LM-04K037
May 27, 2004

Applications of Ab Initio Modeling to Materials Science: Grain Boundary Cohesion and Solid State Diffusion

GA Young, R Najafabadi, W Strohmayer, J Vollmer, C Thompson,
W Hamm, C Geller, E Wimmer, J Sticht, A Mavromaras and J Harris

Applications of Ab Initio Modeling to Materials Science: Grain Boundary Cohesion and Solid State Diffusion

Medea User's Group Meeting, Orcas Island, WA, June 17-20, 2004

George A. Young, Reza Najafabadi, Walter Strohmayer, James Vollmer, Charles Thompson, William Hamm

Lockheed Martin Corporation

Schenectady, NY 12301-1072

Clint Geller

Bechtel Bettis, Inc.

West Mifflin, PA 15122-0079

Erich Wimmer, Jurgen Sticht, Alexander Mavromaras, John Harris

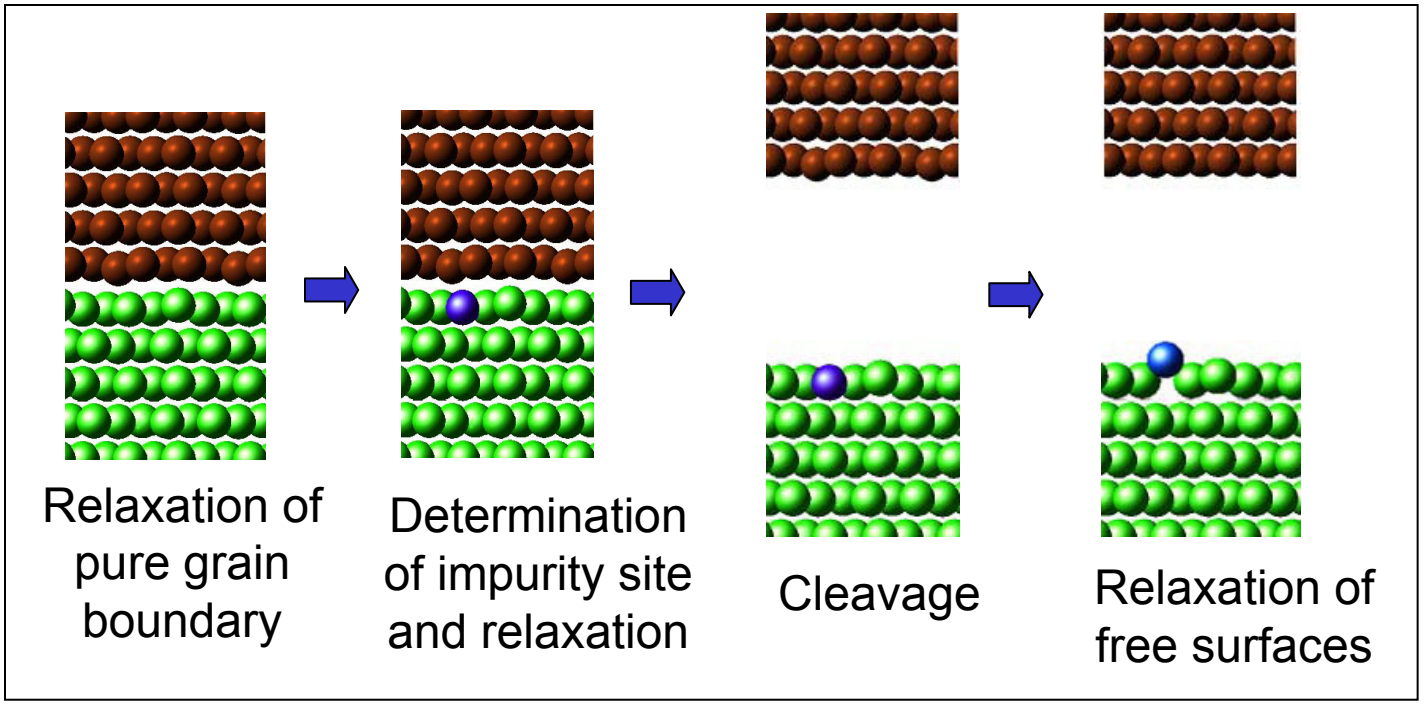
Materials Design Inc.

Angel Fire, NM 87710-1318

Background

- I. Grain boundary cohesion
  - Metallurgical understanding
  - Account for multiple elements
  - Effect of H concentration
  - Mechanisms of embrittlement
    - He embrittlement
    - SCC resistance
- II. Solid State Bulk Diffusion
  - Work of Wolverton *et al*.
  - Proof of principle for H in nickel
  - Determination of D_0 and Q from first principles
  - H diffusion in HCP Ti and Zr
  - H diffusion in FCC Fe – effect of lattice parameter

Computational Procedure: Pure nickel, Σ5-{100} twist grain boundary, 0 K

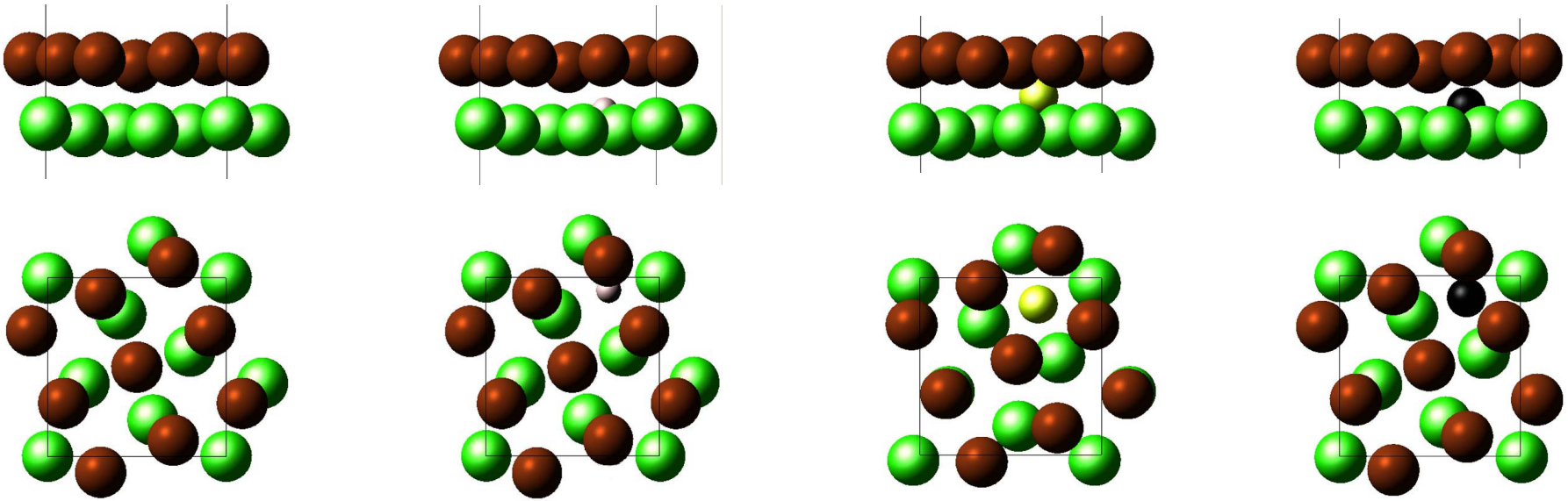


$$\Delta E_{Griffith} = \left(E_{Surface} - E^{impurity}_{Surface}\right) - \left(E_{\substack{Grain \\ Boundary}} - E^{impurity}_{\substack{Grain \\ Boundary}}\right)$$

