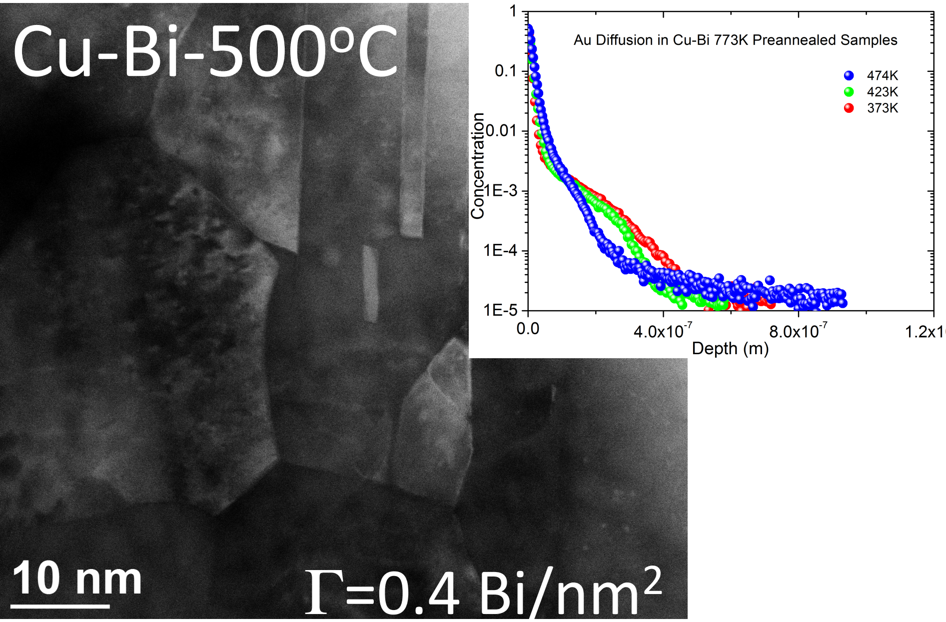
Chang et al. *Acta Mater.* (1999)

