Review of First Principles Comparisons to Pure Elements

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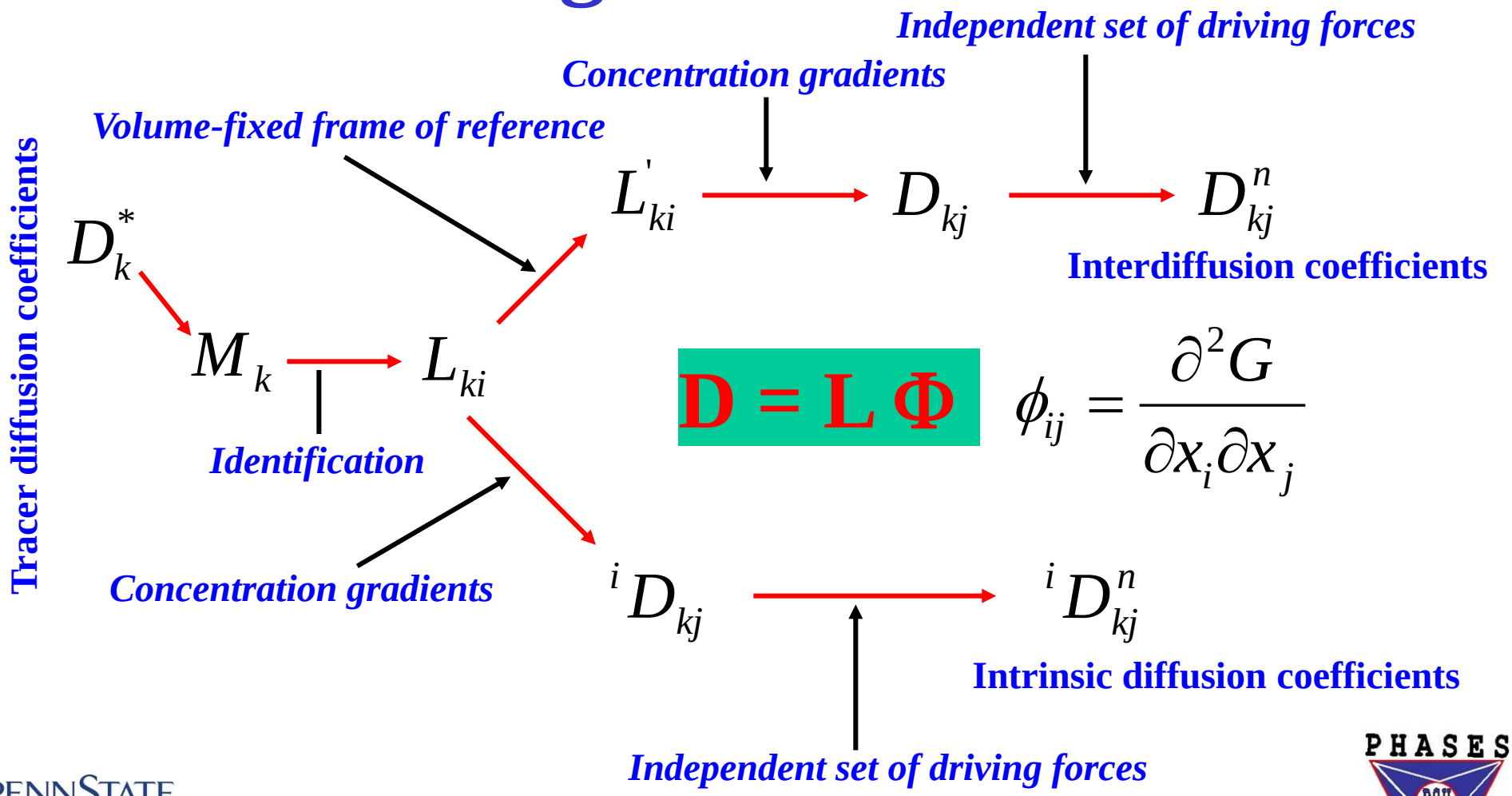
Summary of steps taken when transforming from *M*'s to *D*'s



Andersson and Agren, *J. Appl. Phys.*, Vol.72, 1992, 1350-1355.

Atomic mobility and tracer diffusion coefficient

$$D_i^* = RTM_i$$

$$M_i = \frac{D_i^*}{RT} = \frac{D_i^{0*}}{RT} \cdot e^{-\frac{Q_i^*}{RT}} = \frac{1}{RT} e^{\frac{-Q_i^* + RT \ln\left(D_i^{0*}\right)}{RT}}$$

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Mobility modeling in the similar way as thermodynamic modeling

- **Solution phases** $(A,B,C...)_x(a,b,c...)_y$

$$M_i = \frac{1}{RT}\exp\left(\frac{\Delta G_i}{RT}\right) \qquad \Delta G_i = -Q_i + RT\ln(D_i^{*0})$$

$$\Delta G_i = \sum_j \sum_m y_j^I y_m^{II} \Delta G_i^{j:m} + \sum_j \sum_{k>j} \sum_m y_j^I y_k^I y_m^{II} \Delta G_i^{j,k:m}$$
$$+ \sum_j \sum_n \sum_{m>n} y_j^I y_n^{II} y_m^{II} \Delta G_i^{j:n,m}$$

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Jonsson, *Z. Metallkd.*, Vol.86, 1995, 686-692.

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Mobility model parameters

$\Delta G_i^{j:m}$

- **For species *i* when the first and second sublattices are occupied by species *j* and *m*.**

$\Delta G_i^{j,k:m}$

- **Interaction parameter between *j* and *k* in the first sublattice when the second sublattice is occupied by *m*.**

$\Delta G_i^{j:n,m}$

- **Interaction parameter between *n* and *m* in the second sublattice when the first sublattice is occupied by *j*.**

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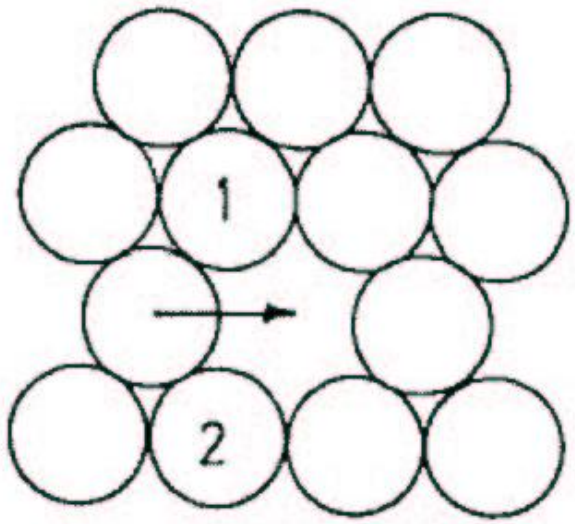
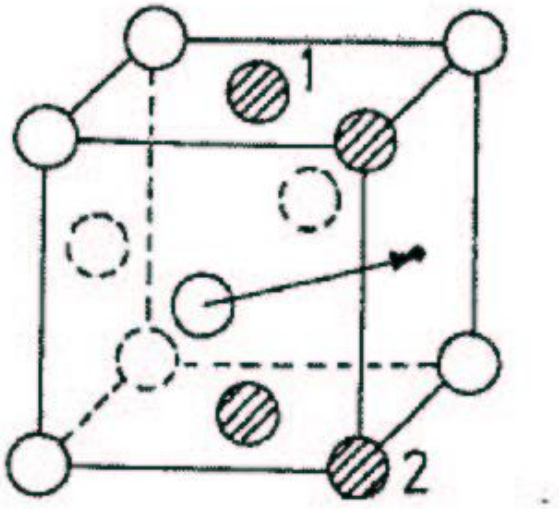
Diffusion: Formation and migration of vacancy





- When between atoms 1 and 2 (saddle configuration), the diffusion atom is in an unstable state with imaginary frequency.

Vacancy formation and migration

$$c = \exp\left(\frac{-\Delta_f G}{k_B T}\right) = \exp\left(-\frac{\Delta_f H}{k_B T}\right)\exp\left(\frac{\Delta_f S}{k_B}\right)$$

$$w = \tilde{\nu}\exp\left(-\frac{\Delta_m G}{k_B T}\right) = \tilde{\nu}\exp\left(\frac{\Delta_m S}{k_B}\right)\exp\left(-\frac{\Delta_m H}{k_B T}\right)$$

However, the entropy and enthalpy at the saddle point could not be evaluated due to the unstable vibrational mode

Mitigate the unstable vibrational mode at the saddle point

$$w = \tilde{\nu} \exp\left(\frac{\Delta_m S}{k_B}\right) \exp\left(-\frac{\Delta_m H}{k_B T}\right) = \nu^* \exp\left(-\frac{\Delta_m H}{k_B T}\right)$$

- **Transition state theory**

$$\nu^* = \frac{\prod_{i=1}^{3N-3} \nu_i}{\prod_{j=1}^{3N-4} \nu'_j}$$

Vineyard, *J. Phys. Chem. Solids* **3**, 121 (1957).