Geometry of impurity atoms on nickel Σ5 {100}

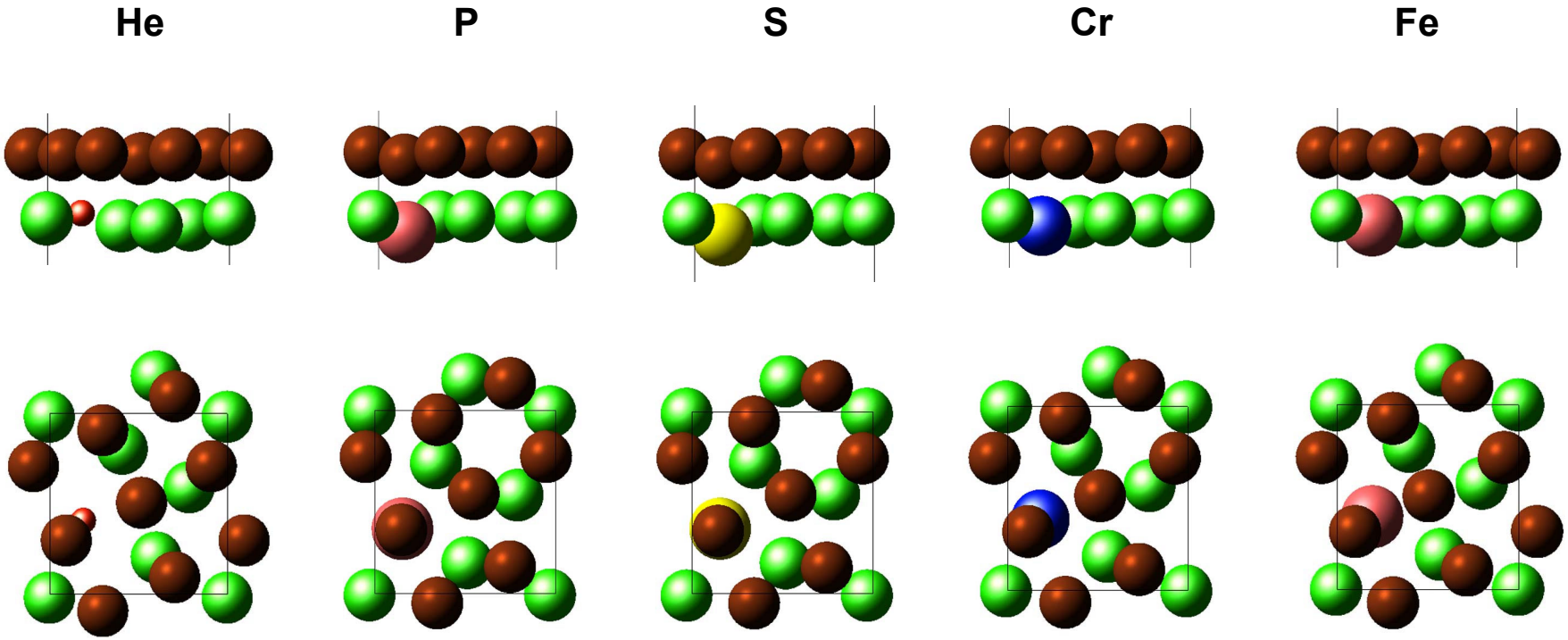
Interstitial impurities

pure Ni | H | B | C



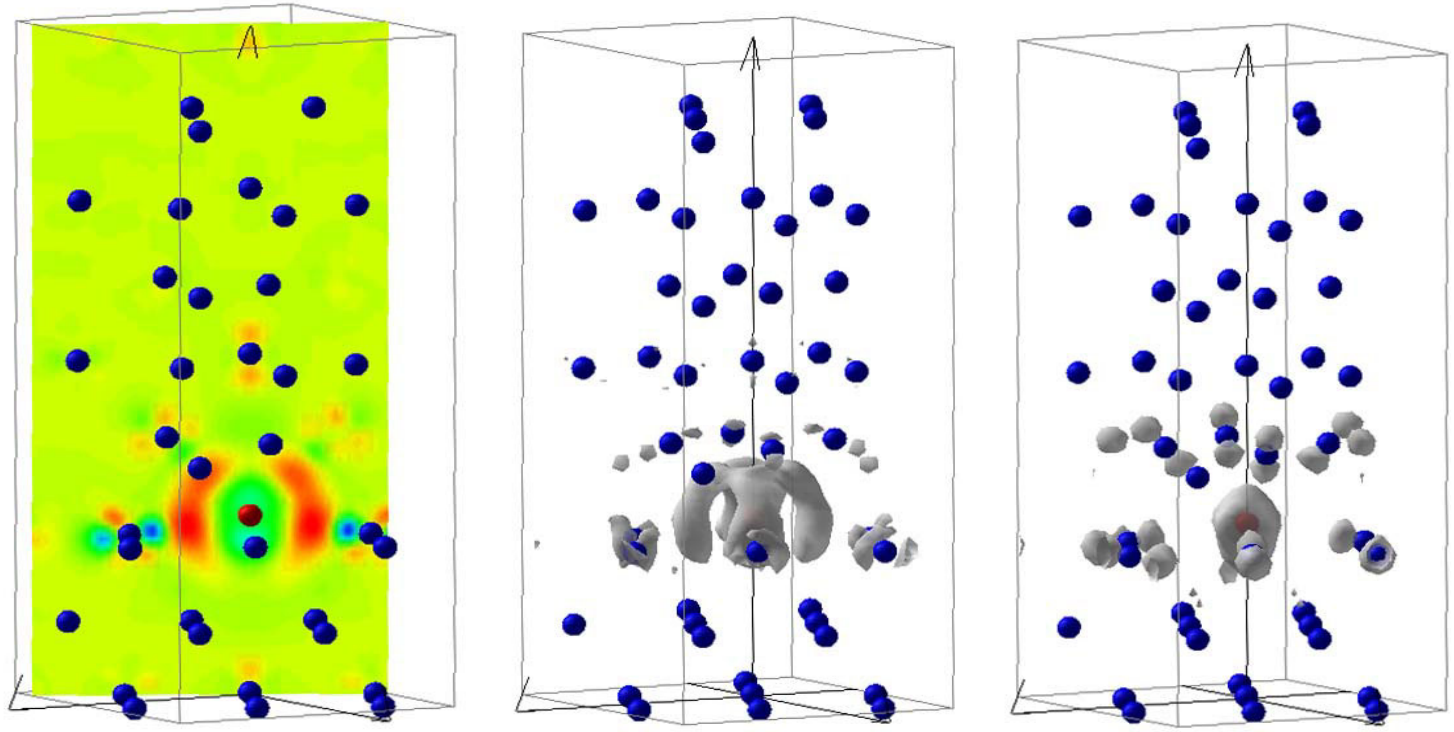
Geometry of impurity atoms on nickel Σ5 {100}

Substitutional impurities



Structure / energy mapping: degree and extent of electronic interactions

Electronic charge changes around a P impurity atom in Ni



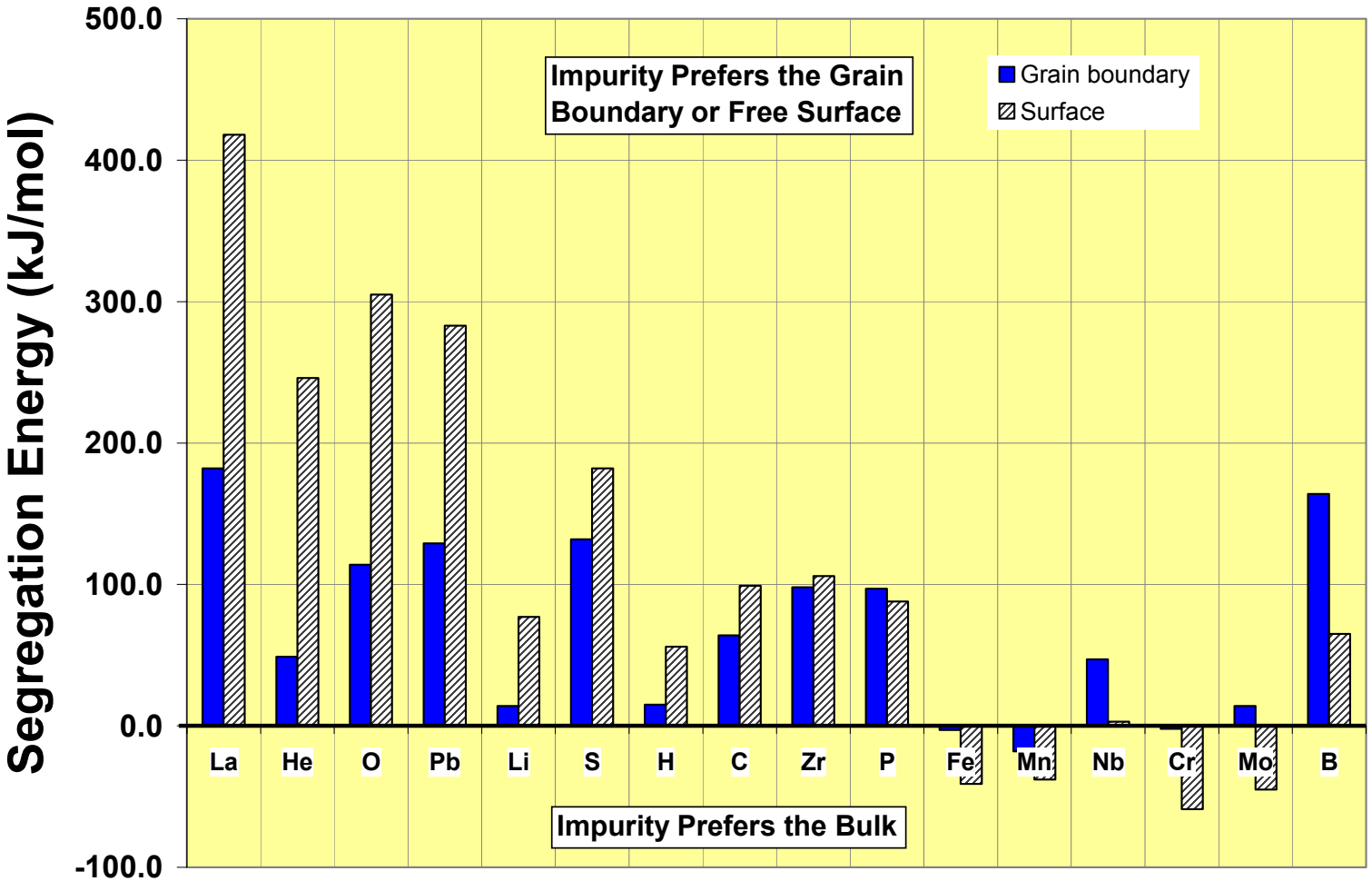
(a) (b) (c)

Gain (red), loss (green)

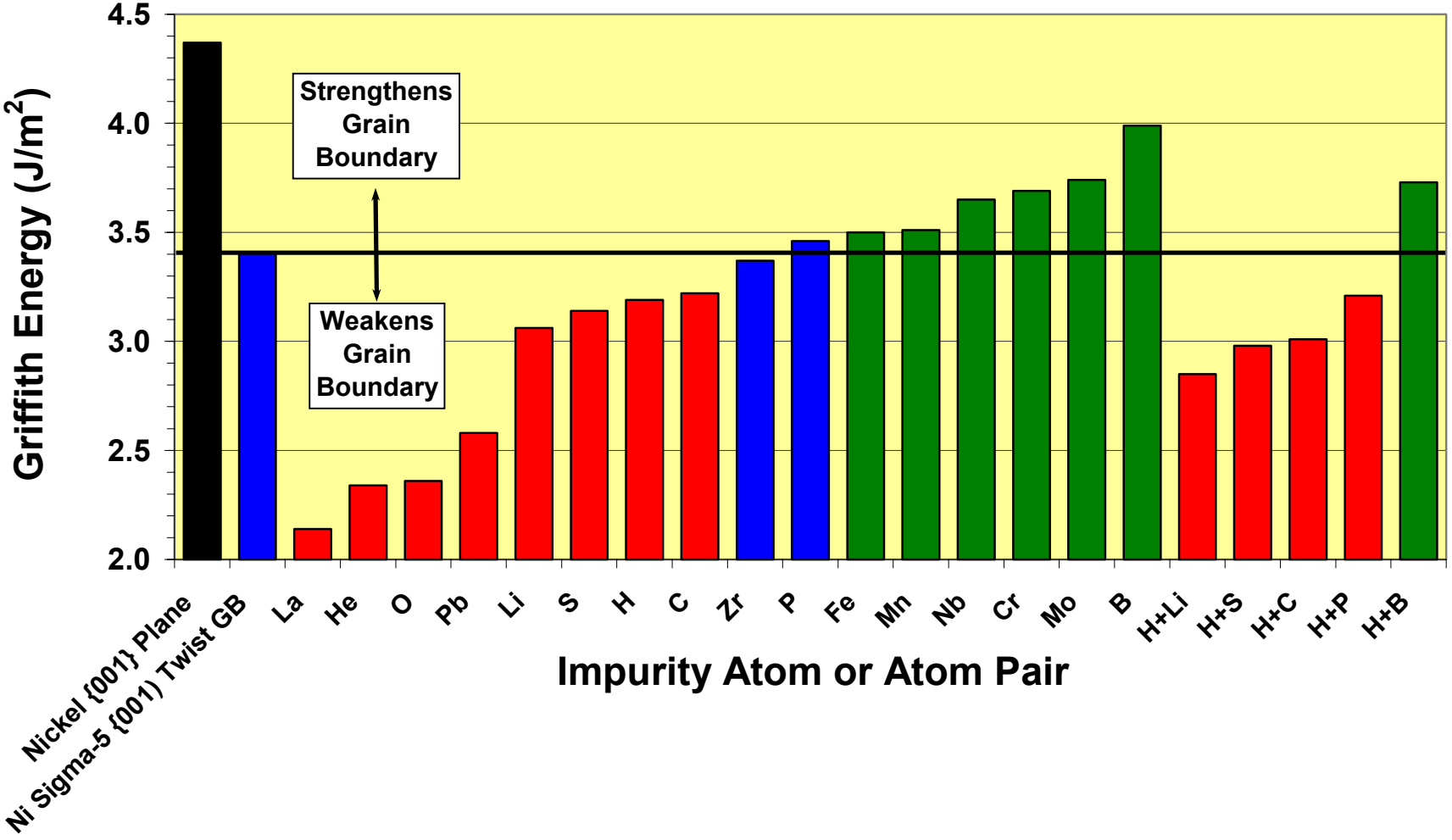
Gain

Loss

Tendency to migrate to grain boundary, surface, or bulk (Note boron)



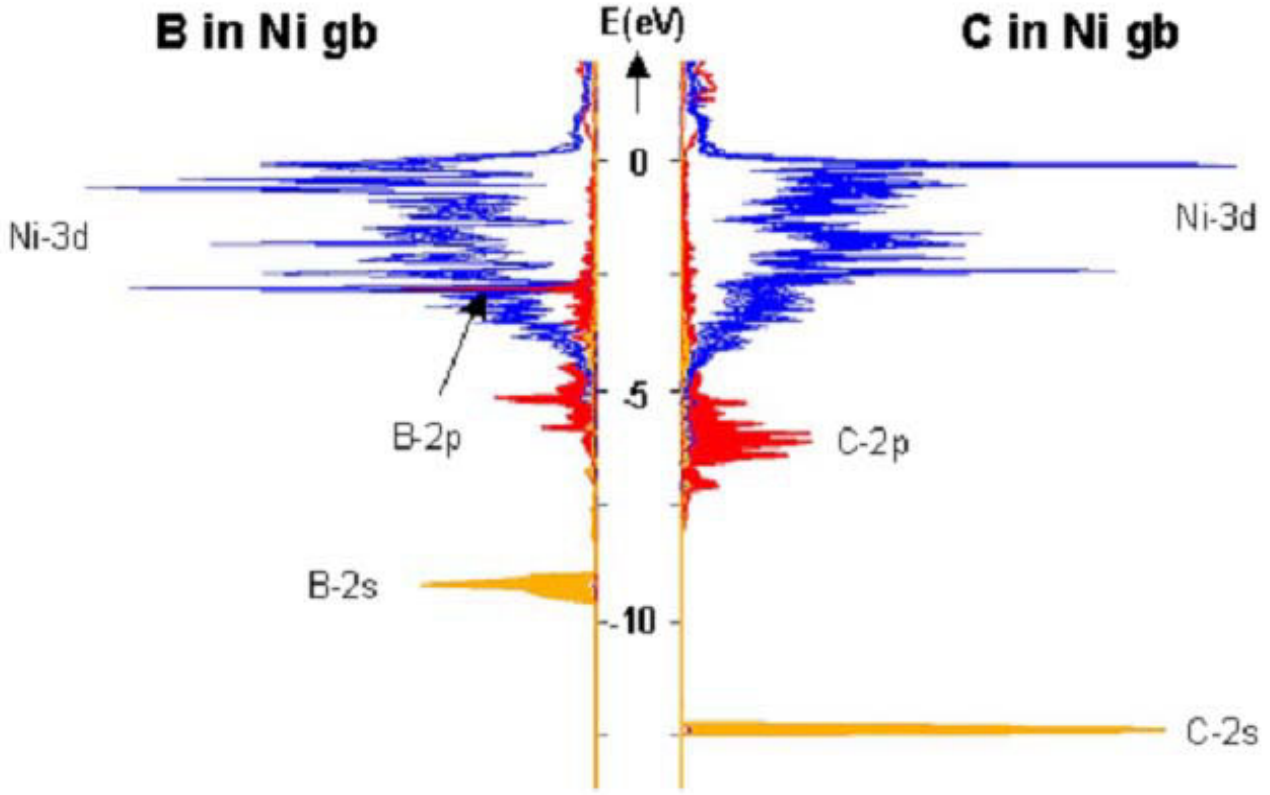
Fundamental effects of impurities on grain boundary strength