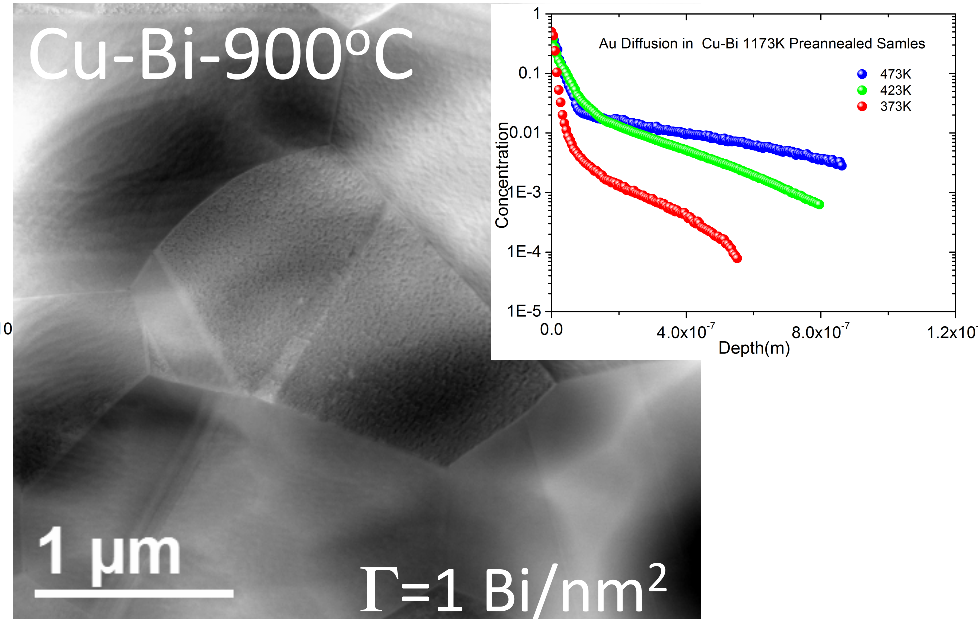


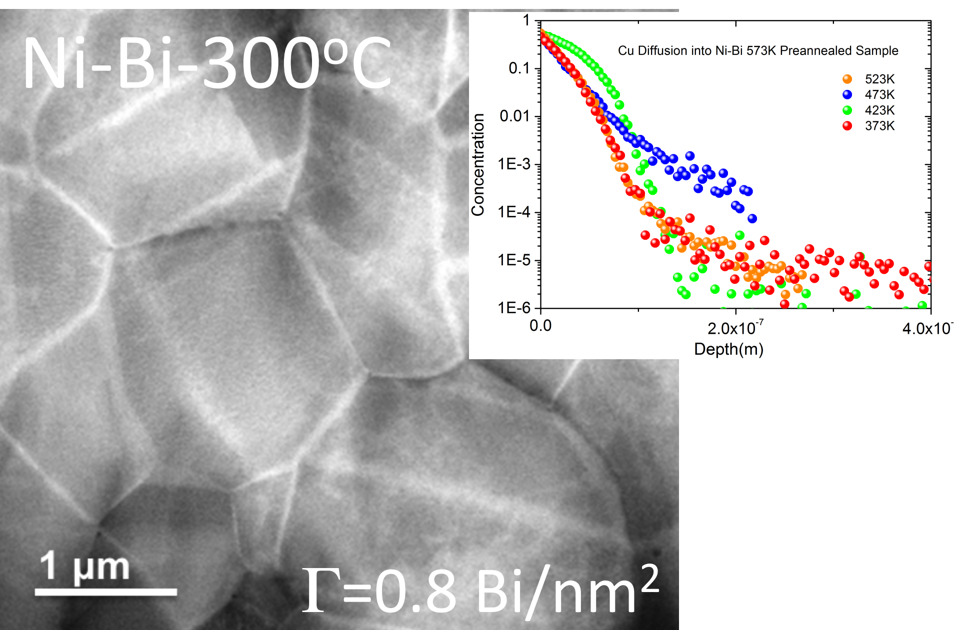


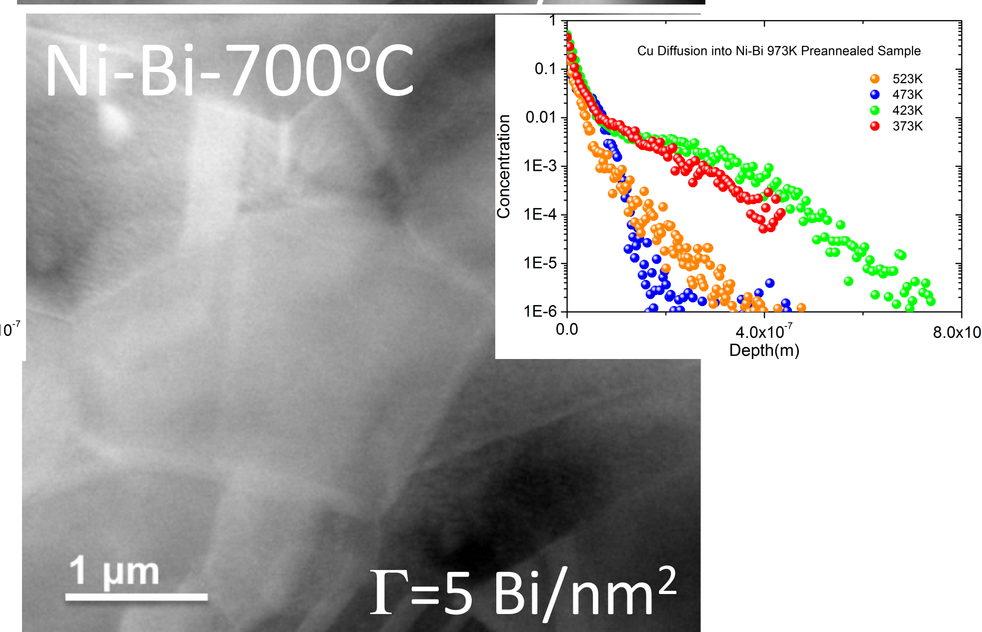
Divinski et al. *PRB* (2005)