Eyring's Reaction Rate Theory

- **Partition function**
- **Atom jump frequency**

$$Z = \exp\left(\frac{-G}{k_B T}\right)$$

$$w = \frac{k_B T}{h}\frac{Z^*_{sd}}{Z_{eq}}$$

* remove the imaginary frequency of the saddle configuration

$$w = \frac{k_B T}{h}\exp\left(\frac{S^*_{sd,N-1} - S_{eq,N-1}}{k_B}\right)\exp\left(-\frac{H^*_{sd,N-1} - H_{eq,N-1}}{k_B T}\right)$$

$$D = fa^2 Cw = \frac{1}{6} fr^2 z \exp\left(\frac{H^*_{sd,N-1} - \frac{N-1}{N}H_N}{k_B T}\right)\exp\left(\frac{S^*_{sd,N-1} - \frac{N-1}{N}S_N}{T}\right)$$

Eyring, *J. Chem. Phys.*, Vol.3, 1935, 107

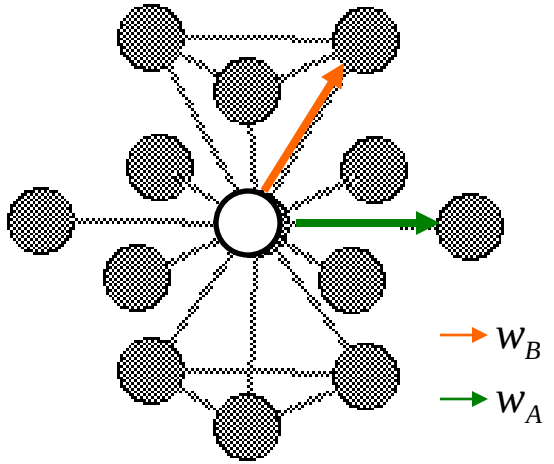
Diffusion in hcp

- **Two diffusion directions**

$$D_x = \frac{1}{2} C a^2 (3 w_A f_{Ax} + w_B f_{Bx})$$

$$D_z = \frac{3}{4} C c^2 w_B f_{Bz}$$

  - w_A - **jump within basal plane**
  - w_B - **jump between adjacent basal planes**
  - f_{ij} - **partial correlation factors for jumps A and B**



- **Correlation factor for host and impurity atom jump - a function of** w_A / w_B
- **Other quantities have similar definitions as cubic system.**

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Mullen, *Phys Rev*. 124, 1723 (1961)

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First-principles calculations based on density functional theory

Many-body Schrödinger's equation

$$\hat{H}\Psi(\vec{R}_1,\vec{R}_2,...\vec{R}_N,\vec{r}_1,\vec{r}_2,...\vec{r}_n) = E\Psi(\vec{R}_1,\vec{R}_2,...\vec{R}_N,\vec{r}_1,\vec{r}_2,...\vec{r}_n)$$

Born-Oppenheimer approximation

Many-electron Schrödinger's equation

$$\hat{H}\psi(\vec{r}_1,\vec{r}_2,...\vec{r}_n) = E\psi(\vec{r}_1,\vec{r}_2,...\vec{r}_n)$$

Density Functional Theory

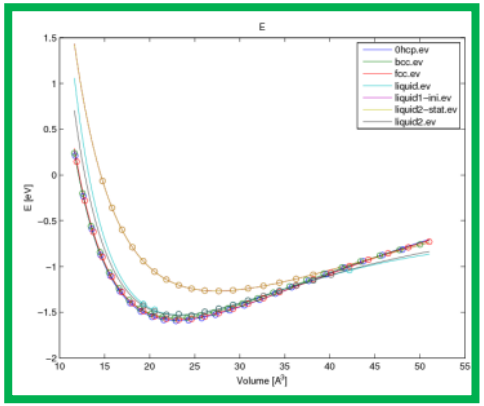
$$E = E[\rho(\vec{r})]$$

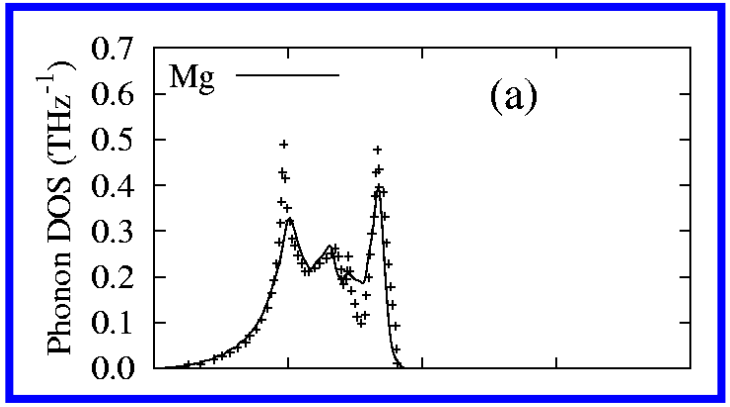
Set of one-electron Schrödinger's equation

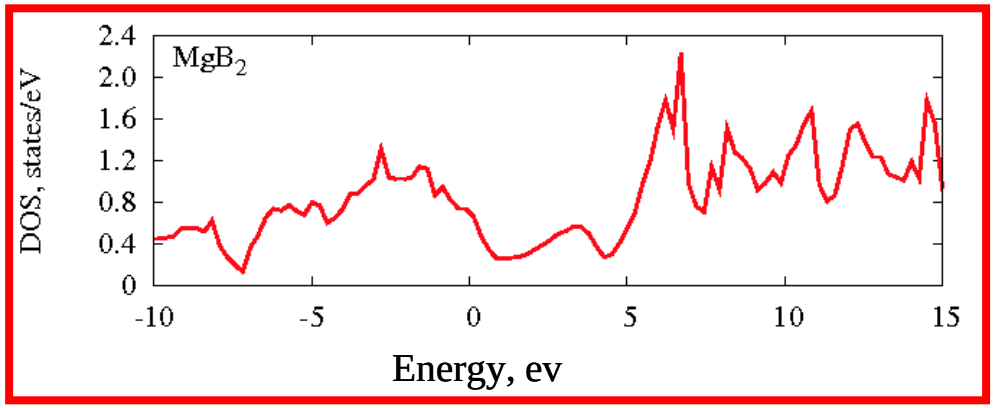
$$\left[-\frac{\hbar^2}{2m_e}\nabla_i^2 - \frac{e^2}{4\pi\varepsilon_0}\sum_{I=1}^{N}\frac{Z_I}{|\vec{r}-\vec{R}_I|} + \frac{e^2}{4\pi\varepsilon_0}\int\frac{\rho(\vec{r}')}{|\vec{r}-\vec{r}'|}d^3\vec{r}' + V_{XC}[\rho(\vec{r})]\right]\psi_i(\vec{r}) = \varepsilon_i\psi_i(\vec{r})$$

Thermodynamic, kinetic & physical properties at finite temperatures

$$F(V,T) = E_c(V) + F_{ph}(V,T) + F_{el}(V,T)$$

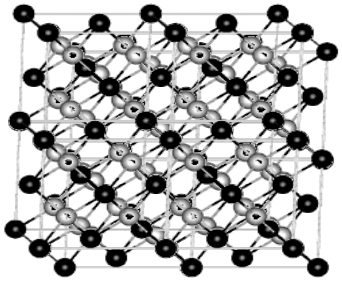






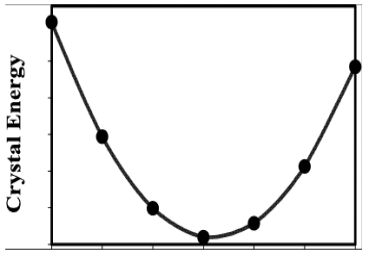
Acta Mater., 52 (2004), 2665, 53 (2005) 1809

Phonon calculations based on the supercell method



Supercell

Lattice Symmetry → Distinct Atomic Displacements → VASP



Poly fit → $\Phi(i,j)$

$$f(i) = \Phi(i, j)u(j)$$

Dynamic matrix → $D_{\alpha\beta}$

Eigenfrequencies & vectors → ν & I

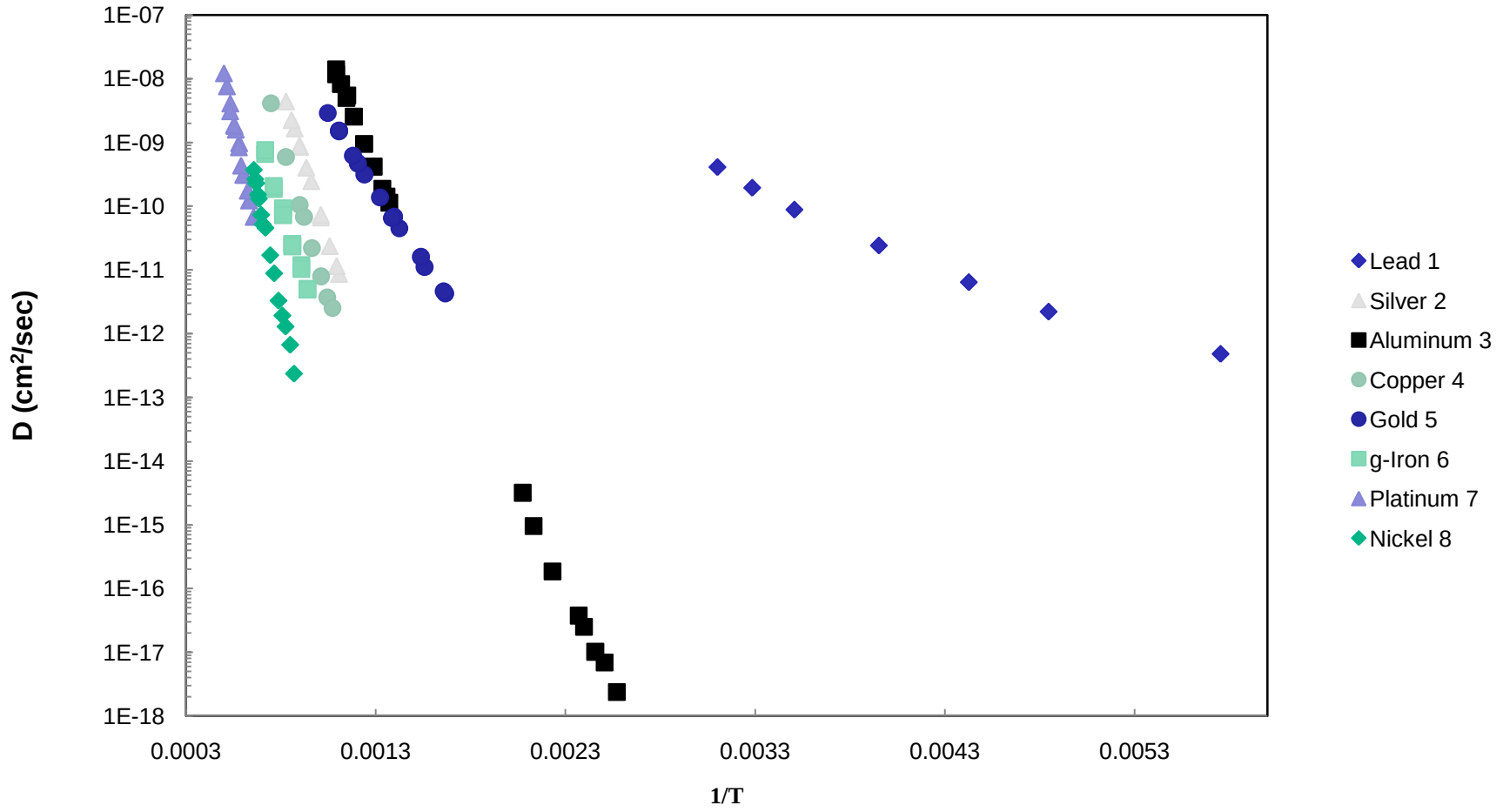
$$S_{vib} = -k_B \int \ln\left[2\sinh\left(\frac{h\nu}{k_B T}\right)\right] g(\nu)\, d\nu$$