Metallurgical strengthening of grain boundaries

- Boron a known strengthener of Ni grain boundaries
- Theories (Donachie from Superalloys Source Book):
  - Boron alters grain boundary precipitate structure
  - Boron has a beneficial interaction with a deleterious element (*e.g.* ties up sulfur ?)
  - Boron reduces the grain boundary diffusivity (slows S segregation ?)

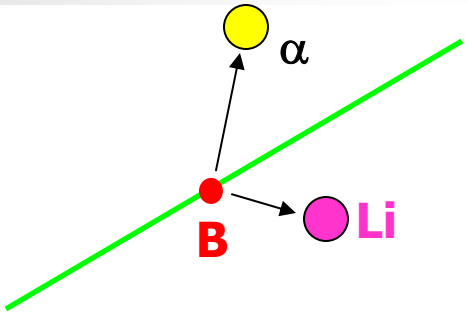
Why does boron promote grain boundary strength (but carbon doesn't) ?



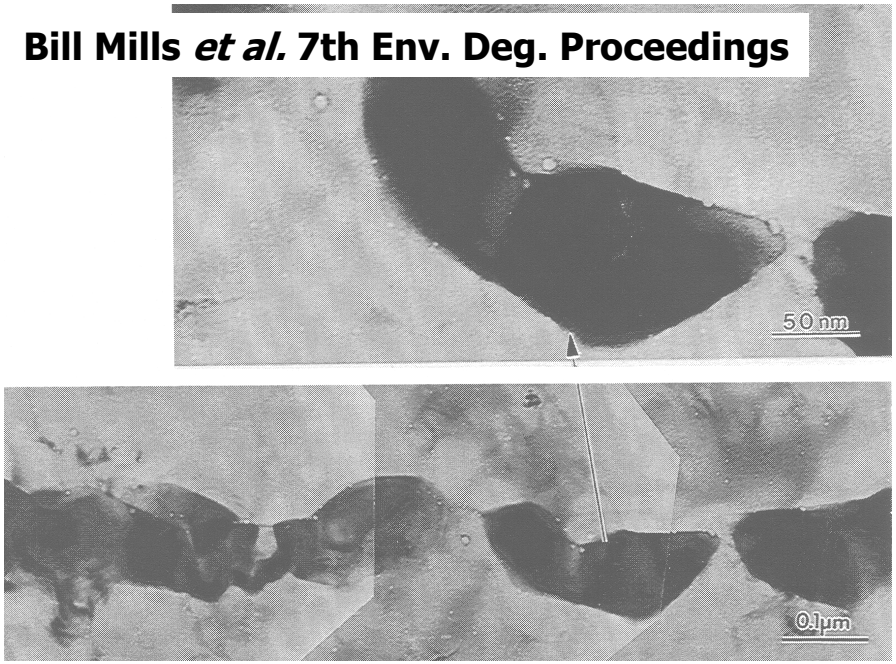
B-2p electrons overlap with Ni-3d → bonding

Mechanism of "He Embrittlement"

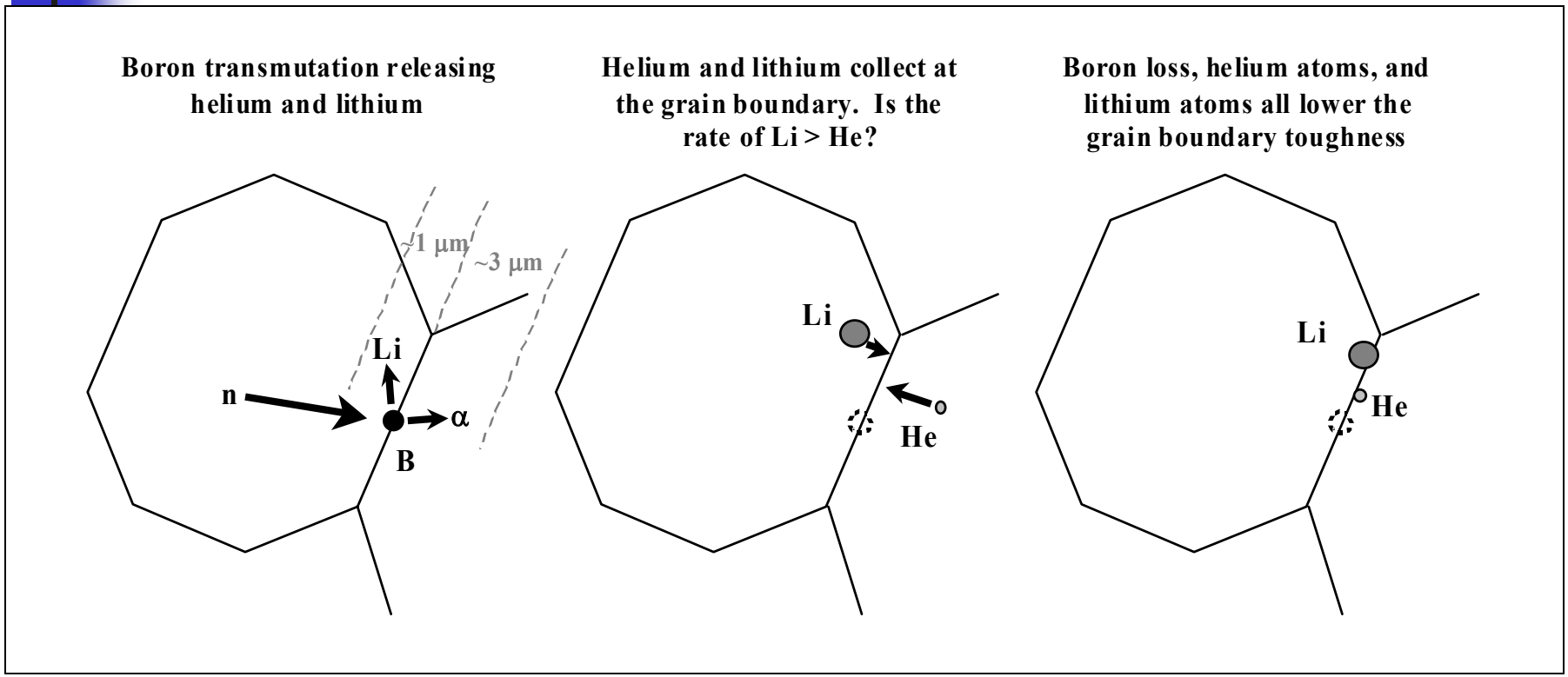
$$^{10}_{5}B + ^{1}_{0}n \rightarrow ^{7}_{3}Li + ^{4}_{2}He$$



- After irradiation *and annealing,* He bubbles on nickel grain boundaries have been observed
- *But* you embrittle before you observe physical bubbles – intrinsic He embrittlement (see Mills *et al.*)
- Need to assess B loss and Li embrittlement, kinetics of He and Li diffusion