Chemical Diffusion into Bi doped Ni/Cu

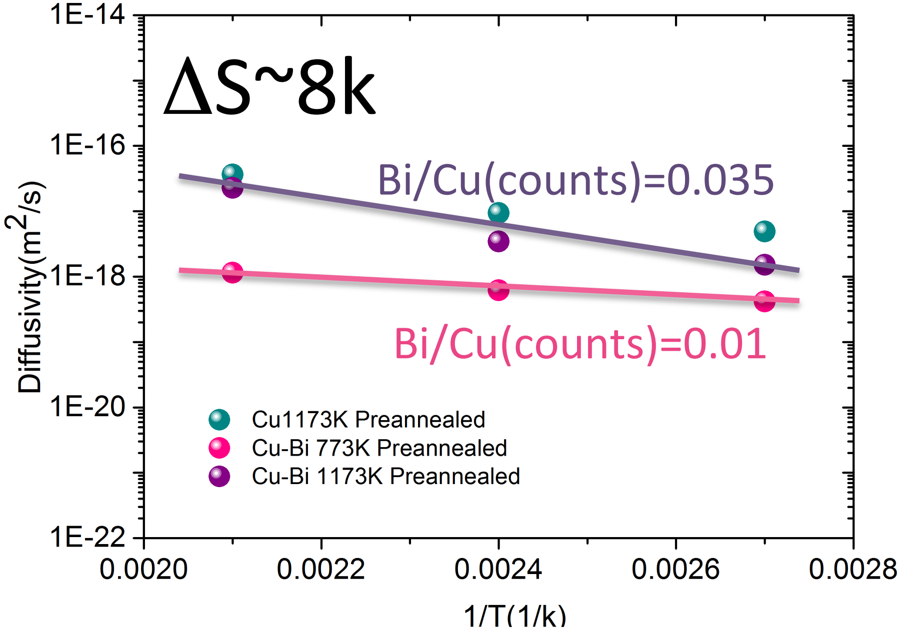


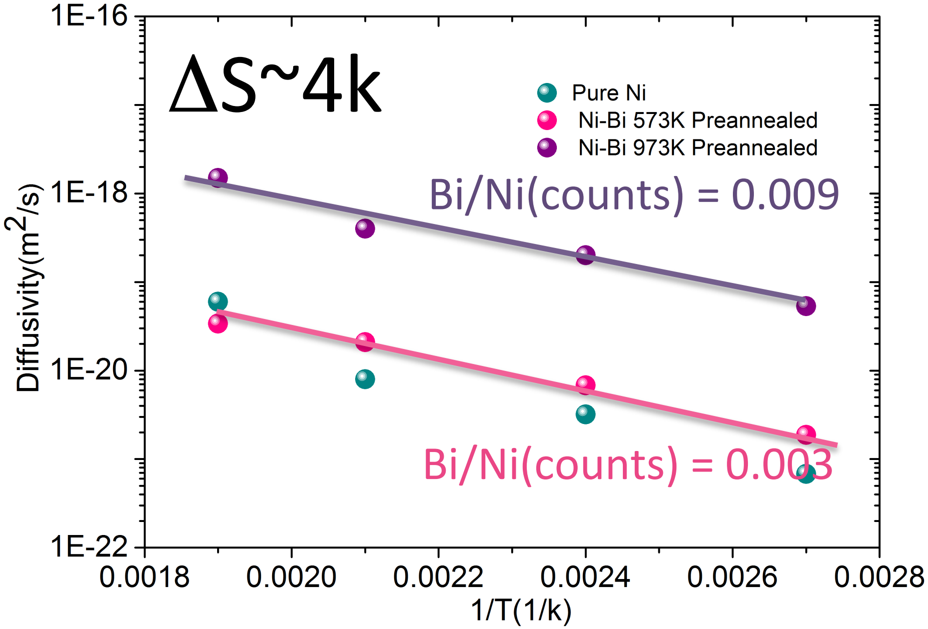






Entropy Difference between Complexions

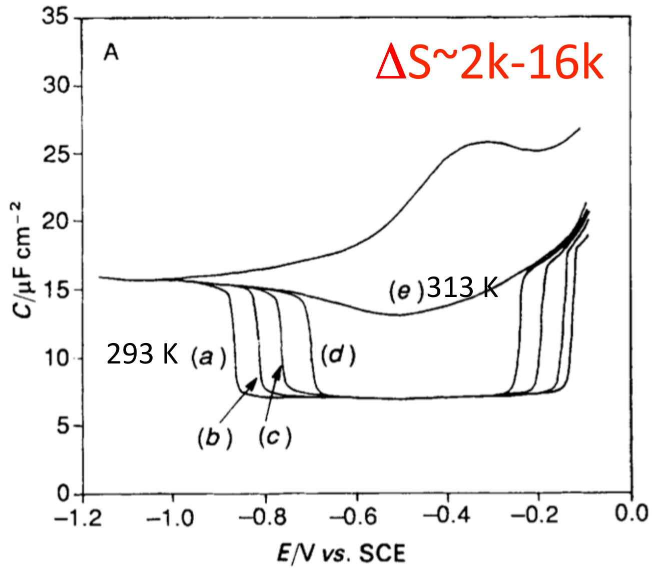




K. Tai et al. *J. Appl. Phys.* In Press

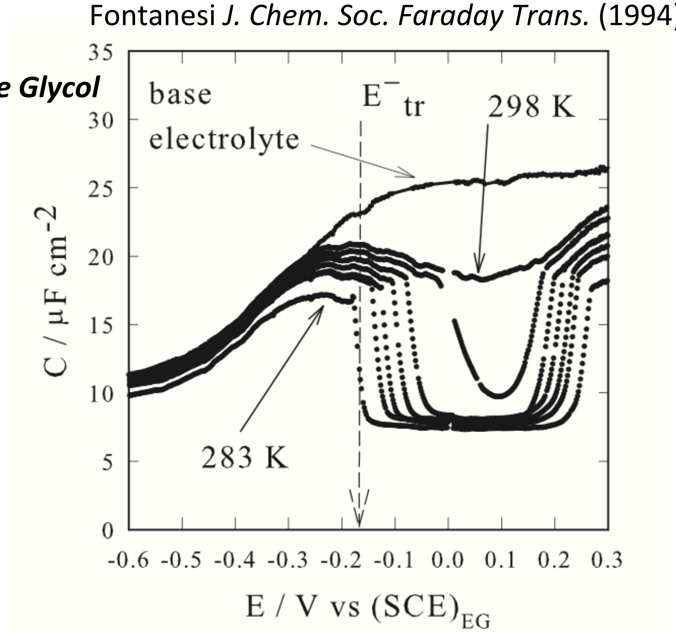
Comparison w/ Related Measurements

Adenine Hg/Aqueous

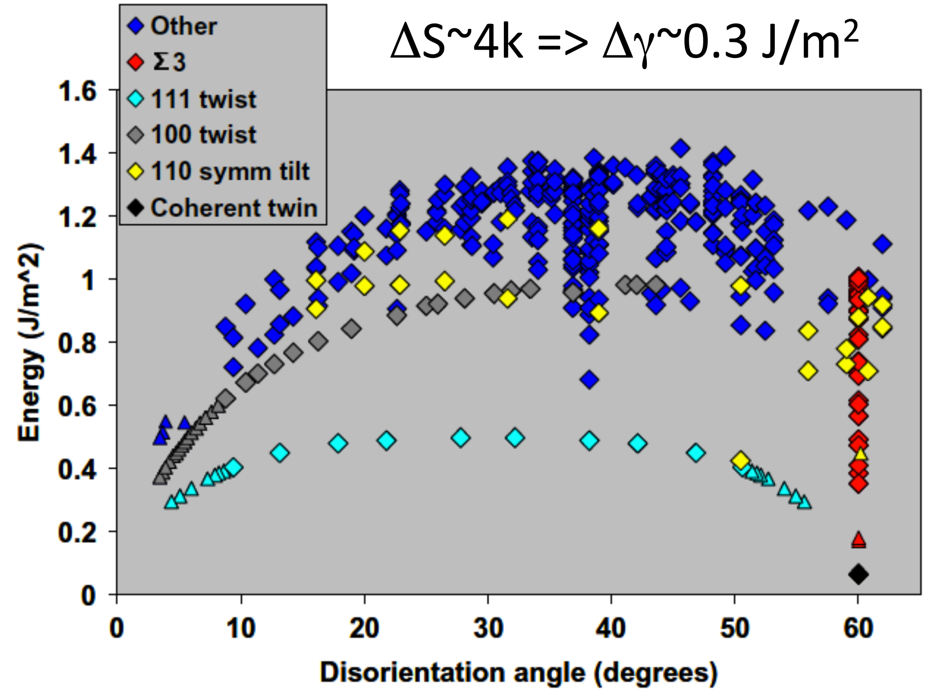


Fontanesi *J. Chem. Soc. Faraday Trans.* (1994)

Anthracene Hg/Ethylene Glycol



Fontanesi *Entropy* (2010)