Integrate PDOS → S_{vib}

van de Walle, *Calphad,* **26**(2002), 539; **33**(2009) issue 2

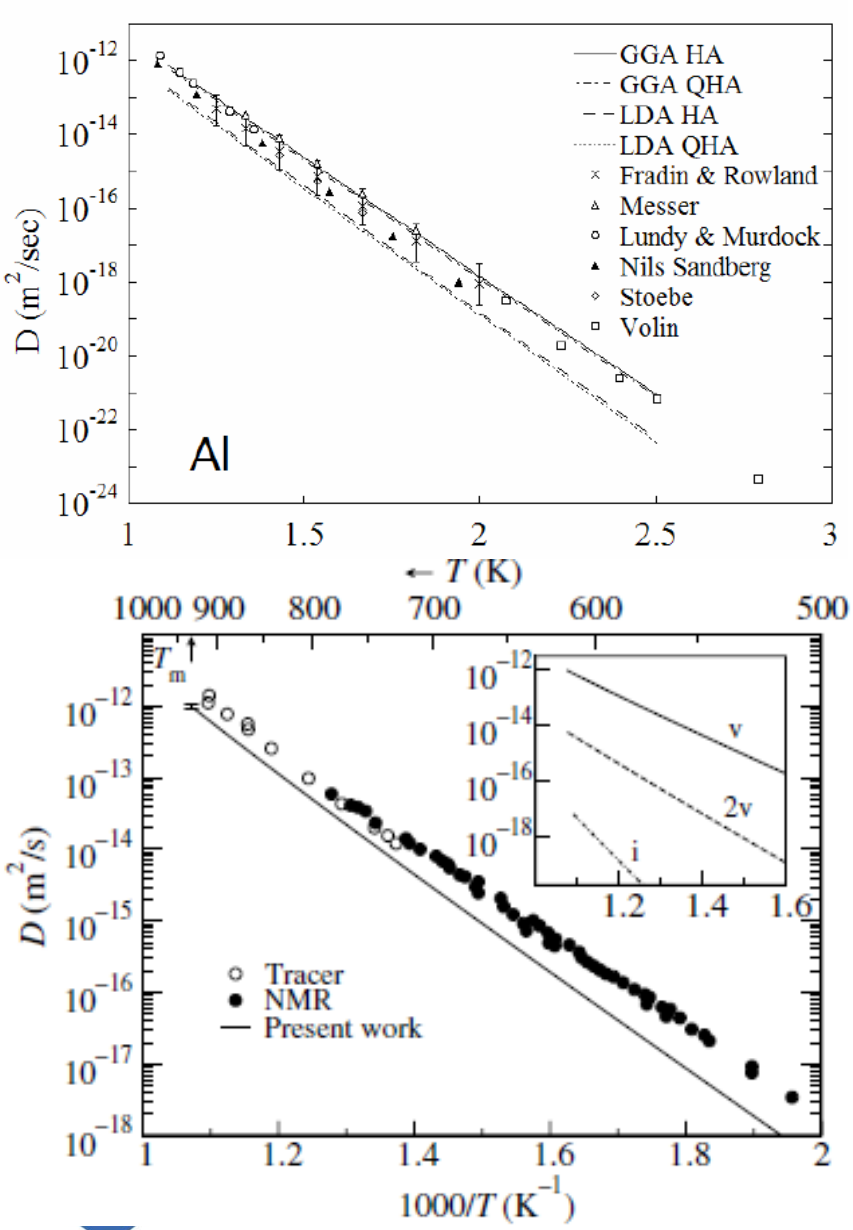
FCC Self-Diffusion Data

Experimental FCC Metal Self-diffusion Coefficients, cm^2/sec

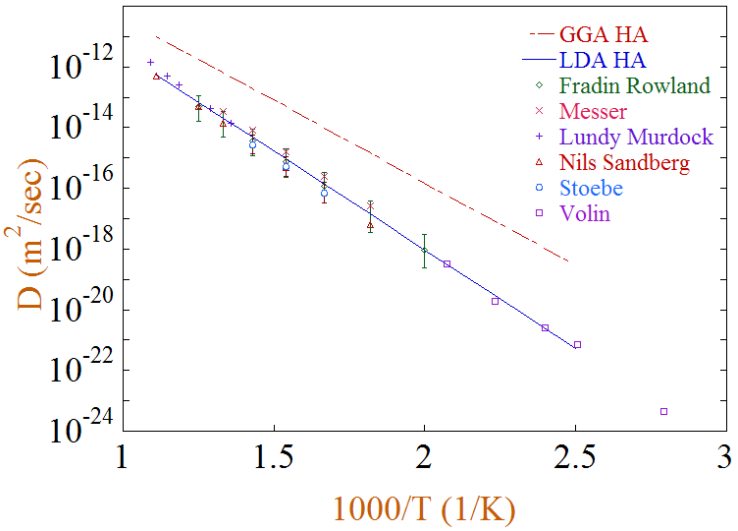


1	**Pb**	Nachtrieb, Handler, Journal of Chemical Physics, 23, 9, 1955
2	**Ag**	Hehenkamp, Th. and Faupel, F., Acta metall., 1983, 31, 691
		C. T. Tomizuka and E. Sonder - 1956 - Self-Diffusion in Silver - Physical Review
3	**Al**	Volin, Annealing Kinetics of voids and self-diffusion coefficient in aluminum
		T. S. Lundy and J. F. Murdock - 1962 - DIFFUSION OF AL-26 AND MN-54 IN ALUMINUM - Journal of Applied Physics
4	**Cu**	A. Kuper, H. Letaw, L. Slifkin, E. Sonder and C. T. Tomizuka - 1954 - SELF-DIFFUSION IN COPPER - Physical Review
5	**Au**	B. Okkerse - 1956 - SELF-DIFFUSION OF GOLD - Physical Review
6	**γ-Fe**	F. S. Buffington, K. Hirano and M. Cohen - 1961 - SELF DIFFUSION IN IRON - Acta Metallurgica.pdf
7	**Pt**	Catteneo, Self-Diffusion in Platinum, Philosophical Magazine
8	**Ni**	Hoffman, Self Diffusion in Solid Nickel, T AIMME, 1956

Aluminum



Mantina, “First-principles calculation of self-diffusion coefficients,” Phys. Rev. Lett., Vol.100, 2008, 215901.



Sandberg, "Self-diffusion rates in Al from combined first-principles and model-potential calculations," Phys. Rev. Lett., Vol.89, 2002, 065901.