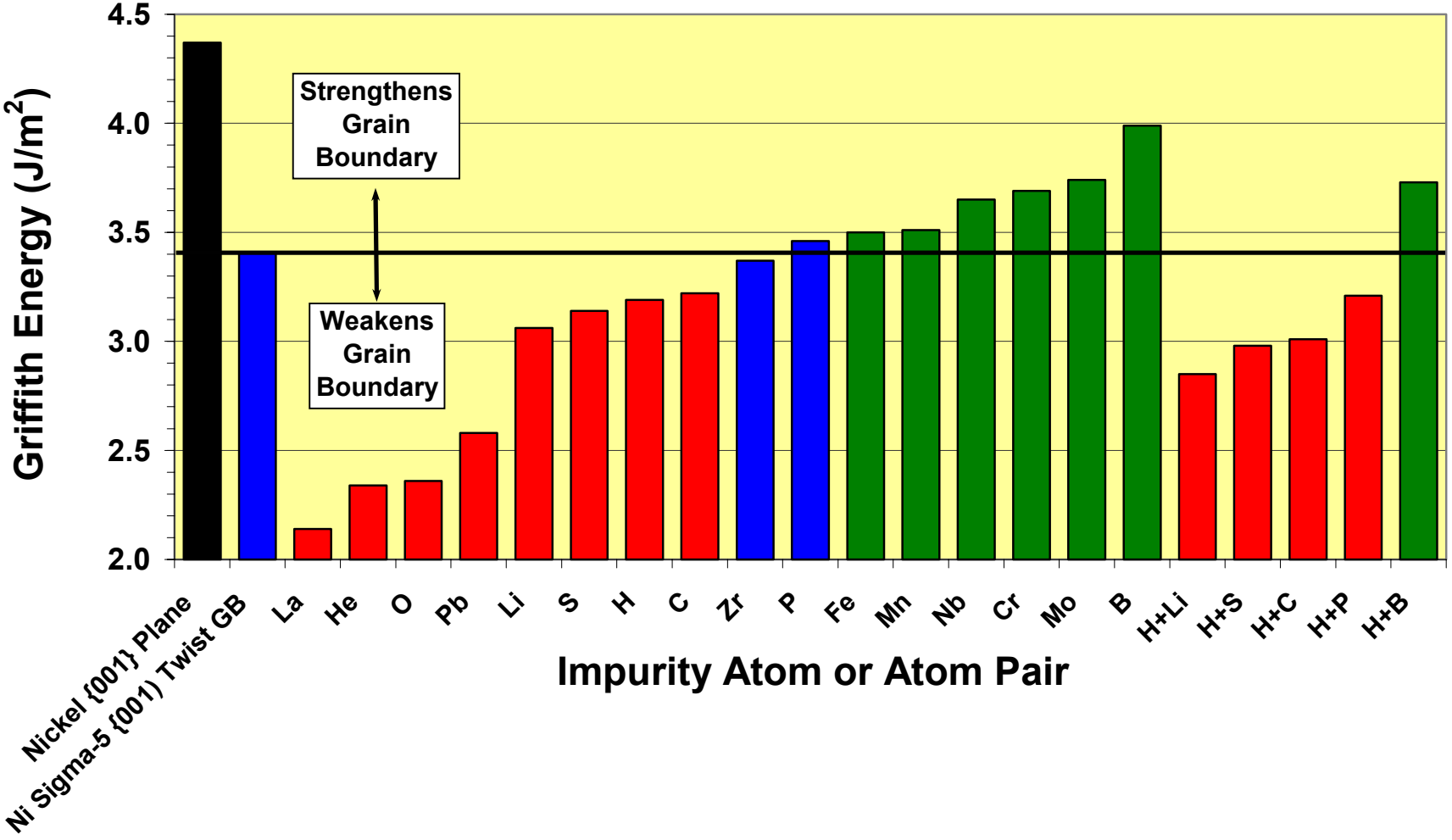


B loss + Li embrittlement + He embrittlement



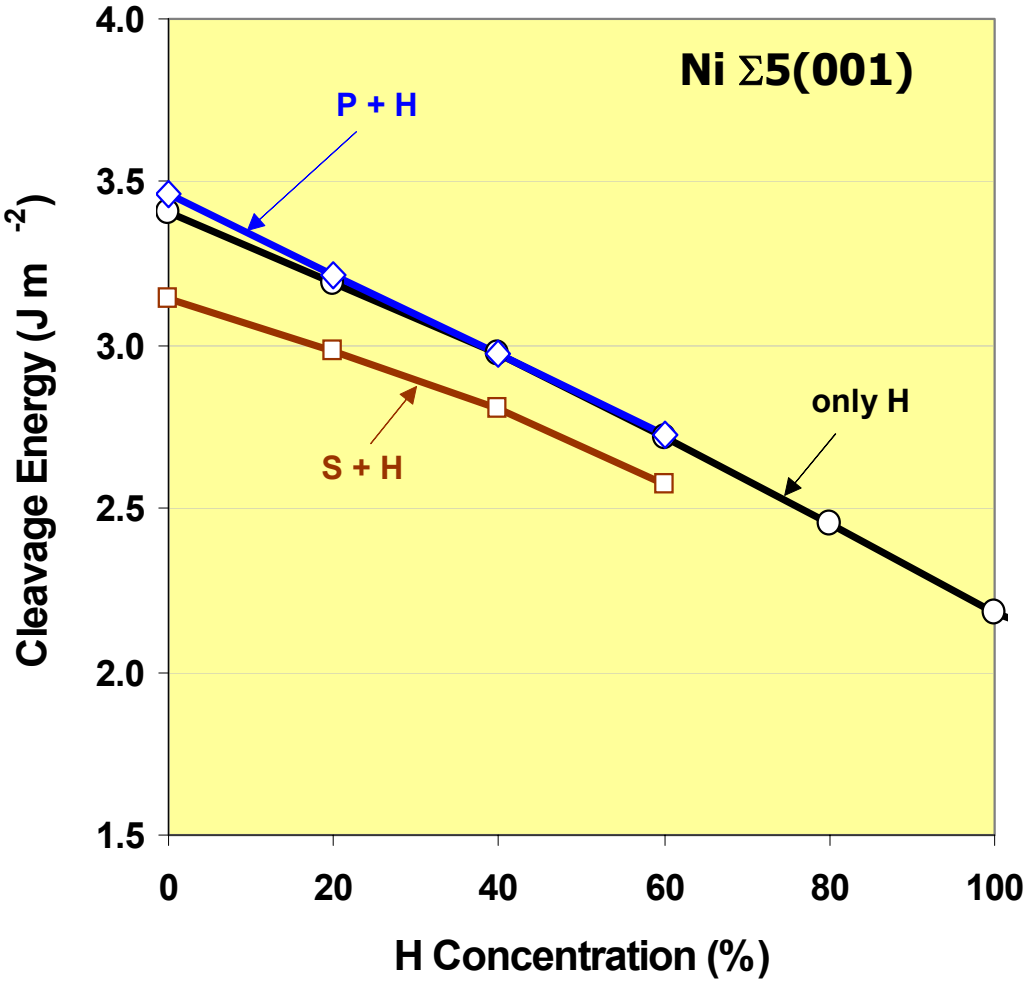
→ Need to understand kinetics of Li and He migration back to grain boundary

He and Li embrittlers, B strengthener

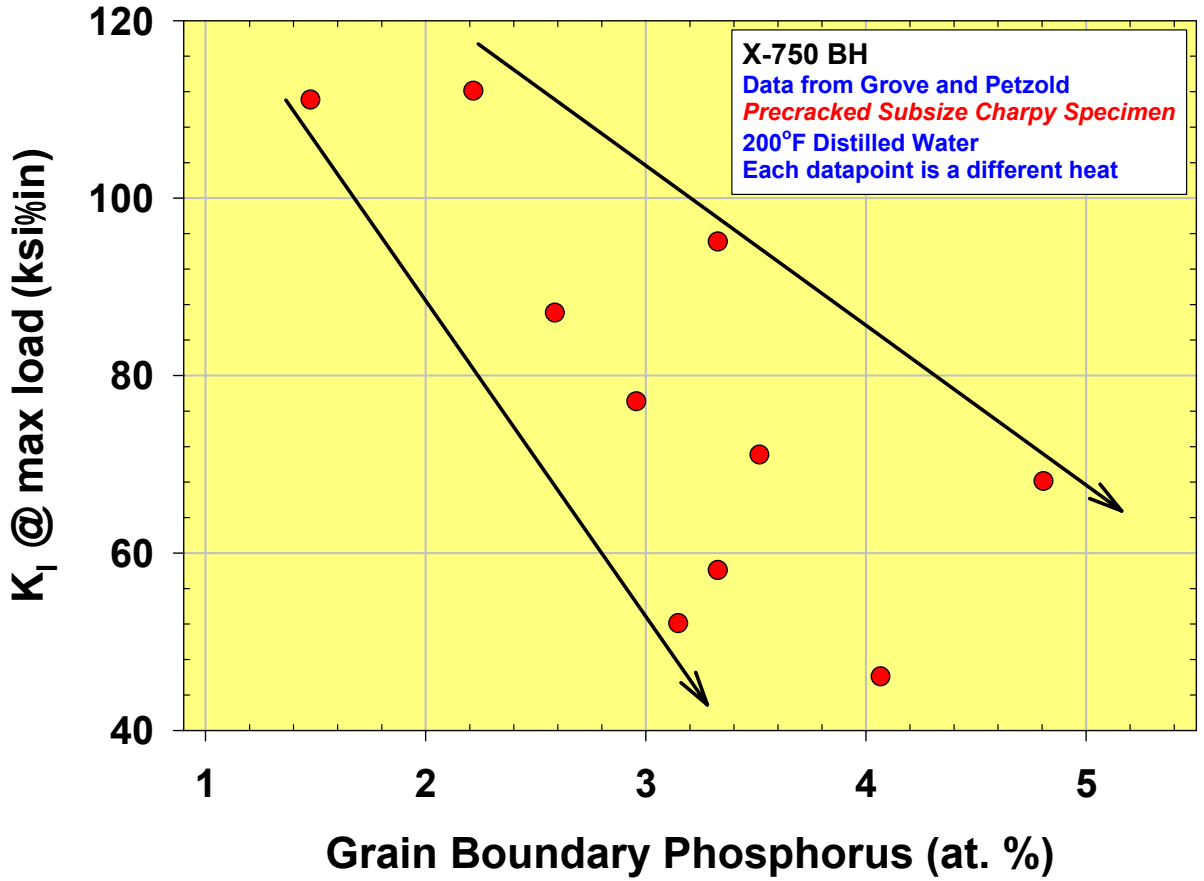


Effect of H concentration on cleavage energy with and without S and P impurities

- Linear superposition good first approximation
- No significant synergistic effects
- S and H act additively



Need to account for multiple effects: (1) GB strength and (2) effect on H uptake



$$\text{Relative Grain Boundary Strength} = -4.86[He] - 3.77[Pb] - 1.58[Li] - 1.00[H] - 0.86[C] - 0.18[Zr] + 0.23[P] + 0.41\{Fe] + 0.45[Mn] + 1.09[Nb] + 1.27[Cr] + 2.64[B]$$

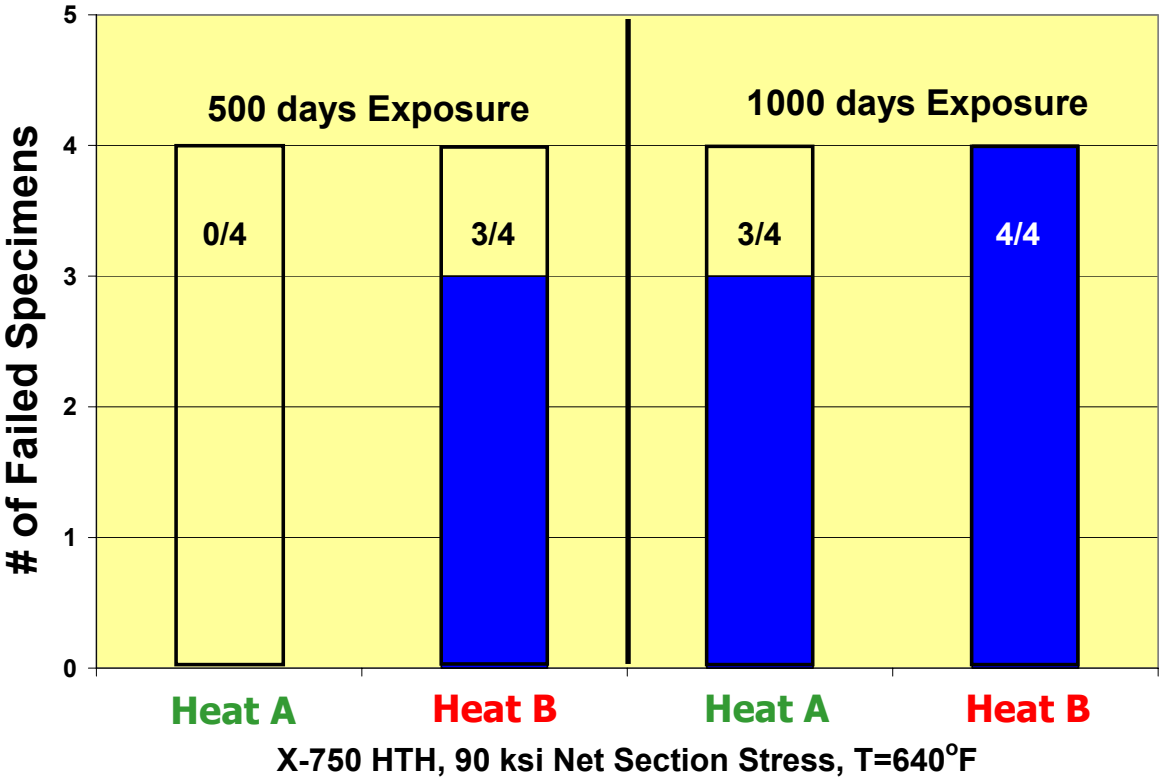
SCC of X-750: Similar heats with different response to SCC initiation and growth

X-750 Condition HTH (2025°F/1hr + 1300°F/20 hrs)

Heat	Ni	Cr	Fe	Ti	Al	Mn	C	B	P	S	Nb+Ta
A	72.43	15.54	7.93	2.60	0.79	0.07	0.039	0.0037	0.007	0.001	0.86
B	71.47	15.25	8.15	2.66	0.73	0.15	0.043	0.0022	0.002	0.002	0.97