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

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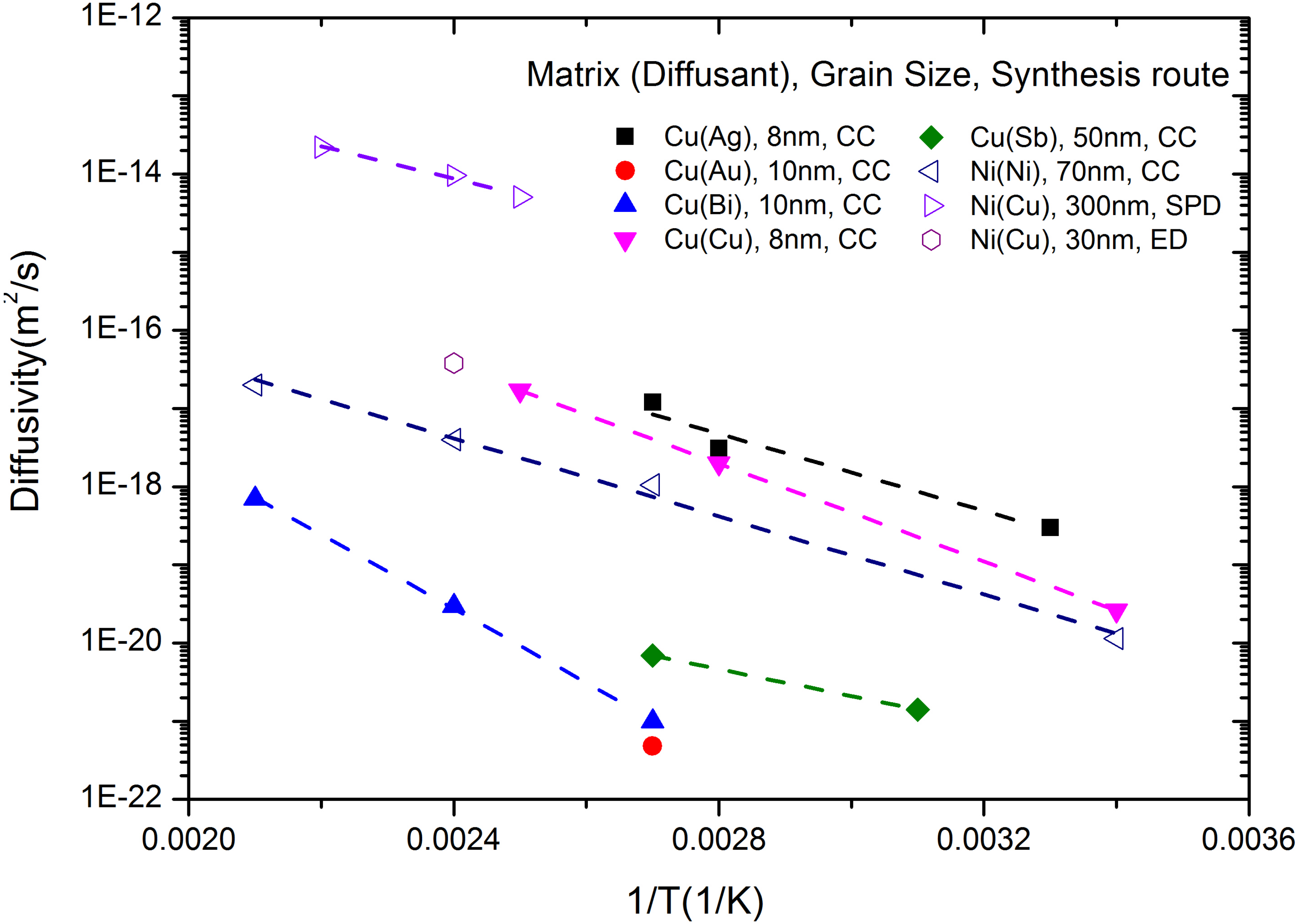
30 ppm-CaO	I (NGG)	0.82	−20
	III (AGG)	0.69	
200 ppm-SiO_2	I (NGG)	0.68	−10
	III (AGG)	0.61	

Dillon et al. *JACerS* 2010

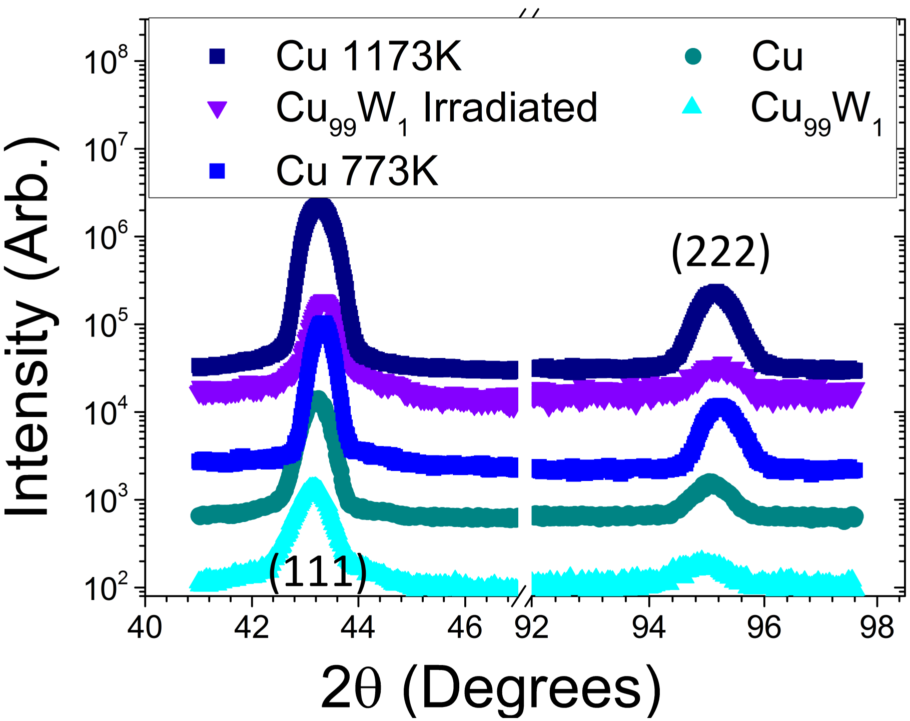
GB Diffusion in Nanograin Alloys- Motivation