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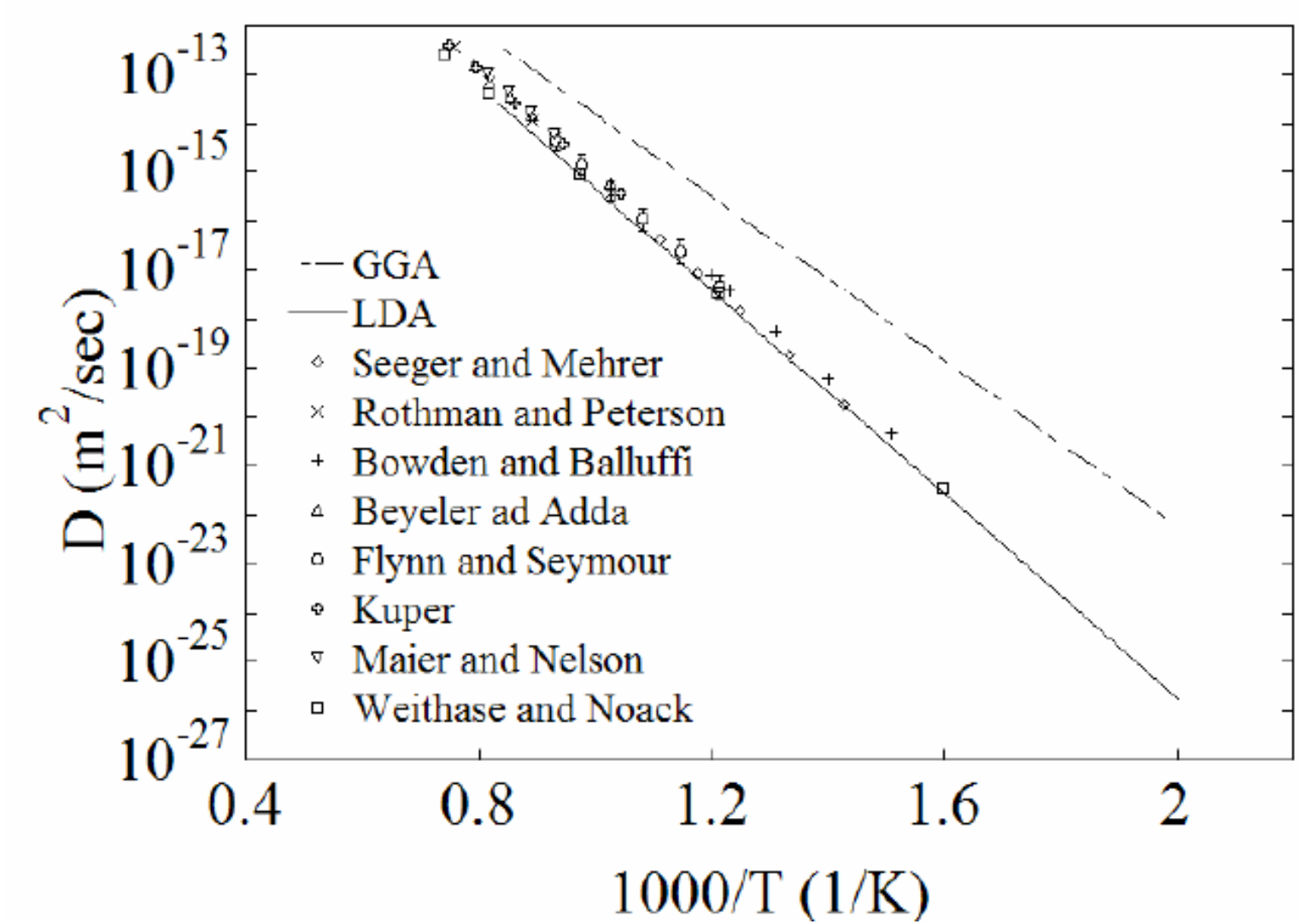
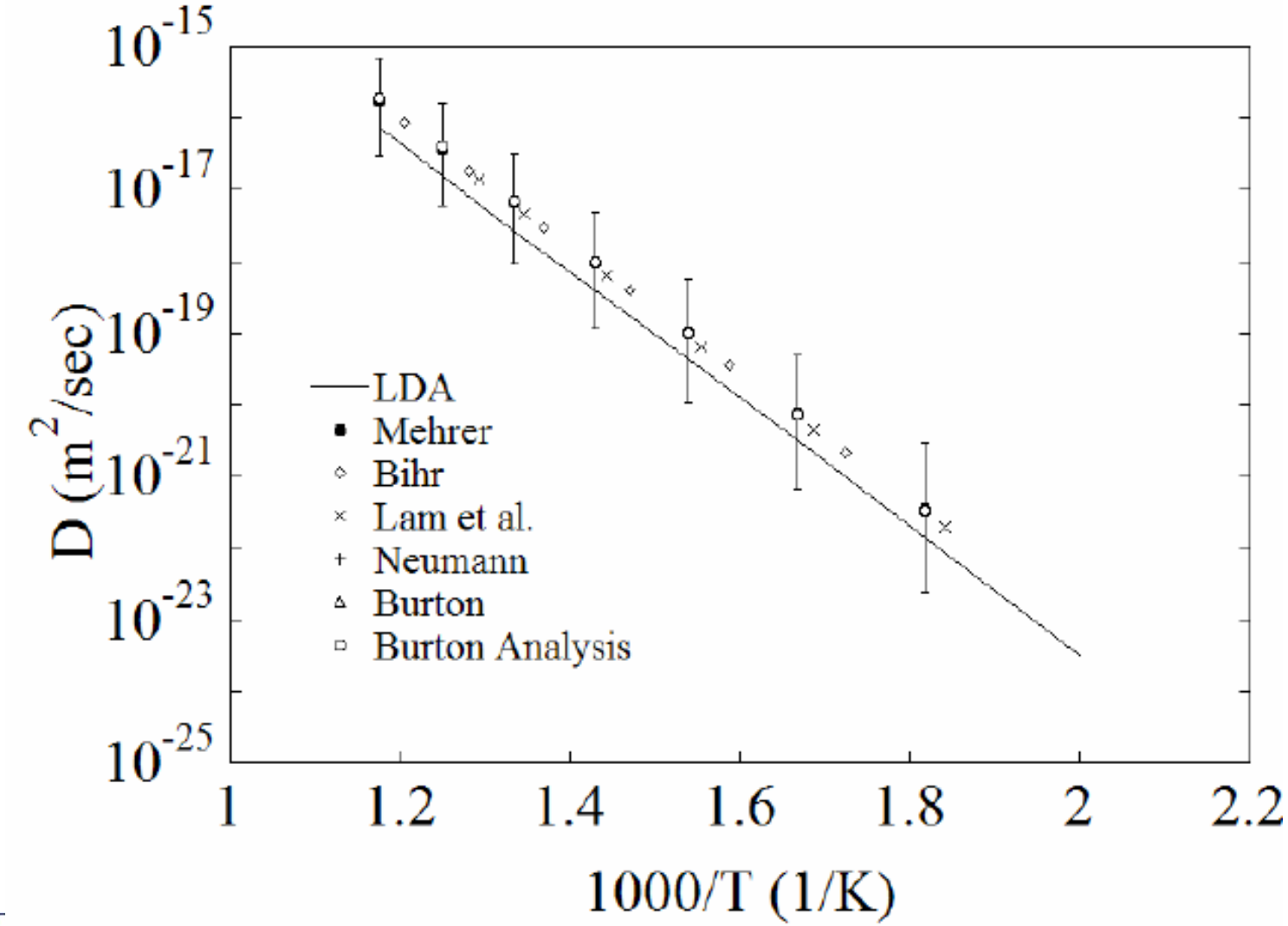
Copper