Heat	YS (ksi)	UTS (ksi)	% El	%RA
A (Good)	118	172	27	32
B (Bad)	117	176	26	36

Heat "B" shows shorter initiation times and faster crack growth rates

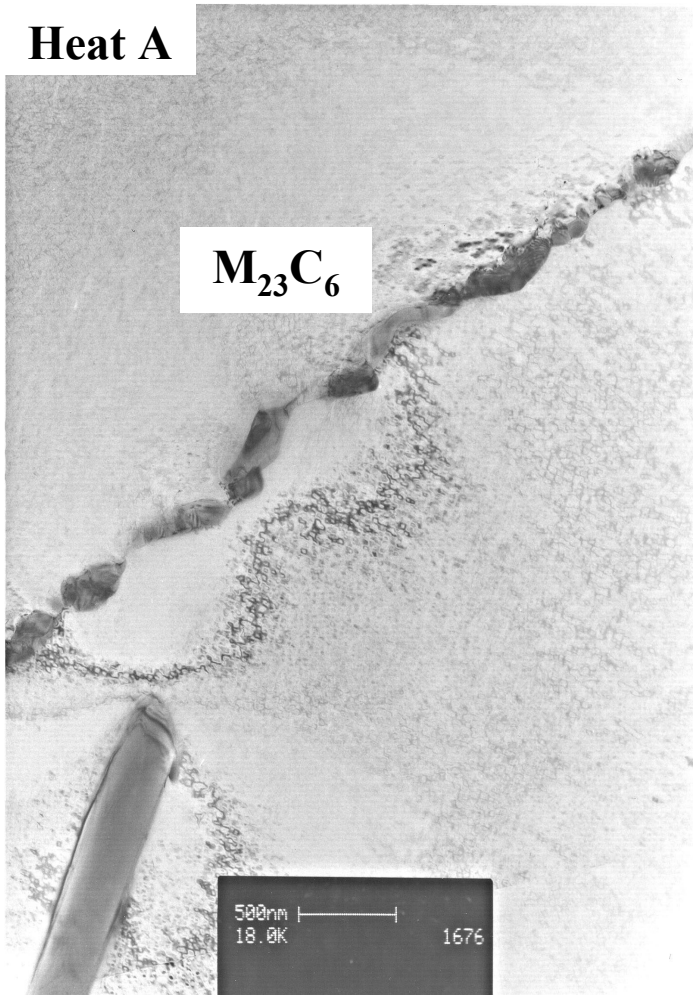


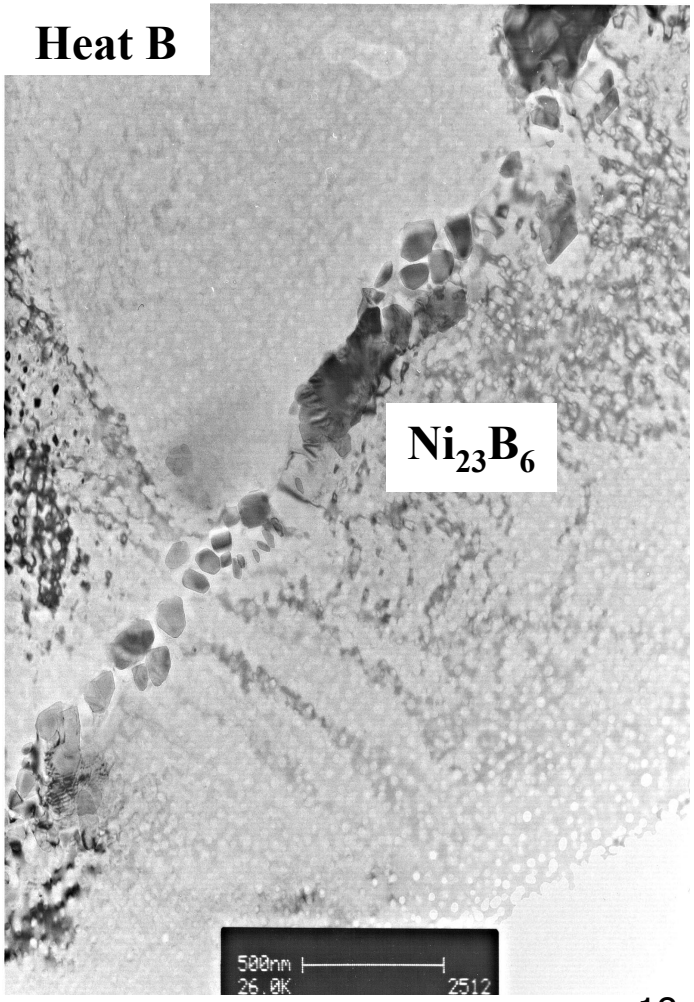
Heat	CGR at 680°F K=35 ksi√in
A	1.1 mils/day
B	1.8 mils/day

See Young *et al.* in 11th International Symposium on Environmental Degradation of Materials in Nuclear Power Systems – Water Reactors, Skamania, WA, August 2003.

Heat A - typical $Cr_{23}C_6$ carbides
Heat B - unusually high # of $Ni_{23}B_6$

- **Loss of atomic boron**
- **No Cr depletion around borides**
- **Faster SCC initiation and growth**





Summary

- Ab Initio atomistic modeling gives unique insight into metallurgical effects
  - Explain alloying effects: Boron intrinsically strengthens Ni grain boundaries by helping to fill the Ni 3d orbital
  - De-convolute complex embrittlement phenomena: boron transmutation / stress corrosion cracking
  - Quantitatively assess the effects of multiple grain boundary impurities

Ab Initio Modeling of Solid State Diffusion: Hydrogen in Structural Metals

Ab initio modeling of solid state diffusion

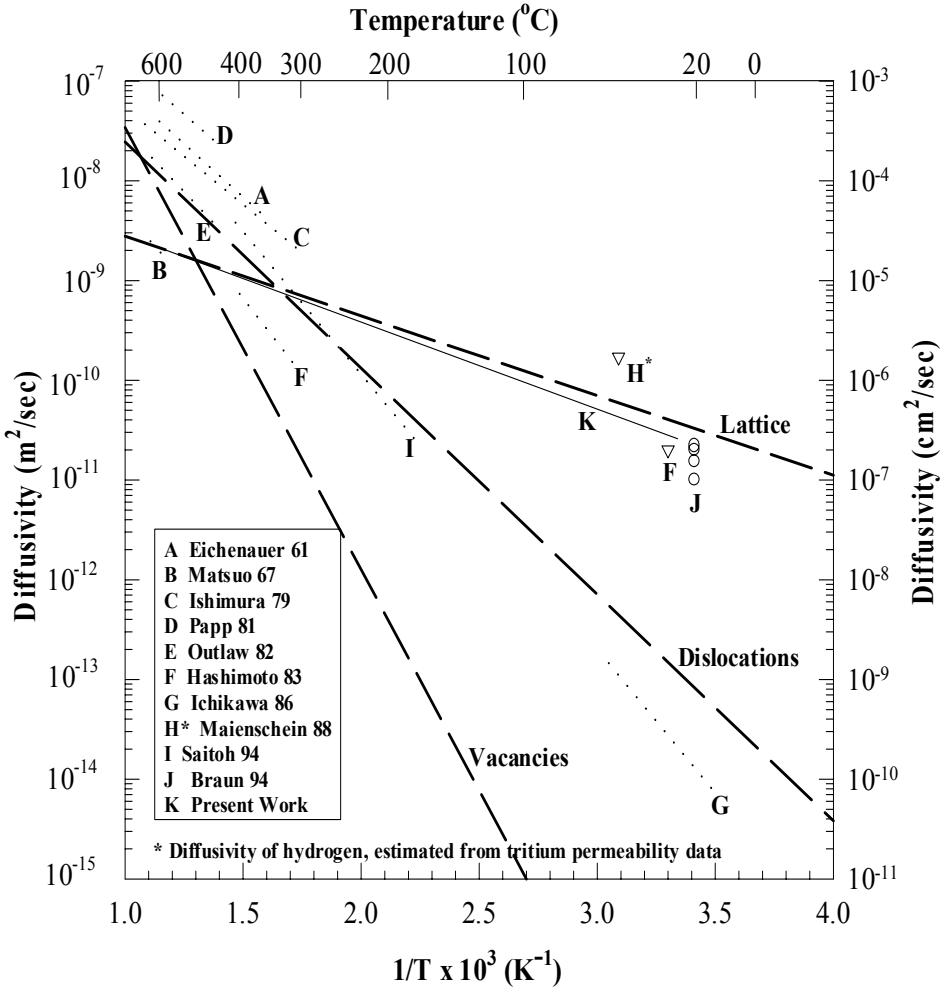
- Phonon capability in MedeA/VASP is a significant advance, allowing accurate determination of things like enthalpy, and entropy *as a function of temperature → free energy*
- Phonons enable first principles studies of diffusion, solubility, etc. that are often experimentally difficult and subject to significant controversy, *e.g.* H diffusion in Al, Ti, O solubility in Ni, etc.
- Examples
  - Chris Wolverton on H in Al
  - Present work on H in Ni, Ti, Zr, and Fe

Experimental difficulties in diffusion

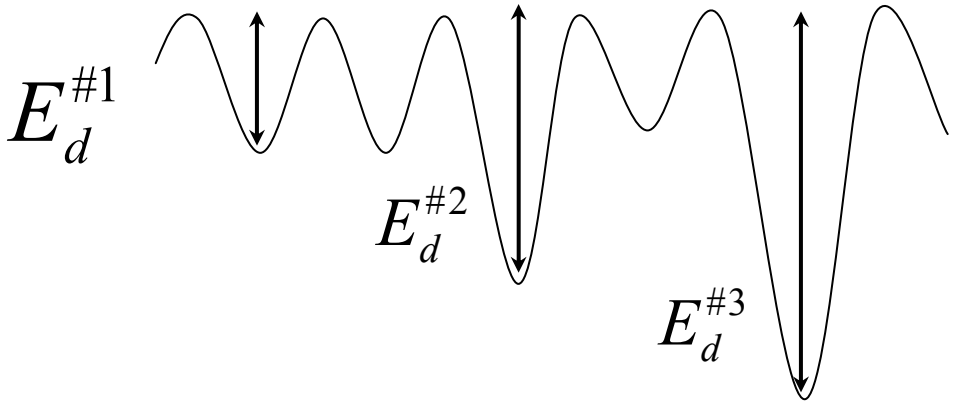
- Often large noise / small signal
- Oxide or other surface films often diffusion barriers
- Effects of traps often not considered
- May be difficult to ensure "lattice diffusion" control
- Electrochemical methods: charging solutions can degrade sample (pitting)
- Vacuum methods: time lag between charging and measurement
- etc., etc.

Hydrogen diffusion in aluminum

- H diffusion both fundamental and technically important to Al and Al alloys
- Large controversy in literature
- See:
  - Young and Scully, Acta Mat. Vol. 46, No. 18, pp. 6337-6349
  - Wolverton *et al.,* Phys. Rev. B, 69, 144109, 2004



Barrier for lattice diffusion is relatively low, vacancies are strong trapping states



Desorption Energies in Aluminum (kJ/mol)			
Researcher	**Lattice**	**Dislocation**	**Vacancy**
Young (experimental)	15.3 ±4.8	43.5 ±17.5	84.8±32.2
Wolverton (*ab initio*)	17	---	52

Diffusion Equation – see Wert and Zener Phys. Rev. Vol. 76, No. 8, Oct. 15, 1949, pp. 1169-1175.

$$D = \underbrace{n\,\alpha\,a^2\,\nu\,\exp\{\Delta S / R\}}_{D_0}\exp\{-\Delta H / RT\}$$

- n: number of nearest neighbor jump sites
- α: numeric coefficient that depends on the location of the interstitial positions
- a: lattice parameter (net jump distance, l)
- ν: vibrational frequency
- ΔS: activation entropy
- ΔH: activation enthalpy (Q)
- R: gas constant, T: temperature

Diffusion procedure: consider temperature dependence of ΔS and ΔH (and ν)

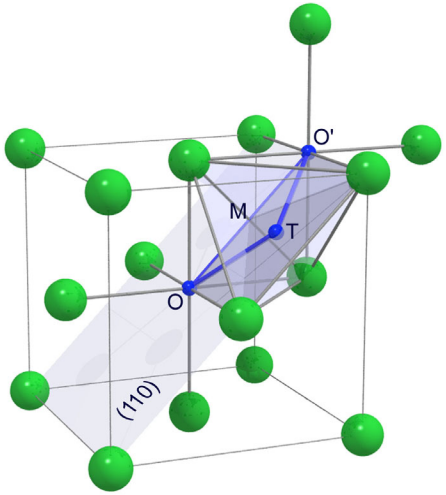
$$D = n\,\alpha\,l^2\,\nu\,\exp\{\Delta S(T)/R\}\exp\{-\Delta H(T)/RT\}$$

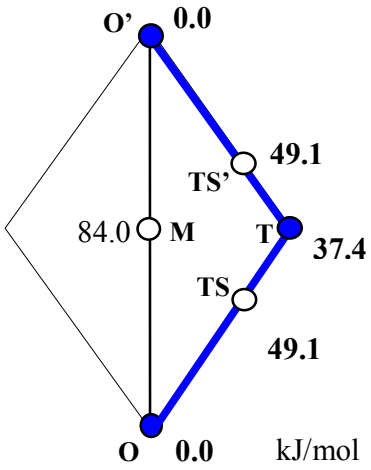
- Determine low energy site
- Determine low energy path