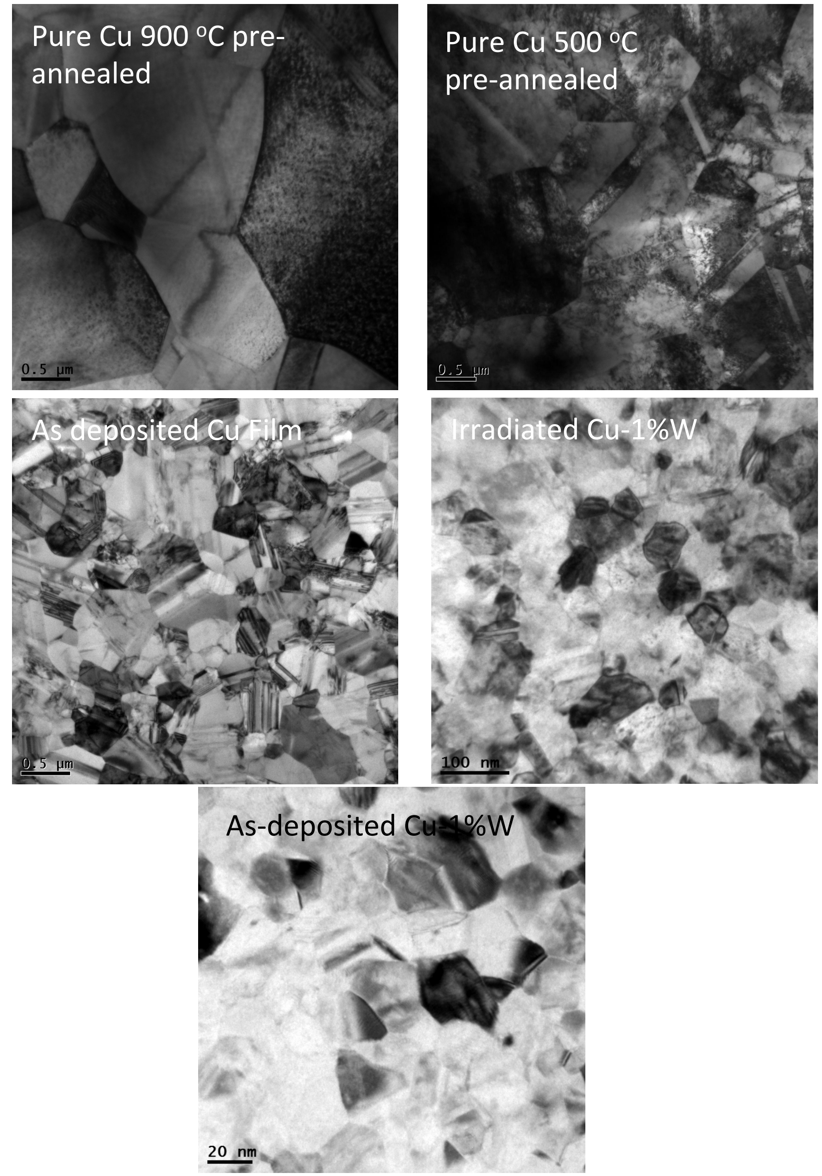
Kolobov et al. Russian J. Phys. (2008)

Wurschum, Herth, Brossmann, Advanced Engineering Materials (2003)

Cu Thin Films of Varying Grain Size

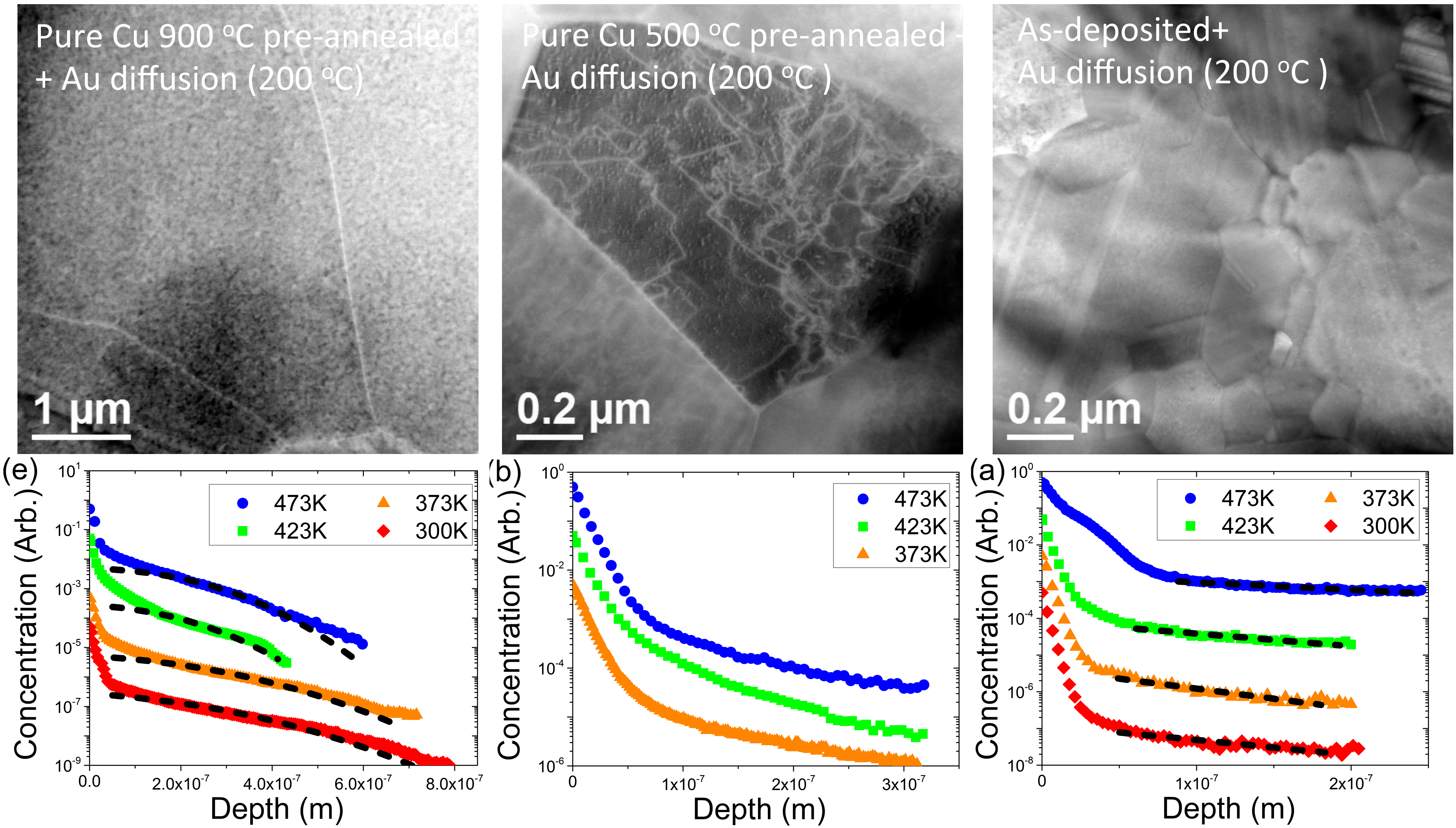


Sample	Average Grain Size (nm)		
	X-ray	TEM	
		w/o twins	w/ twins
Cu	15.0	~150	~20
Cu-W	14.7	~30	~15
Irrad. Cu-W	17.0	~80	~25
773K Cu	23.5	~2000	~280
1173K Cu	47.0	~4000	~550