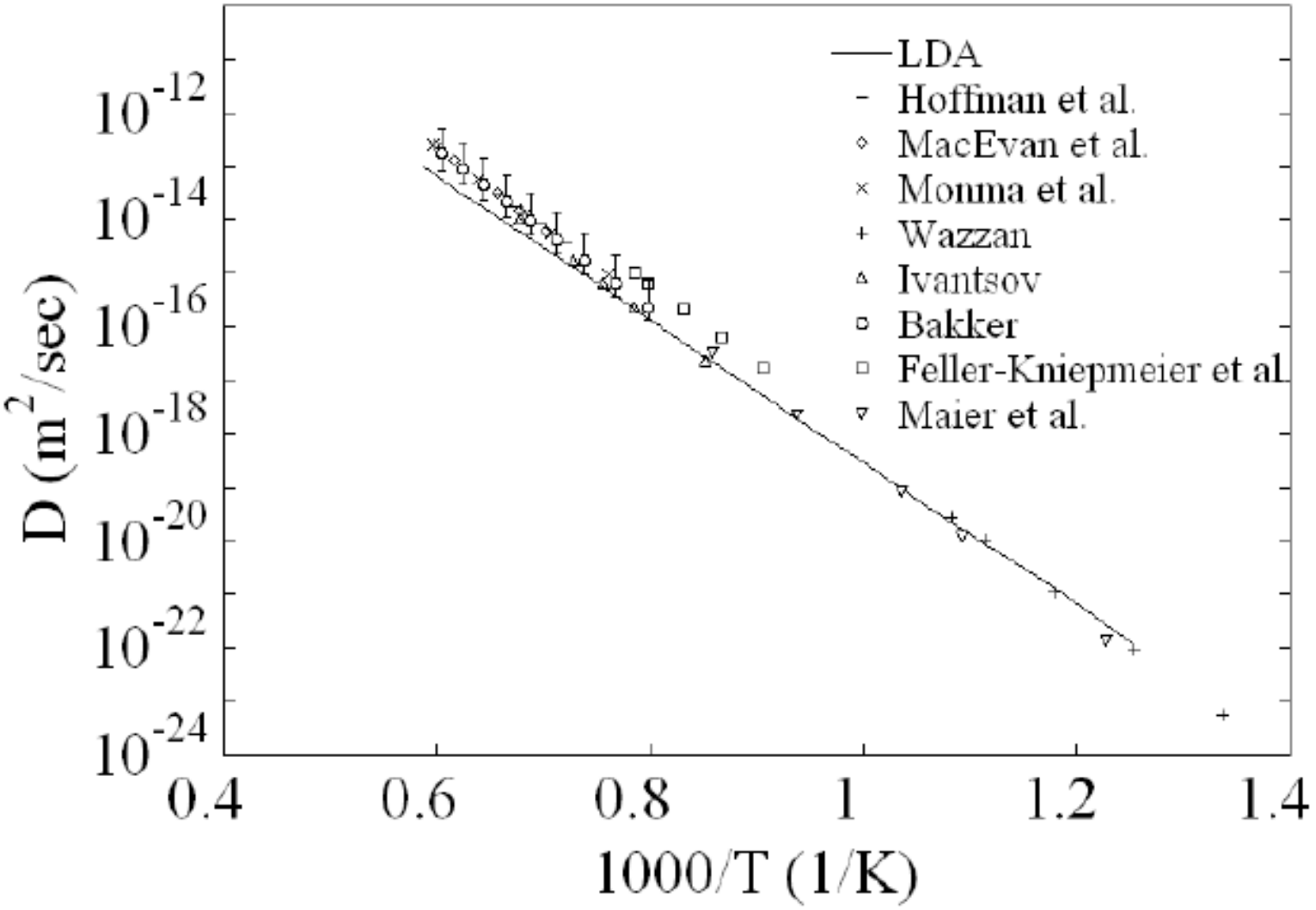
Mantina, PhD Thesis, Penn State, 2008

Silver



Mantina, PhD Thesis, Penn State, 2008

Nickel



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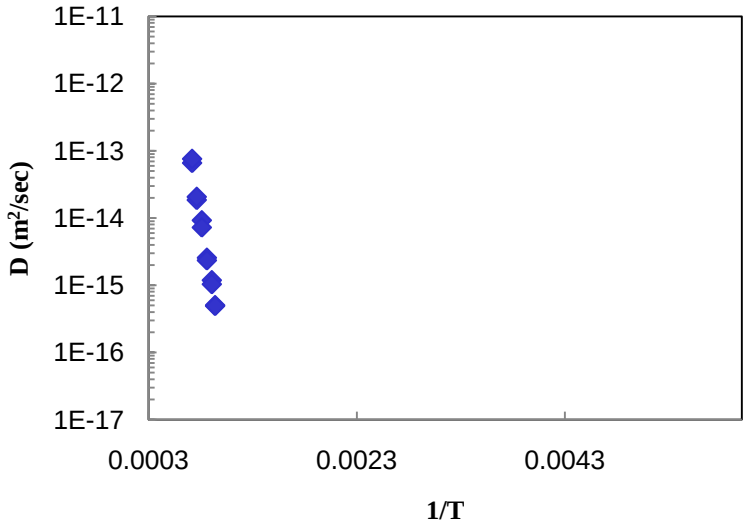
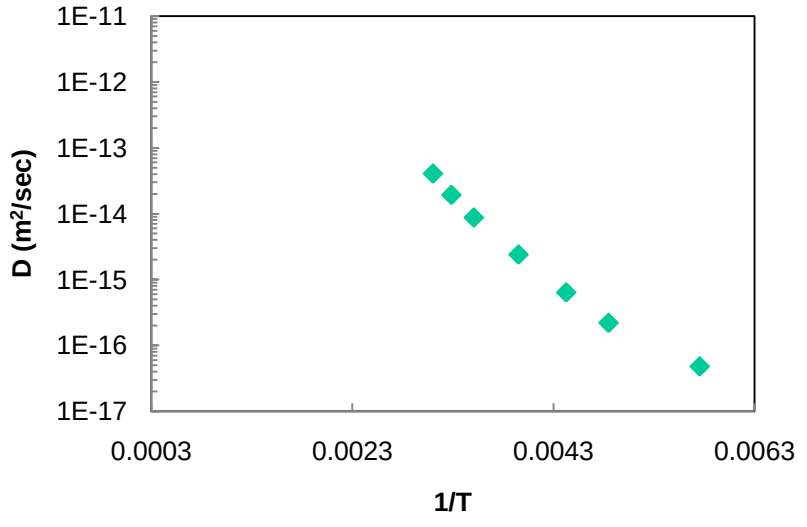
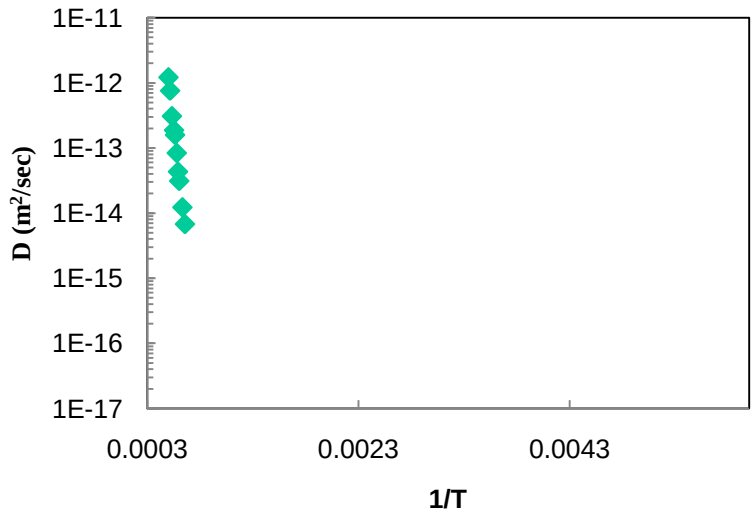
Iron