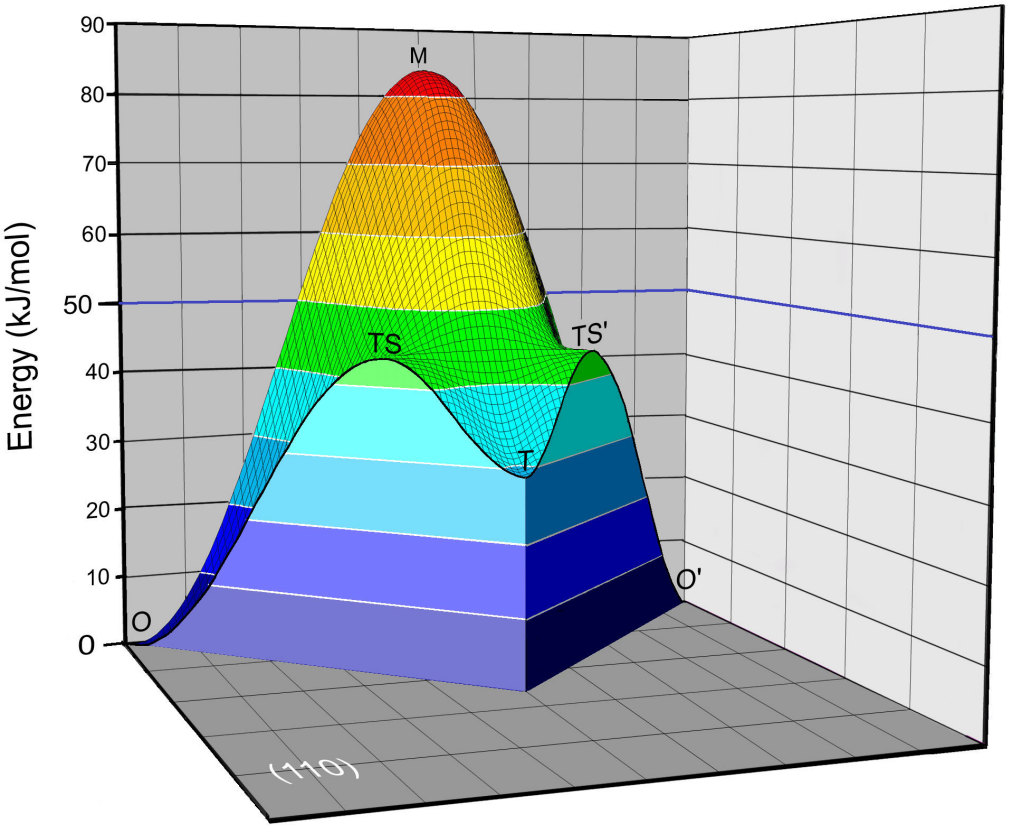
} n, α, and l

- Vibrational frequency (relatively T independent) } ν
- Entropy change $f(T)$ } ΔS
- Enthalpy change $f(T)$ } ΔH