K. Tai et al. *Acta Mater.* (2013)

Au diffusion in Cu (Different G.S.'s)

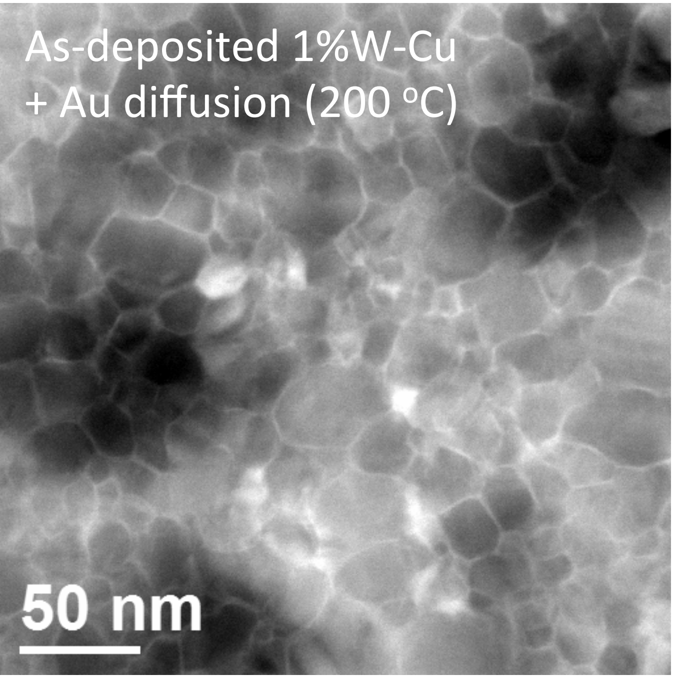


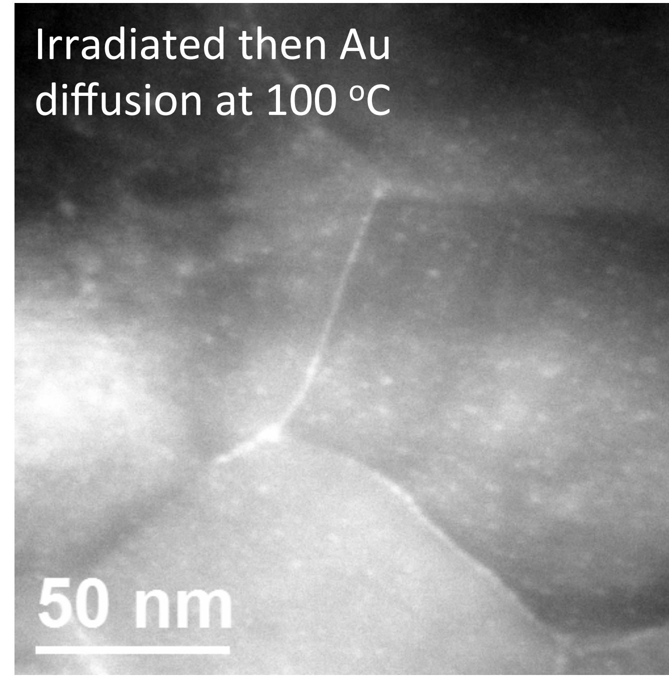
$$\bar{c}(z) \approx \bar{c}_{gb}(z) \propto \mathrm{erfc}\left(\frac{z}{2\sqrt{D_{gb}t}}\right)$$

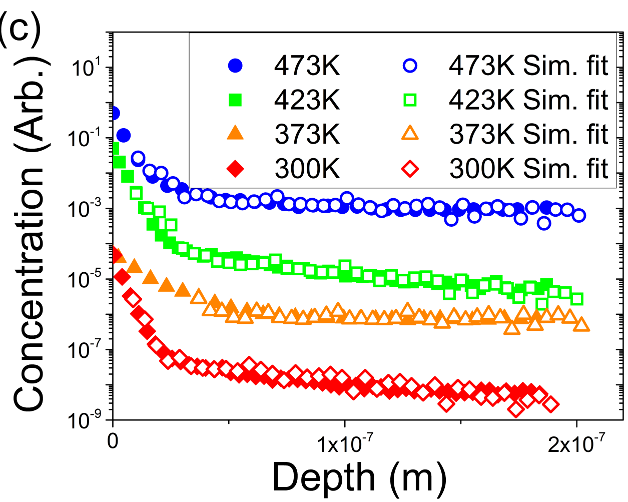
No Model

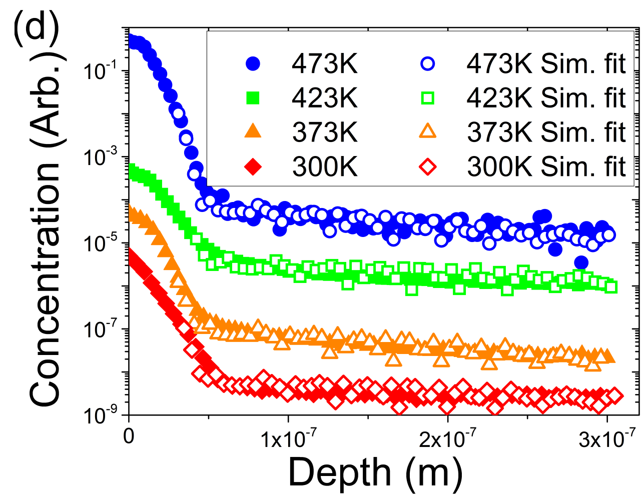
$$\delta D_{b} = v\left(\frac{\partial \ln \bar{c}}{\partial z}\right)^{-2}$$