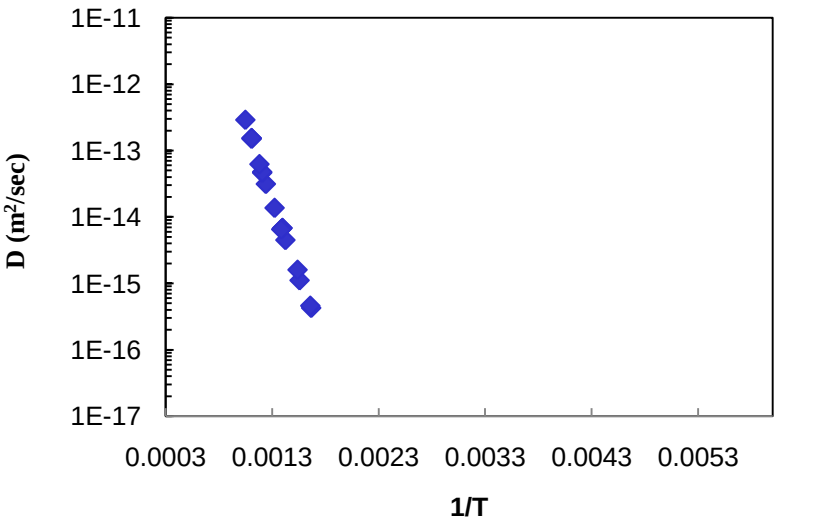
Lead



Platinum

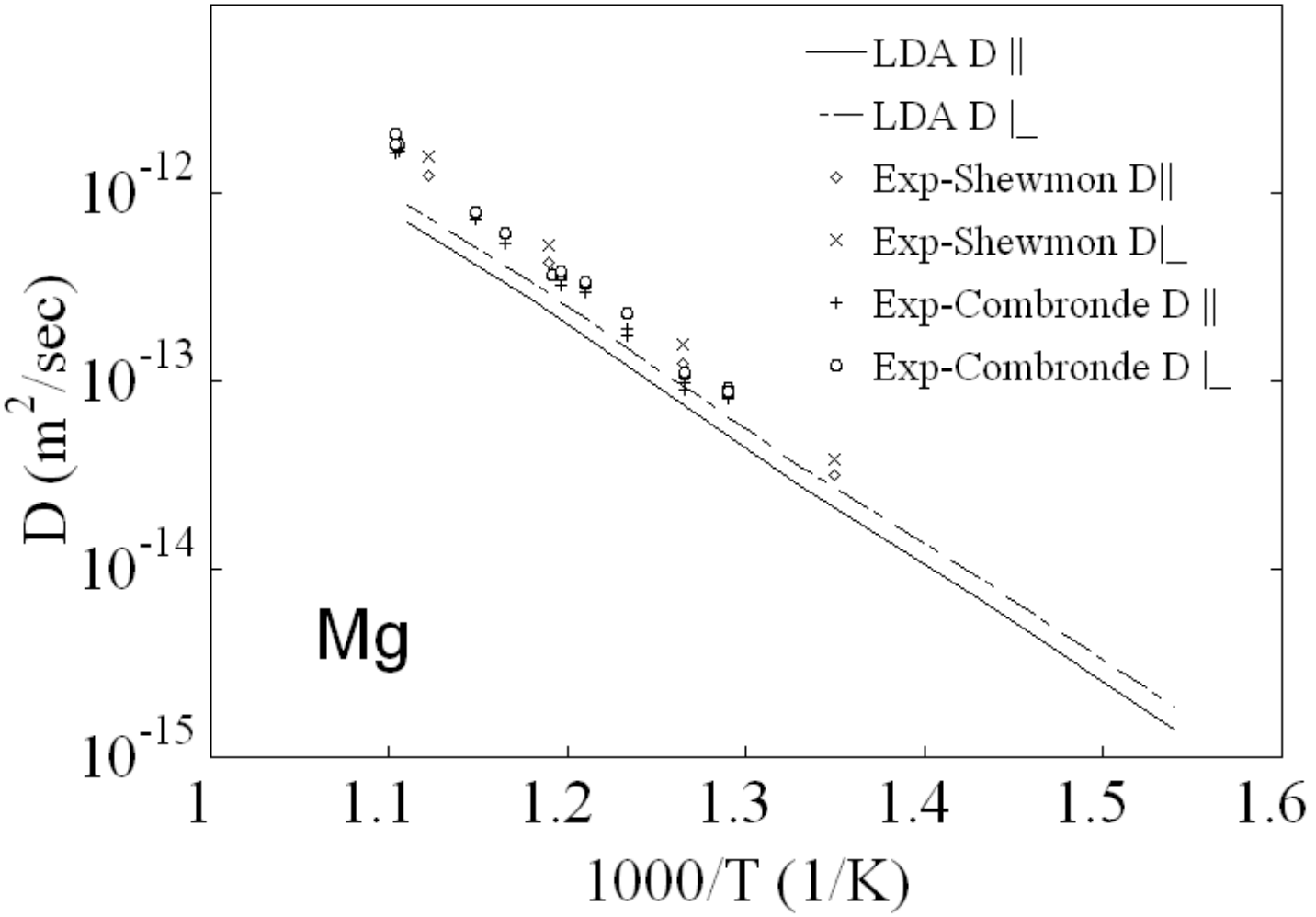


Gold



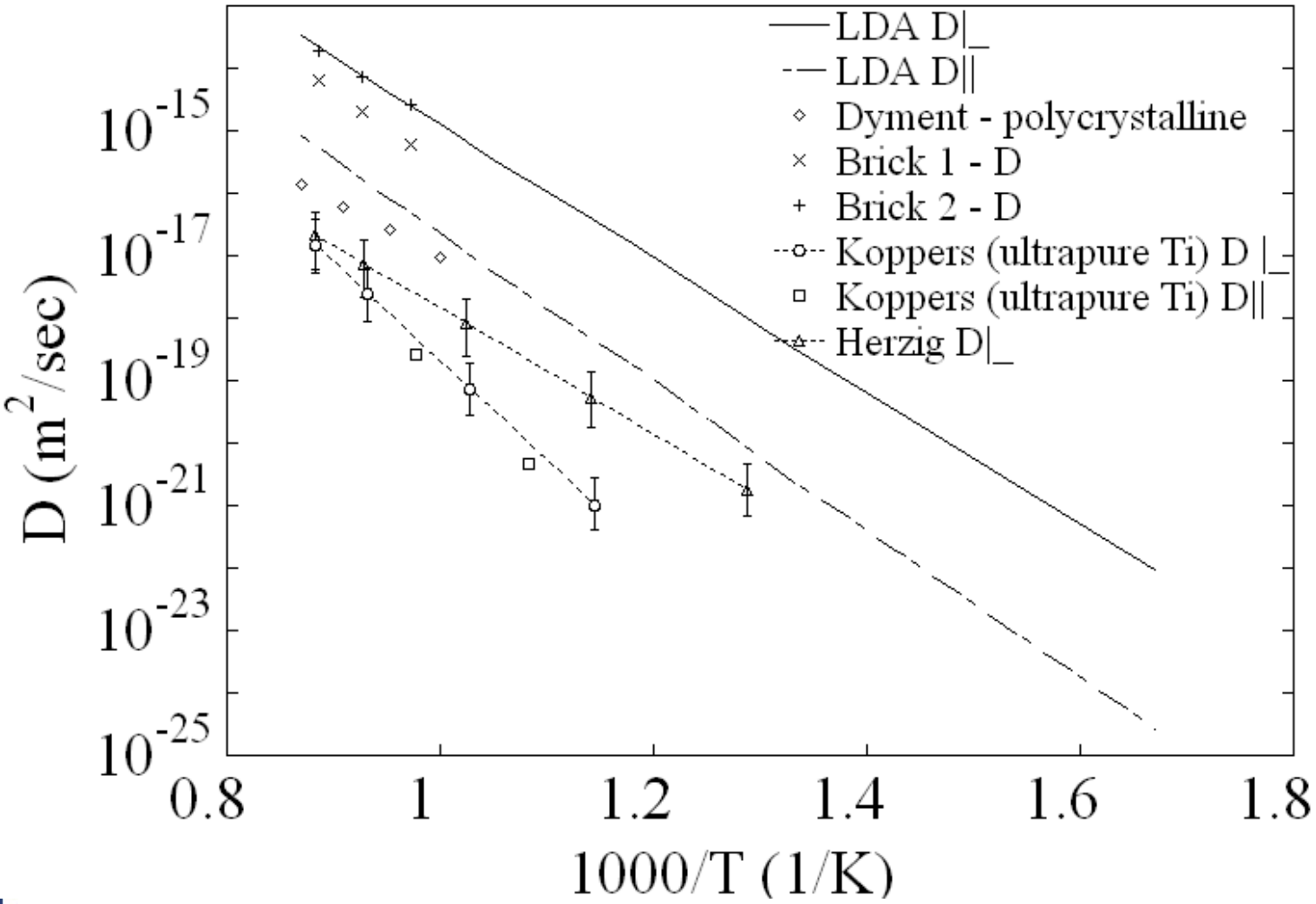
HCP Self Diffusion Data

Mg



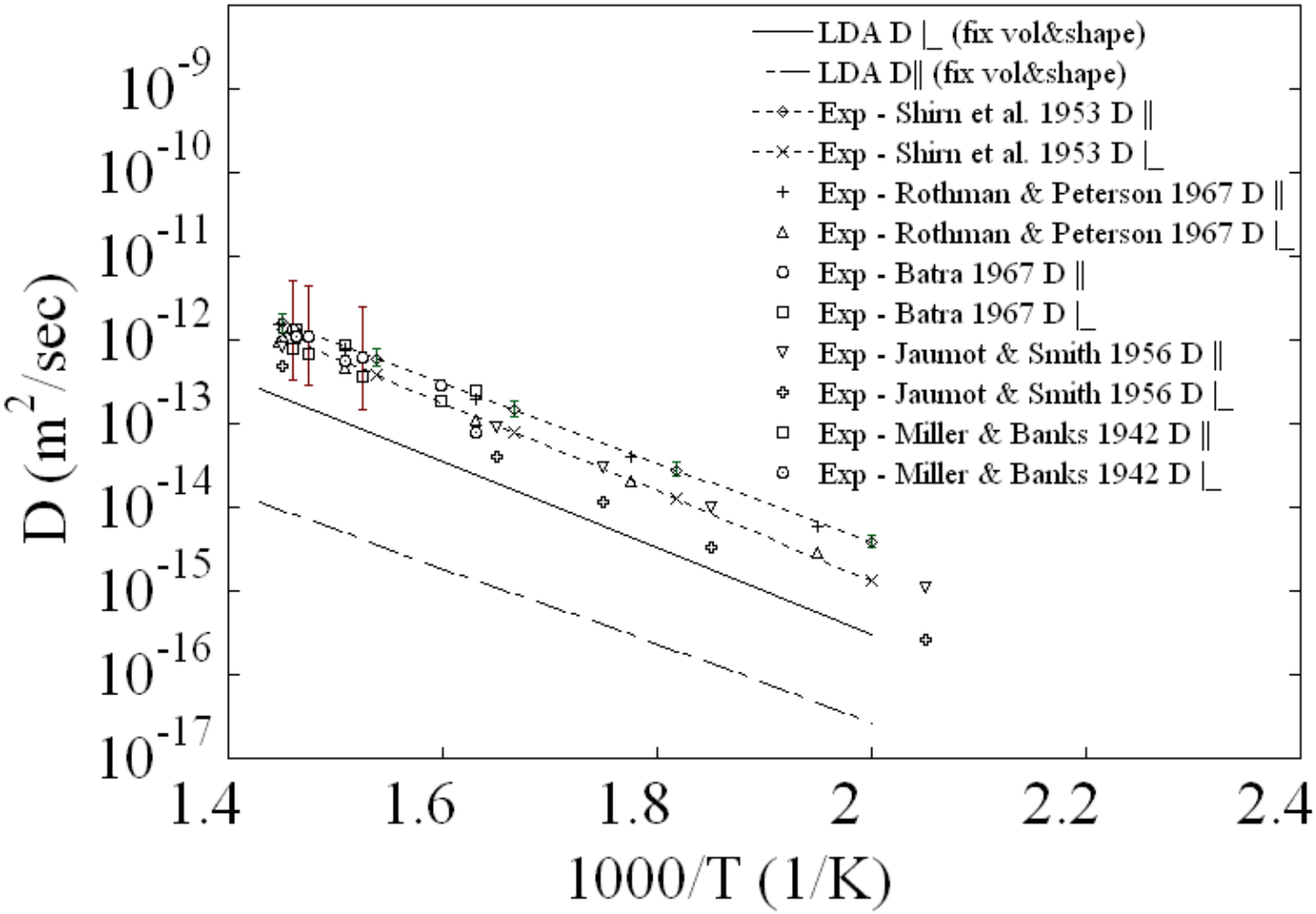
Mantina, PhD Thesis, Penn State, 2008

Ti



Mantina, PhD Thesis, Penn State, 2008

Zn



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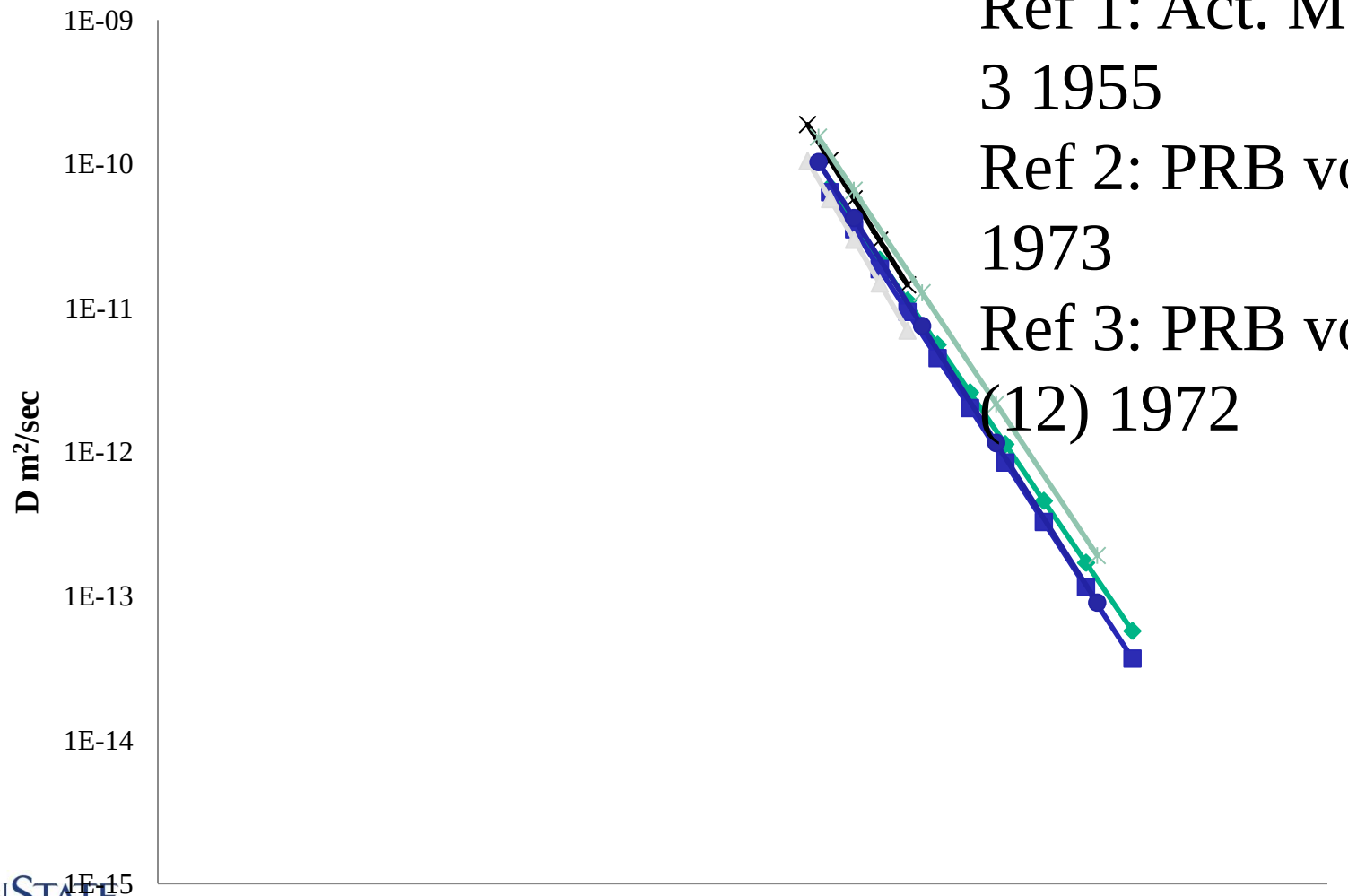
Cd