Octahedral site and indirect diffusion path via transition state

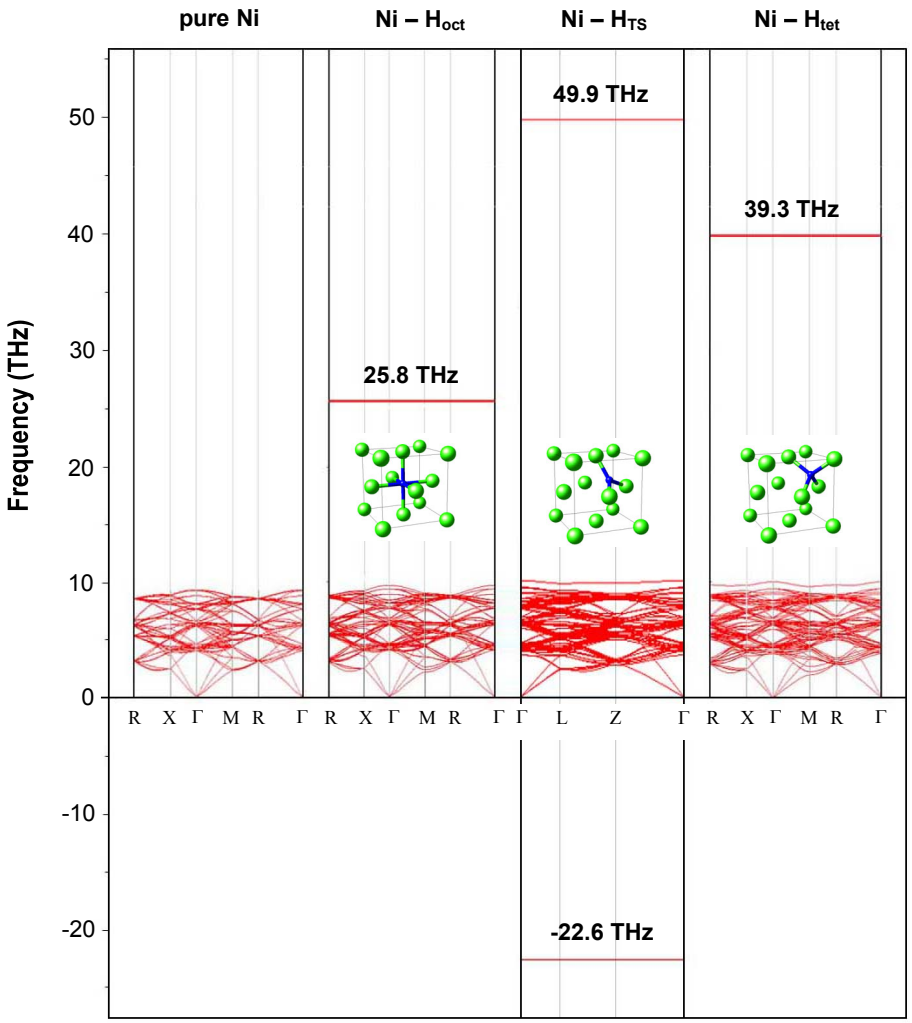




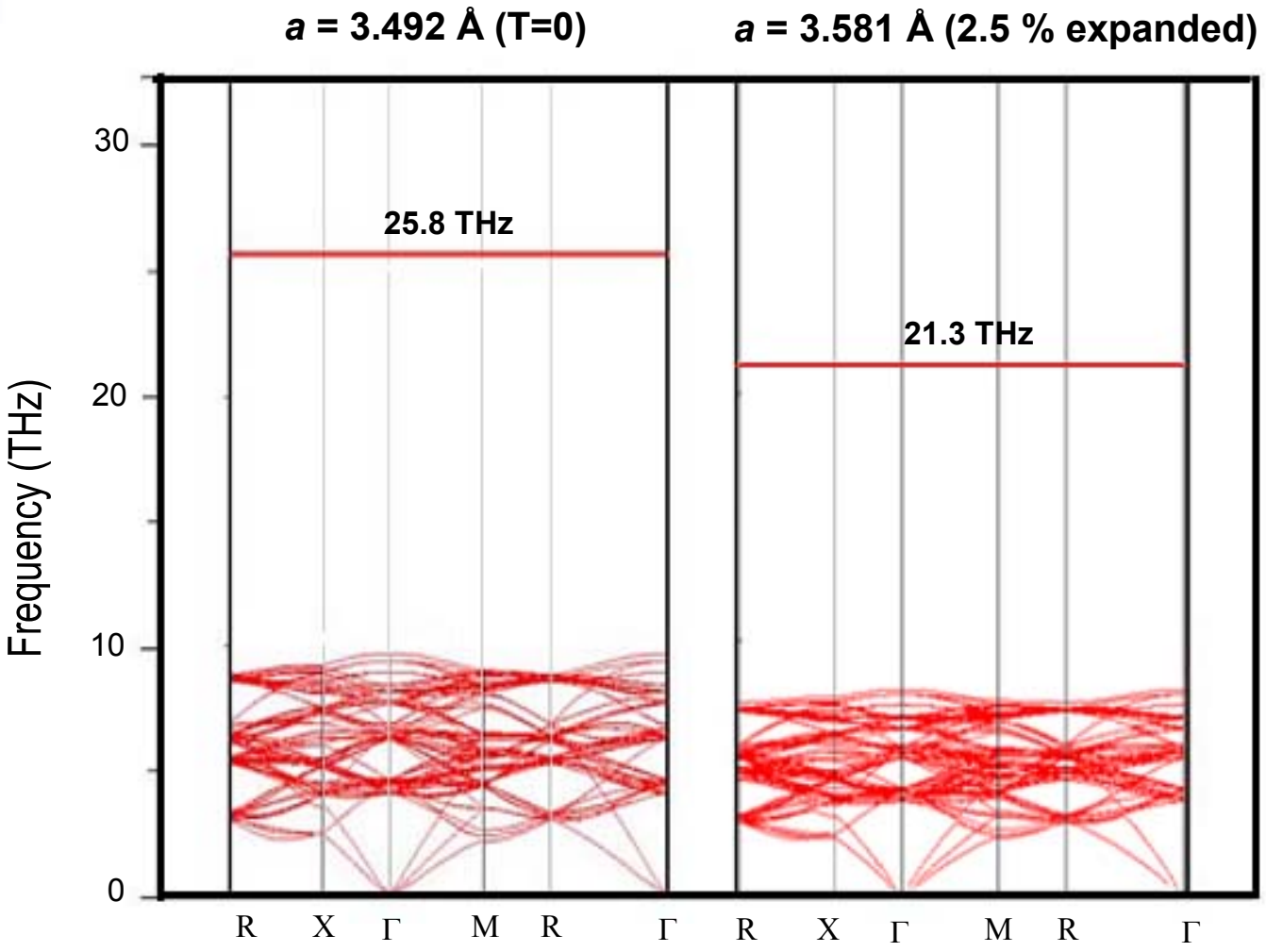


Vibrational frequency via VASP/Phonon

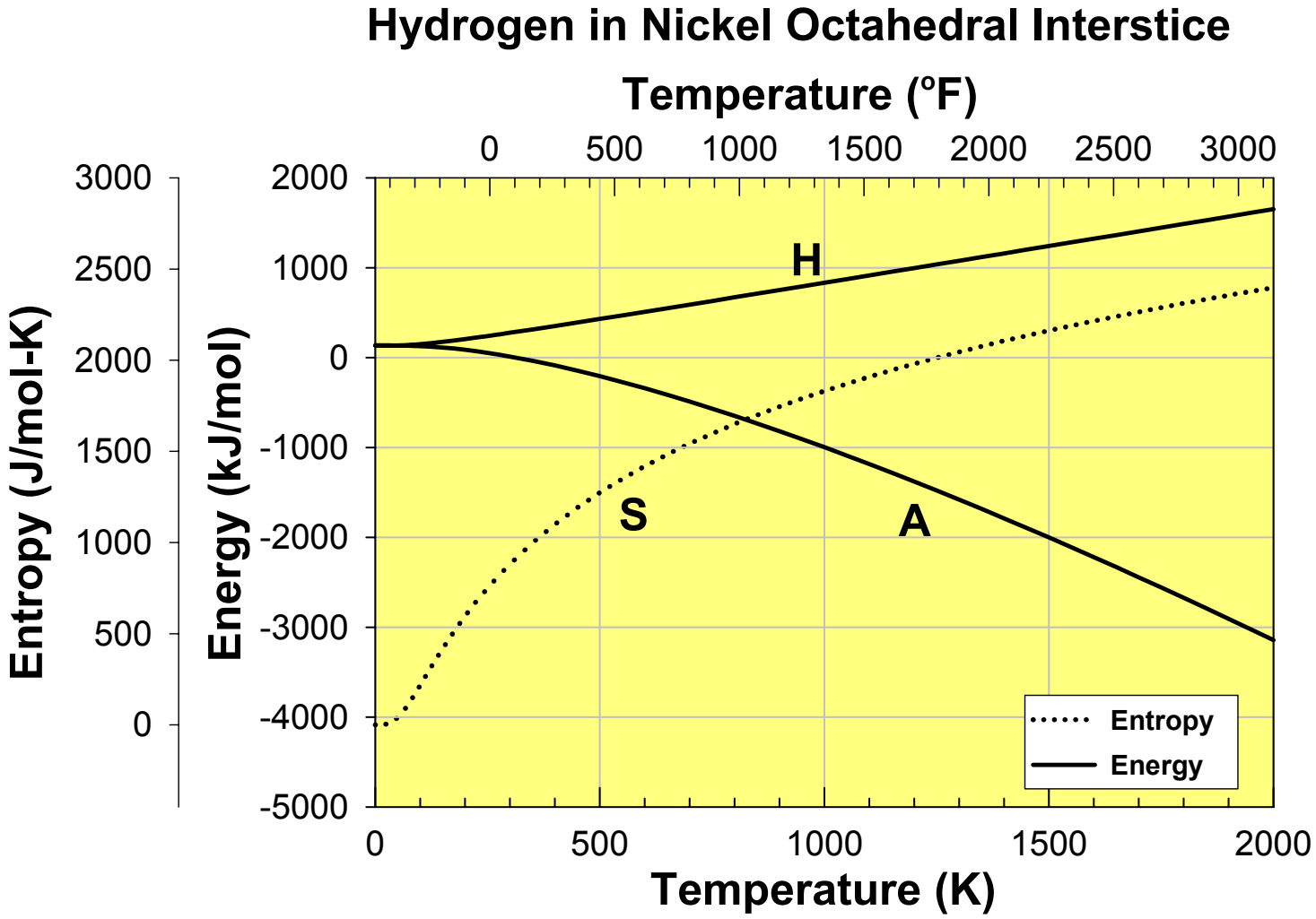
- Frequency at stable octahedral site =25.8 THz
- Frequency in tetrahedral site =39.9 THz (less space than octahedral interstice)
- At the transition state, negative eigenvalue → imaginary frequency



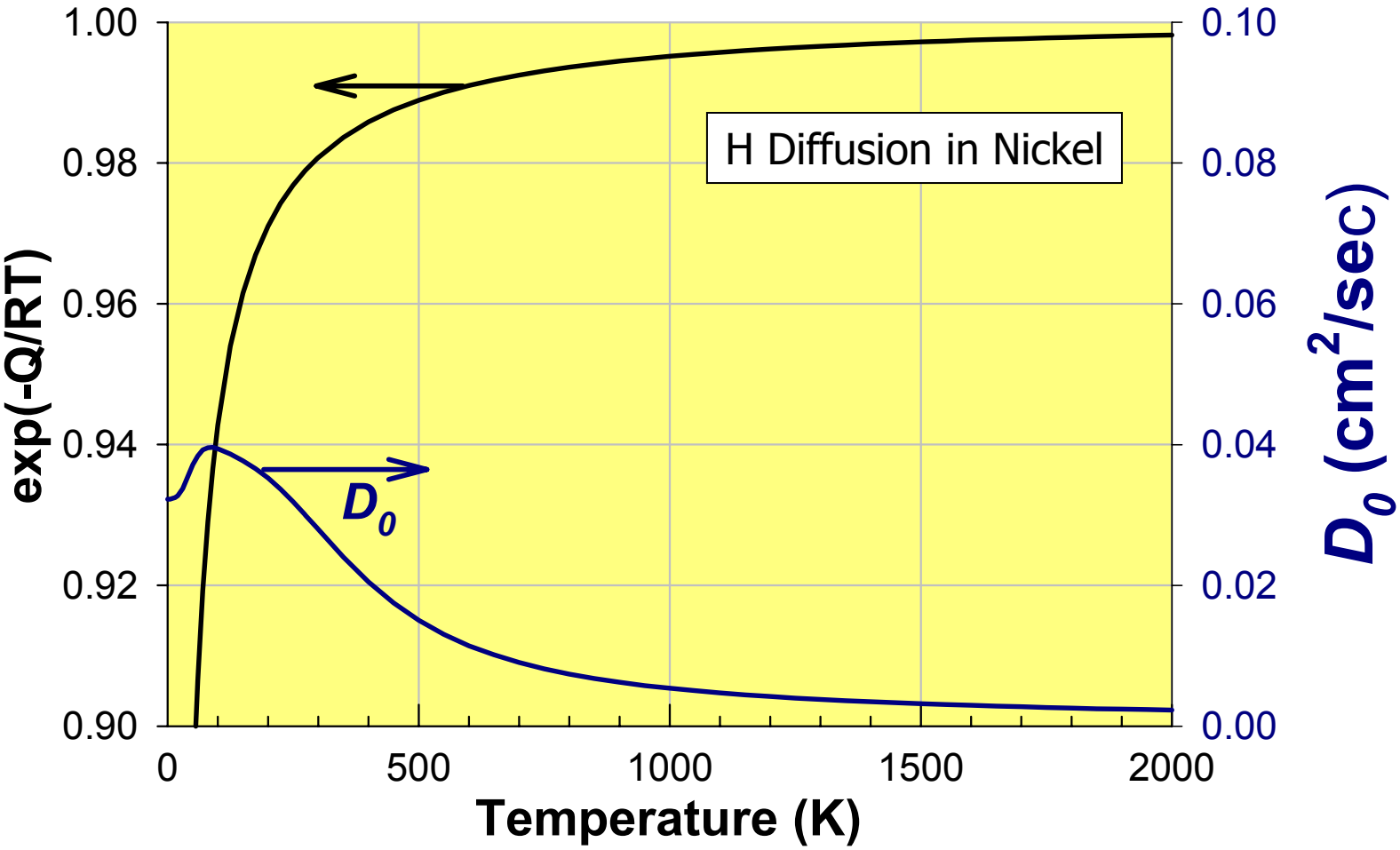
Temperature has little effect on the vibrational frequency of H in nickel (0 K to ~1000 K)



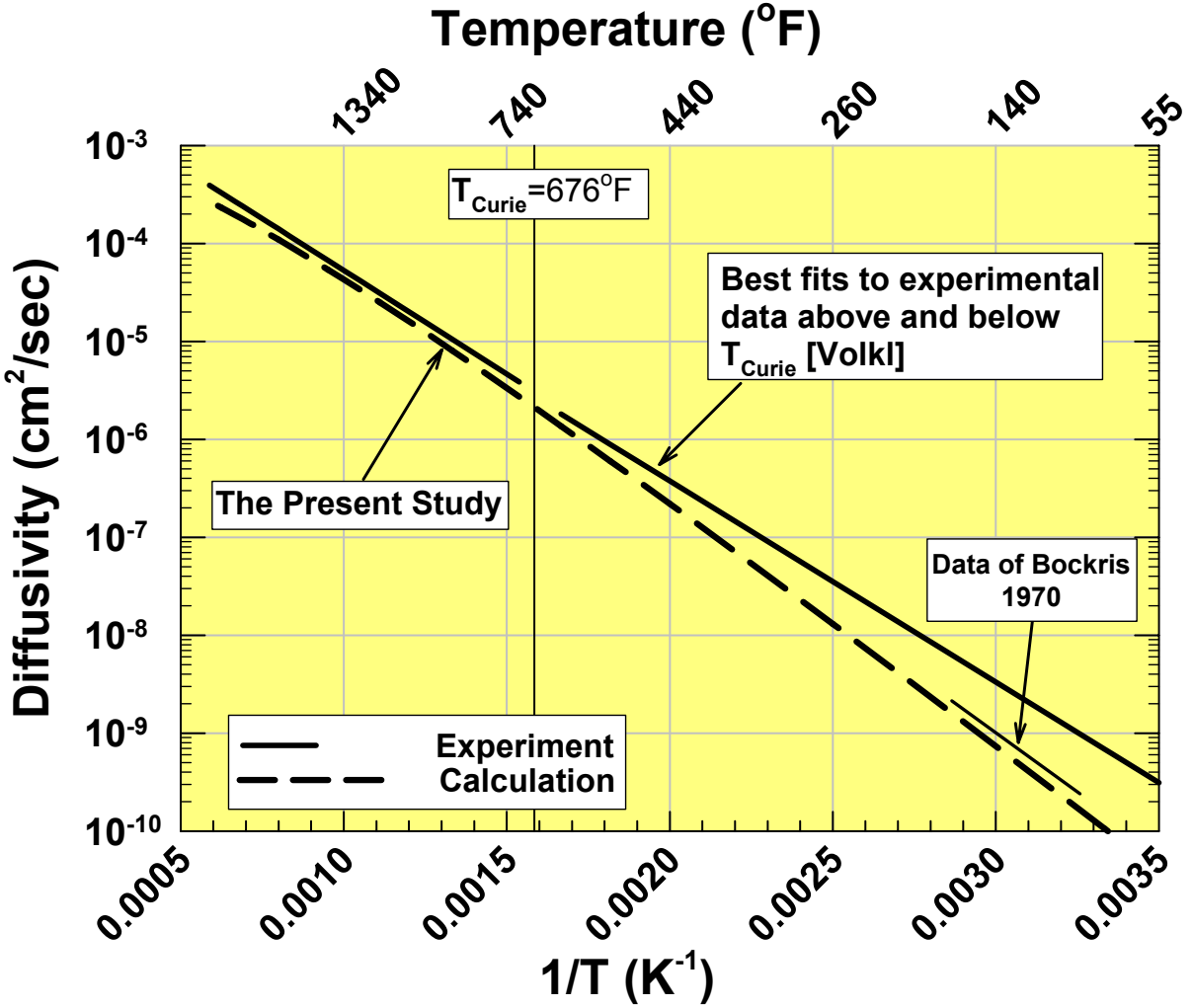
ΔS and ΔH vary with temperature. Typical assumption of constant D_0 is an approximation



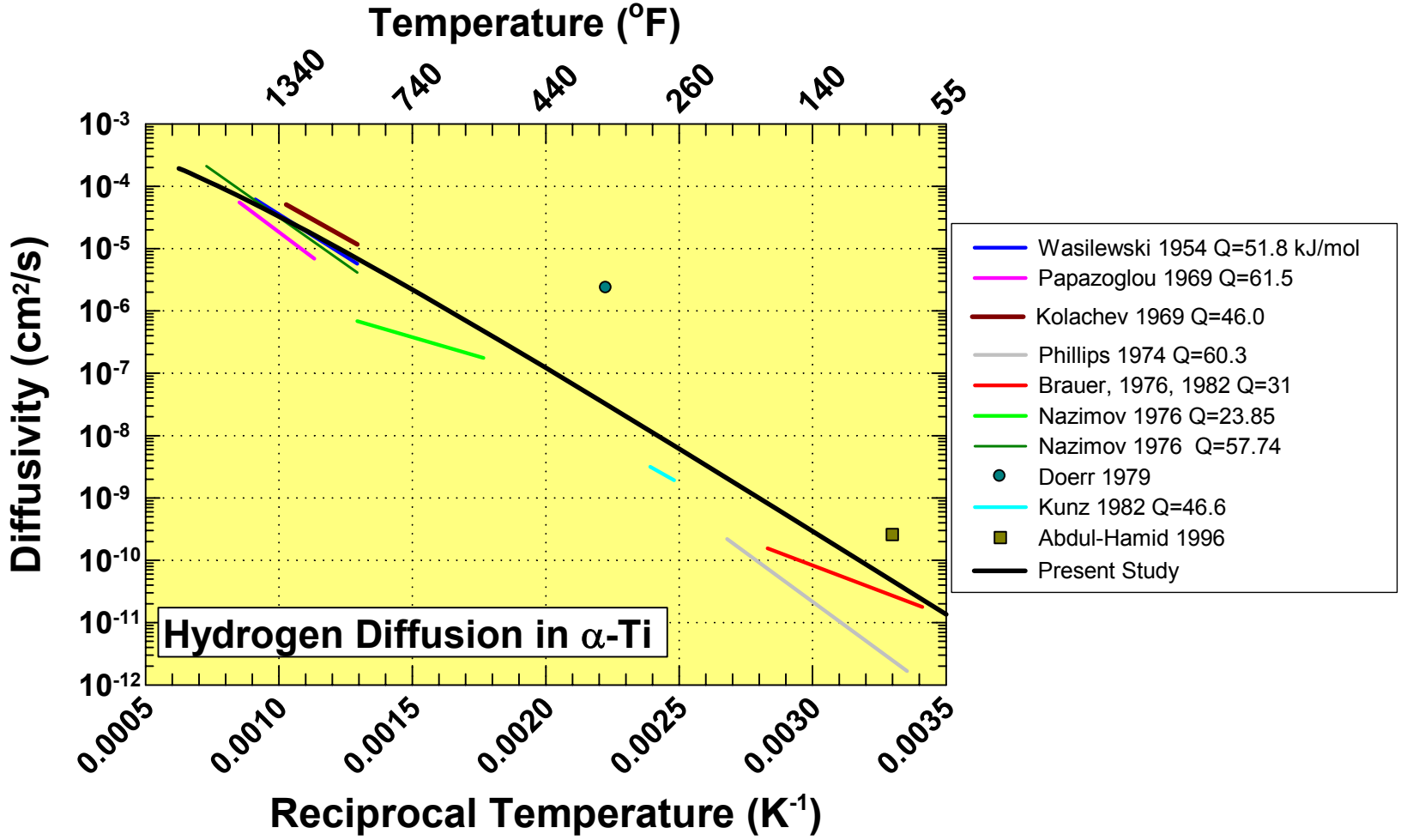
Variation of Q and D_0 with temperature: note "balance" at temperatures >200 K