Au diffusion in Cu (Different G.S.'s)









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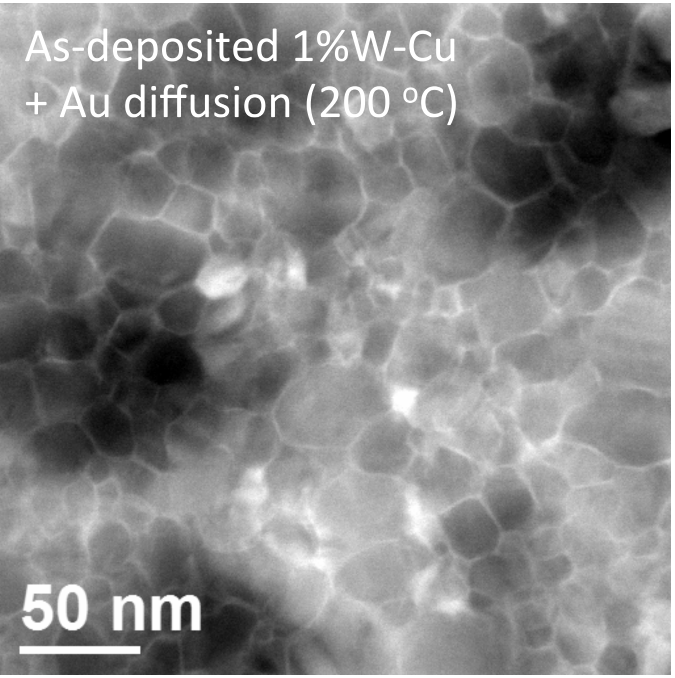
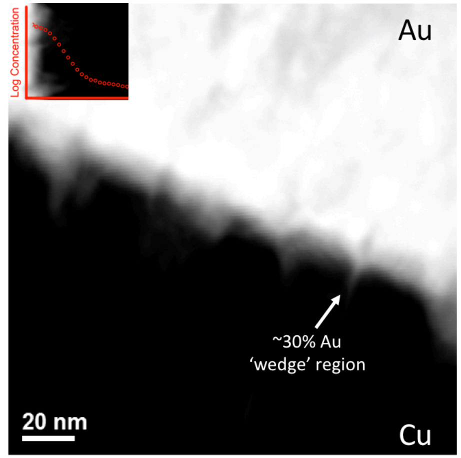
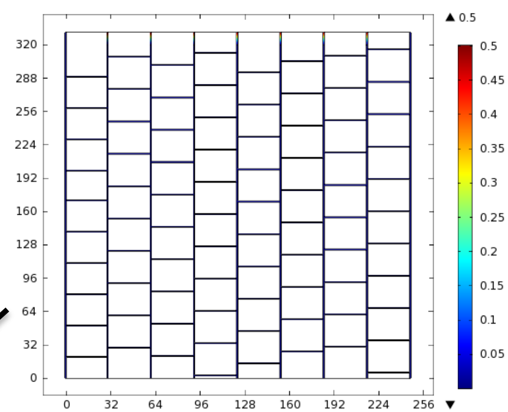
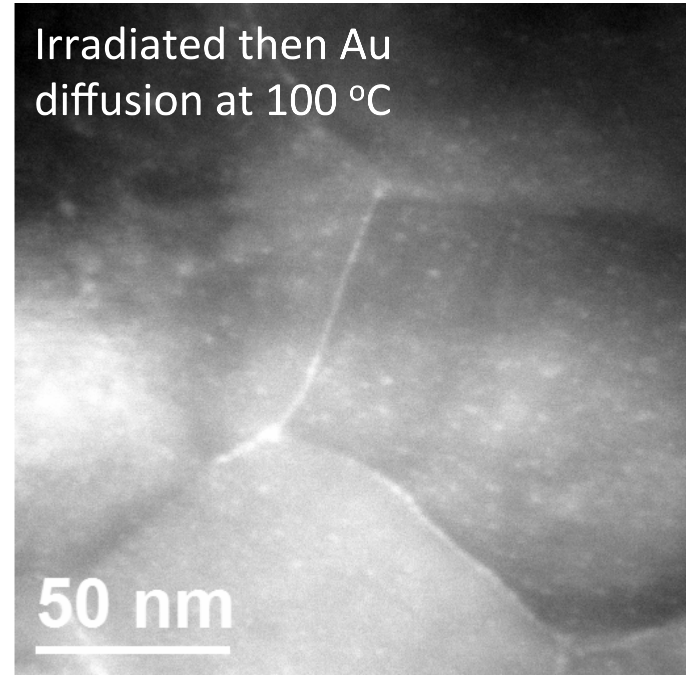
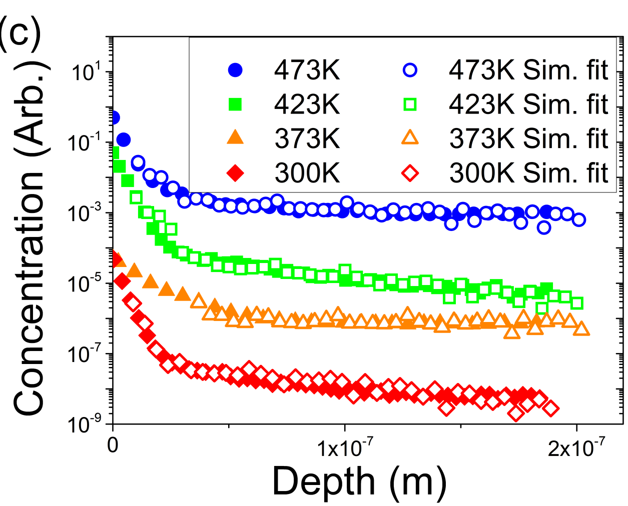
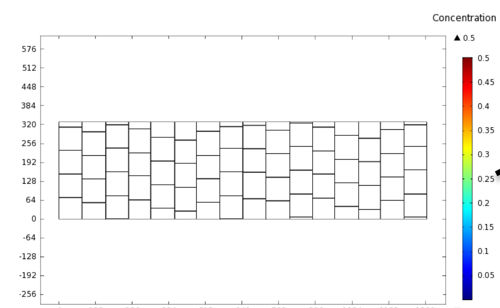