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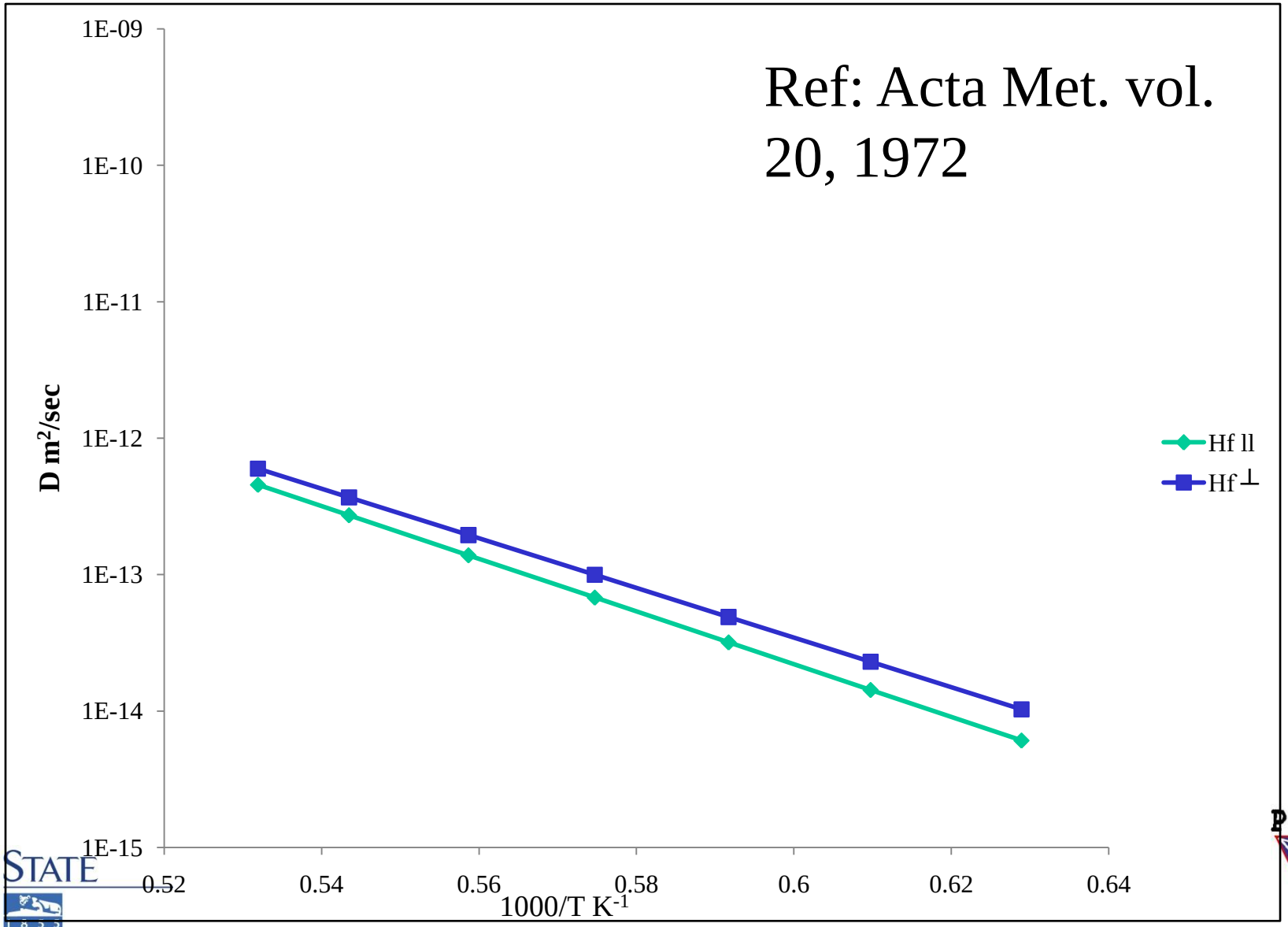
Hf



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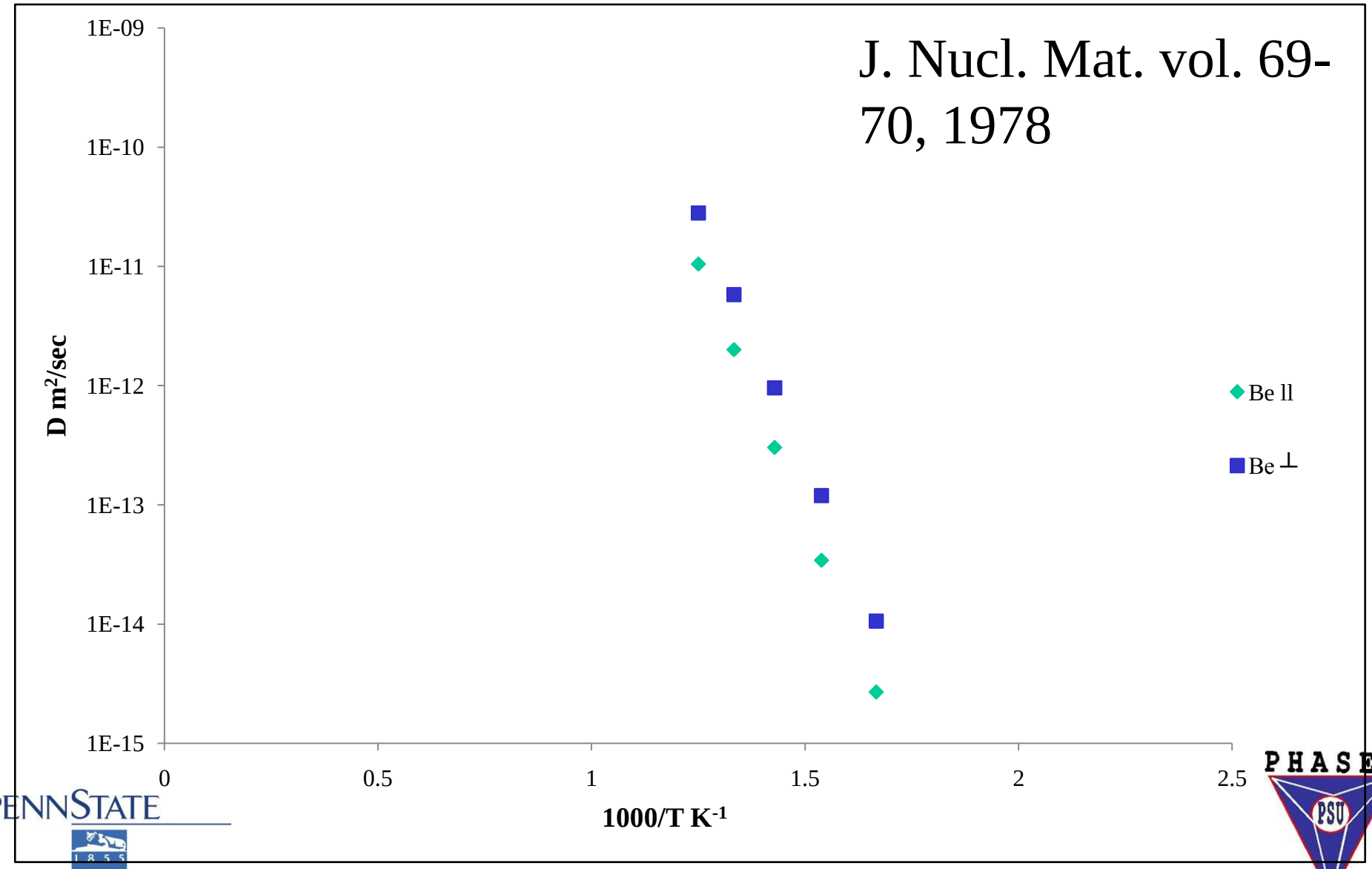
Be



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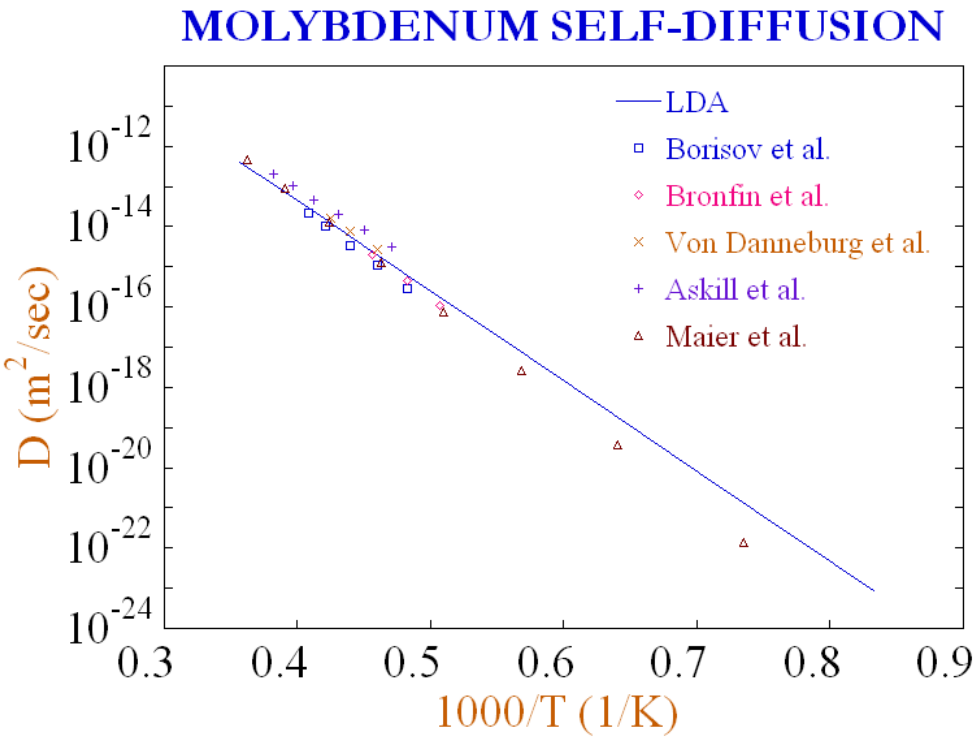
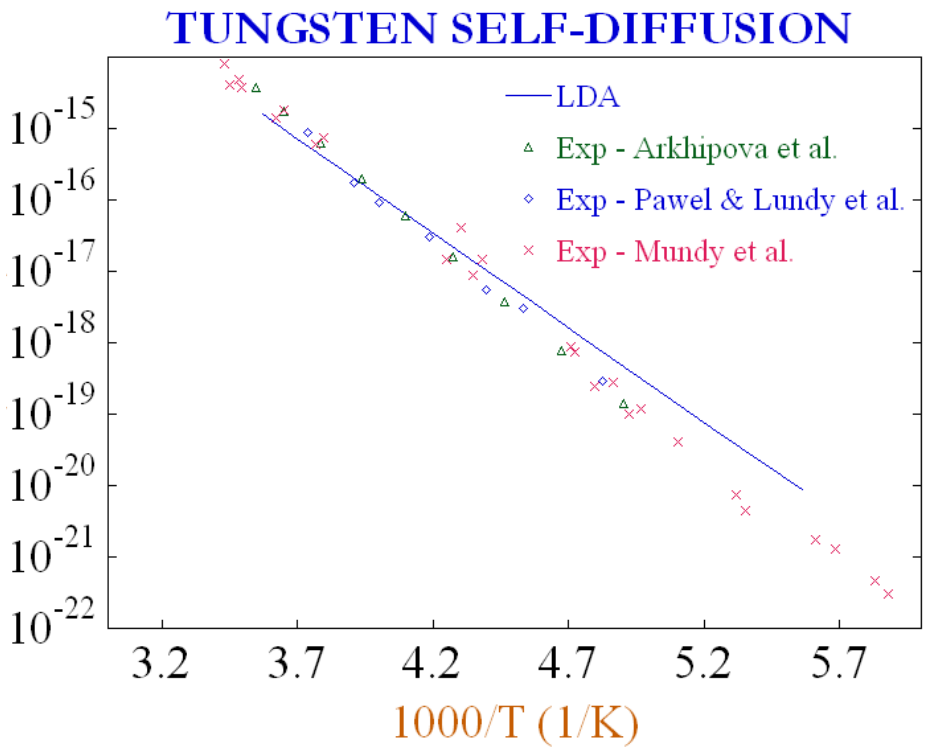
BCC Self Diffusion Data