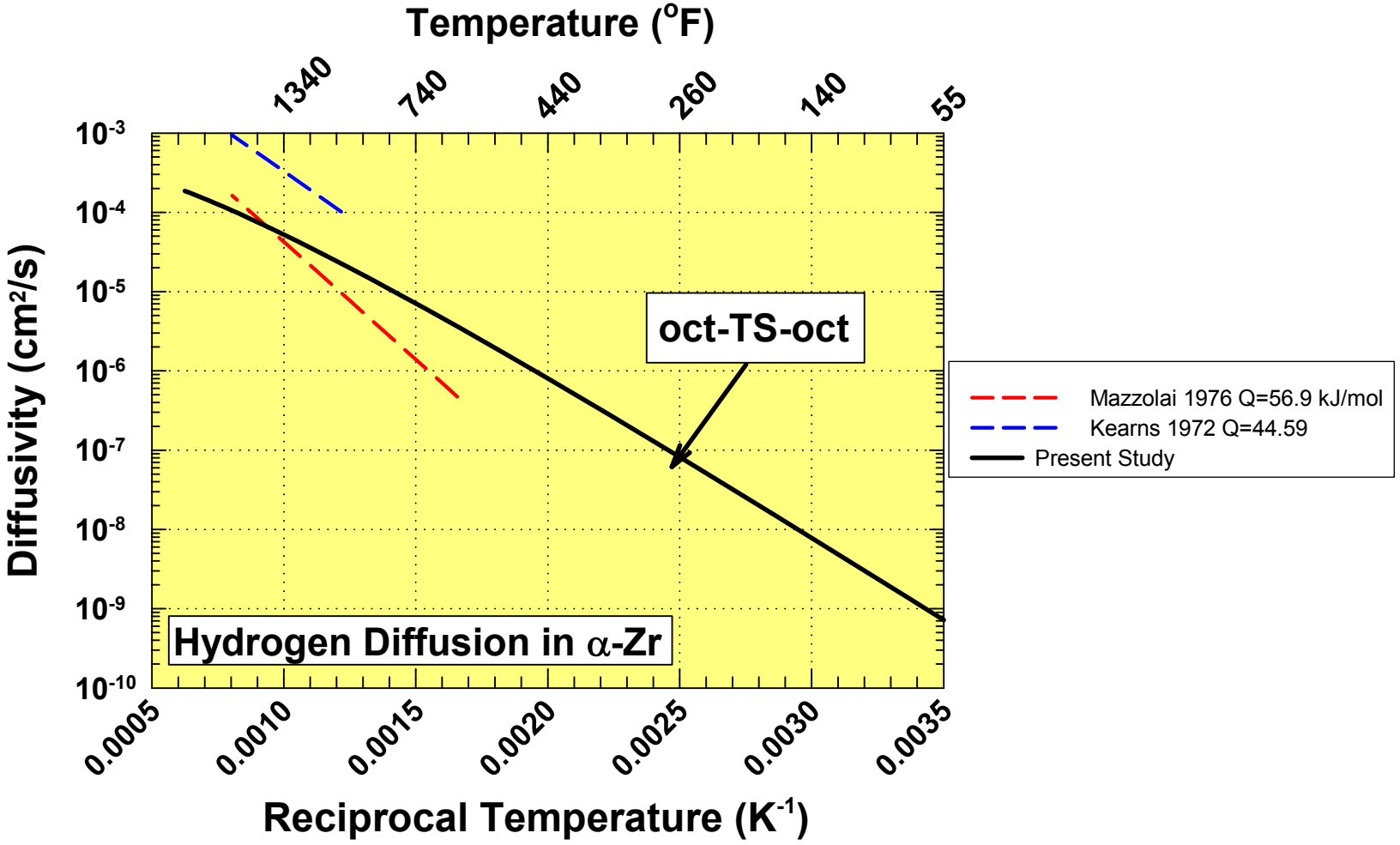
Excellent agreement between first principles calculations and experimental methods



Large disagreement in experimental data for α-Ti. Modeling line gives an impressive "best fit"



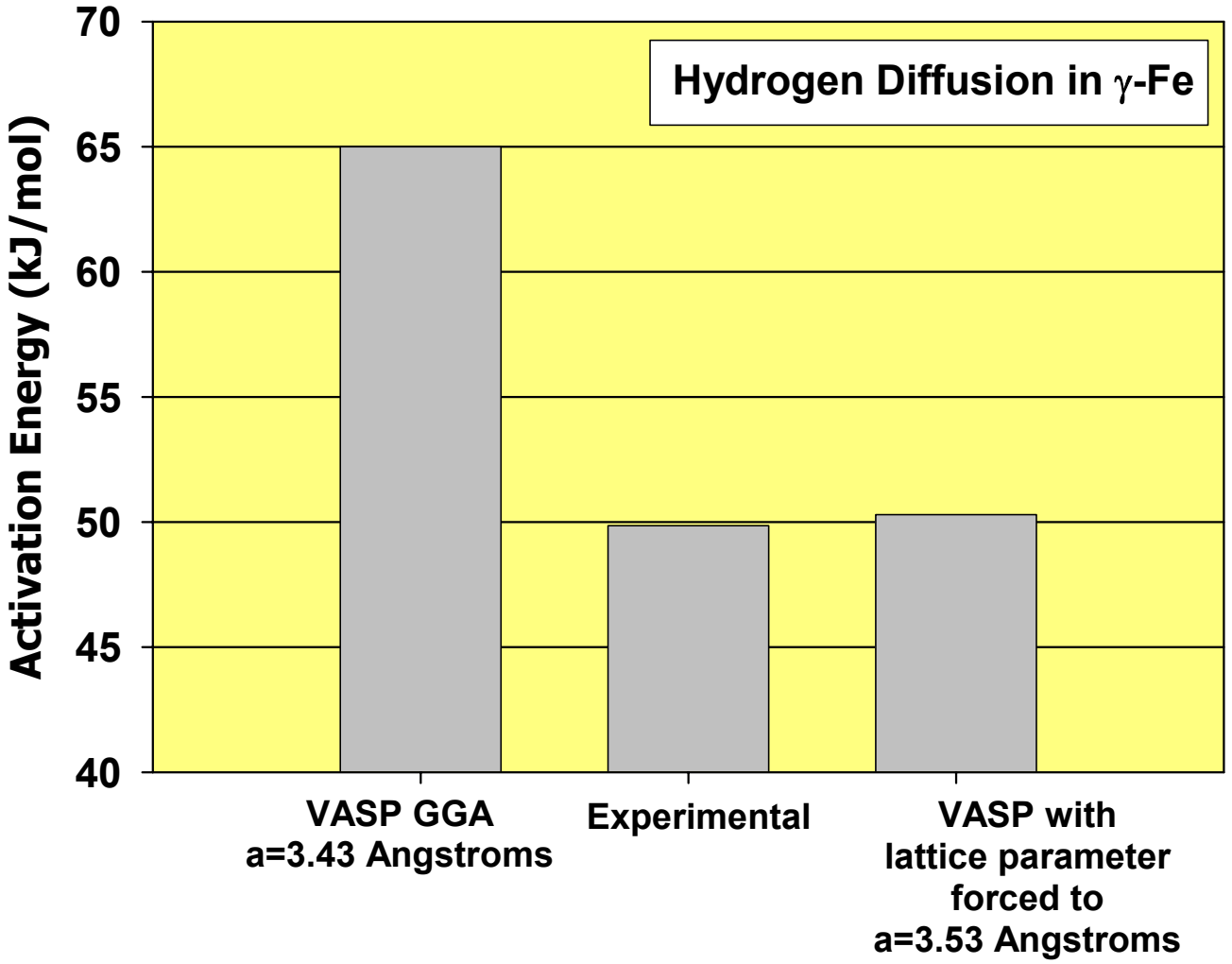
Limited data for H in α-Zr. Results for H in Ni and α-Ti give confidence that modeling is accurate



For γ-Fe: Larger than typical error between calculated and experimental lattice parameter

Metal	Computed Lattice Parameters (Å)	Experimental Lattice Parameters (Å)	Deviation (%)
Ni	a=3.492	3.5239	-0.9
Ti	a=2.904 c=4.652	2.950 4.683	-1.6 -0.7
Zr	a=3.213 c=5.210	3.233 5.148	-0.6 +1.2
γ-Fe	a=3.433	3.6599	**-6.2**

Calculations for H diffusion in γ-Fe highlight the strong effect of the lattice parameter, *a*



Summary of parameters

Table I. *Summary of Calculated Diffusion Parameters*

Metal	Crystal Structure	Interstitial Site	n	α	Approximate *l*‡ (cm)	ν (THz)		ΔS (J/mol-K)		ΔH (kJ/mol)	
						0 K	1000 K	0 K	1000 K	0 K	1000 K
Ni	fcc	octahedral	24	1/12	2.5×10^{-8}	25.8	21.3##	0	-14.9	49.1	40.2
Ti	hcp	octahedral	$(n\alpha) \approx 1$		2.3×10^{-08}	27.7	Not Calculated	0	-8.3	52.7	42.4
Zr	hcp	octahedral			2.6×10^{-08}	21.8	Not Calculated	0	-16.0	40.7	30.9
		tetrahedral			1.7×10^{-08}	37.1	Not Calculated	0	-5.5	35.5	30.8
Fe*	fcc	octahedral	24	1/12	2.5×10^{-8}	28.4	Not Calculated	0	0.2	50.3	43.7

*Results based on lattice parameter of *a*=3.53 Å

‡$l = (a\sqrt{2}/2)$ for the fcc oct.-oct. transition, ~c/2 for the hcp oct.-oct. transition and ~c/3 for the hcp tet.-tet. transition

##Estimated from expanding the lattice parameter from *a*=3.492 Å to *a*=3.581 Å, since the effect of temperature is relatively small; the 0 K attempt frequencies are used in the subsequent calculations.

Summary

- Excellent agreement between first principles calculation of H diffusion in nickel
- Calculations help resolve controversy in systems where experimental data are in disagreement:
  - H in α-Ti

  and guide predictions where there are sparse data:
  - H in α-Zr
- Results for H in γ-Fe show *strong influence of lattice parameter*
- Calculations give new insight into diffusion paths and temperature dependencies
- Techniques have broad applicability to Materials Science, *e.g.* diffusion, solubility, entropy, enthalpy, free energy, …