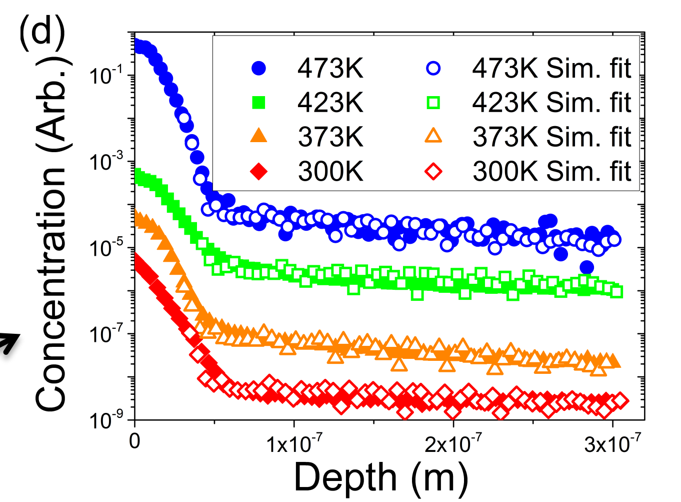






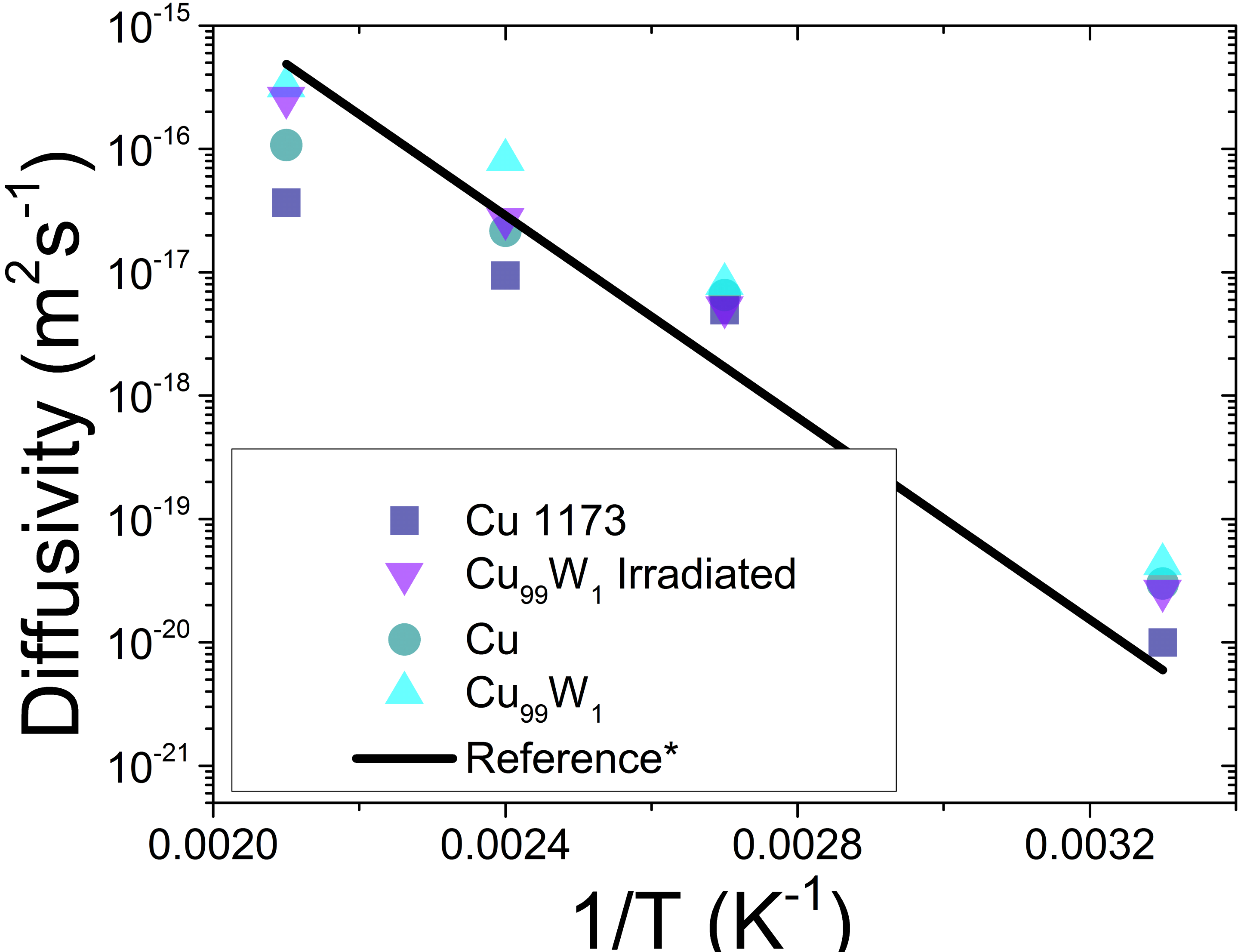






G.B. Kirkendall see: Klinger, *Acta Mater.* 2011

Results of Au G.B. Diffusion in Cu



Au diffusivity in the Cu – Limited 'nano-effect'

K. Tai et al. *Acta Mater.* (2013)

*Ref. Surholt, Mishin, Herzig, *Phys. Rev. B* (1994).

Conclusions

- Significant entropy contribution, ~4-8k, associated with G.B. complexion transitions
- The excess entropy is manifest as enhanced diffusivity / G.B. mobility
- G.S. effect on diffusivity weak on thin film samples
- Thermal relaxations are qualitatively 'rapid' at temperatures where vacancy hops active