Have not systematically collected yet

Self-diffusion coefficients in bcc





$$D = fa^2Cw = fa^2\frac{k_BT}{h}\exp\left(\frac{S^*_{sd,N-1} - \frac{N-1}{N}S_N}{T}\right)\exp\left(\frac{H^*_{sd,N-1} - \frac{N-1}{N}H_N}{k_BT}\right)$$

Mantina, submitted

Impurity diffusion data from our first-principles calculations

- In fcc Al
  - Cu, Mg, Si, Li
  - 3d: Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn
- In hcp Mg: Cd, Sn
- In bcc Mo: W
- In bcc W: Mo

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Mantina, PhD Thesis, Penn State, 2008

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Capability and Challenges

- **First-principles procedures to calculate self-diffusion coefficients and *impurity diffusion coefficients* are developed for fcc, bcc, hcp structures.**
- **Challenges for diffusion in**
  - **Magnetic elements**
    - **Wang, Phys. Rev. B, Vol.78, 2008, 104113.**
  - **Unstable phases at 0 K, such as hcp-Al**
    - **Ozolins, Phys. Rev. Lett., Vol.102, 2009, 065702.**

Magnetic phases

- **Gibbs energy of vacancy formation and migration as a function of temperature**
- **Treatment of magnetic property as a function of temperature**
  - **A magnetic phase at finite temperatures is a mixture of various magnetic states such as non-magnetic (NM), anti-ferromagnetic (AFM), ferromagnetic (FM)**
  - **Its partition function is a sum of the partition function of individual magnetic states**

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Wang, Phys. Rev. B, Vol.78, 2008, 104113.

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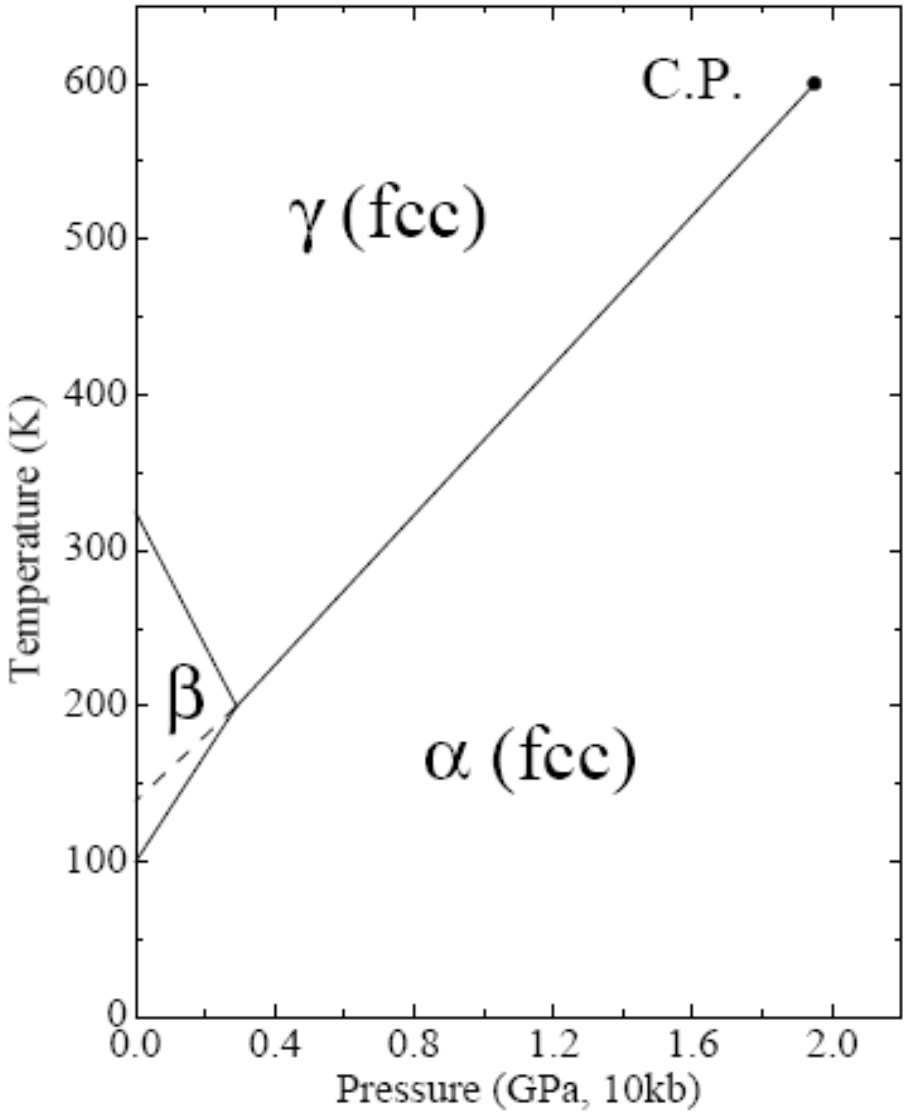
Magnetic transition in Ce from non-magnetic α to magnetic γ



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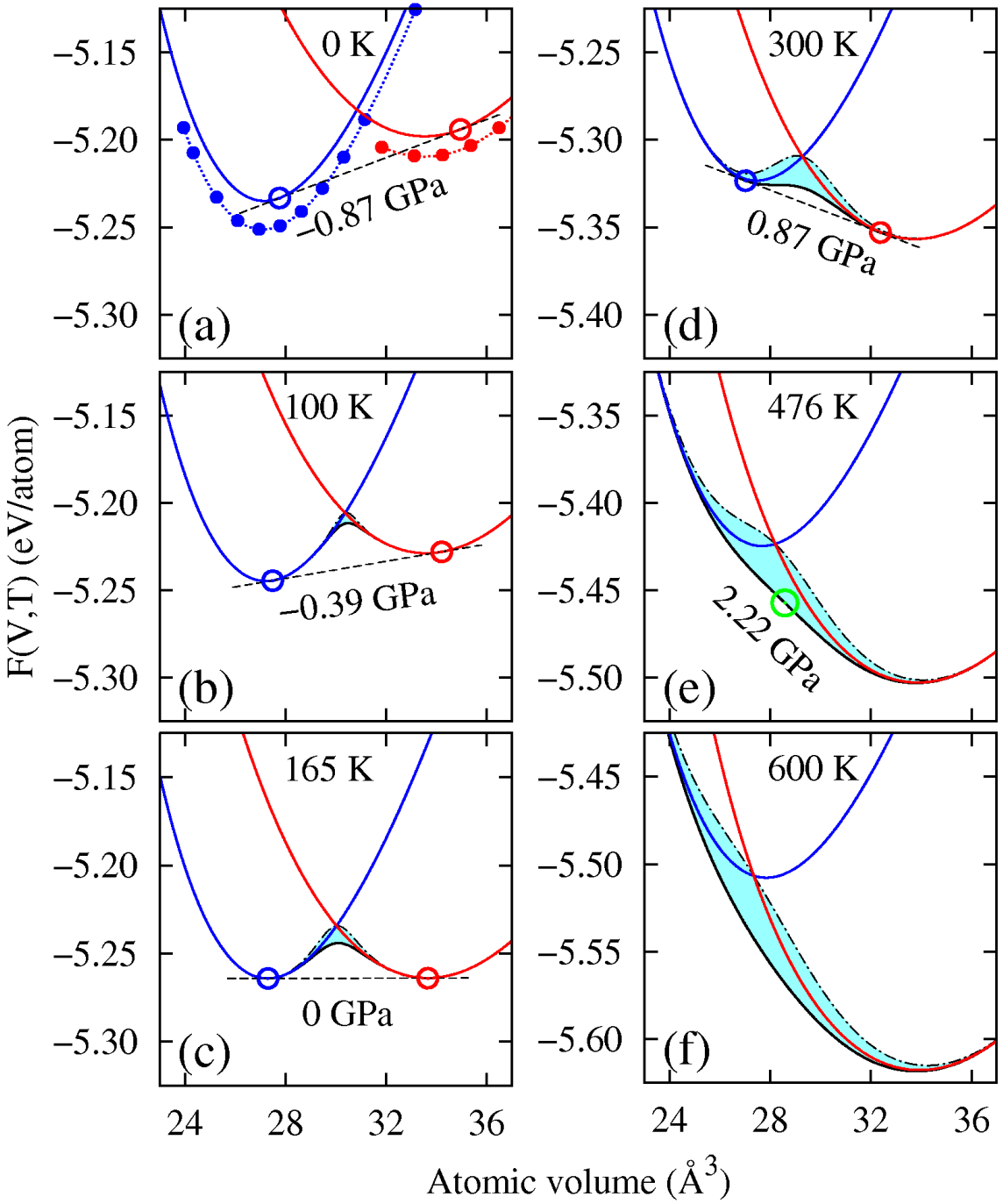
Helmholtz Free energy diagram for Ce

$$F^{\sigma}(V,T) = -k_B T \log Z^{\sigma}$$

$$F(V,T) = \sum_{\sigma} x^{\sigma} F^{\sigma}(V,T) - TS_{conf}$$

$$S_{conf} = -k_B \sum_{\sigma} x^{\sigma} \log x^{\sigma}$$



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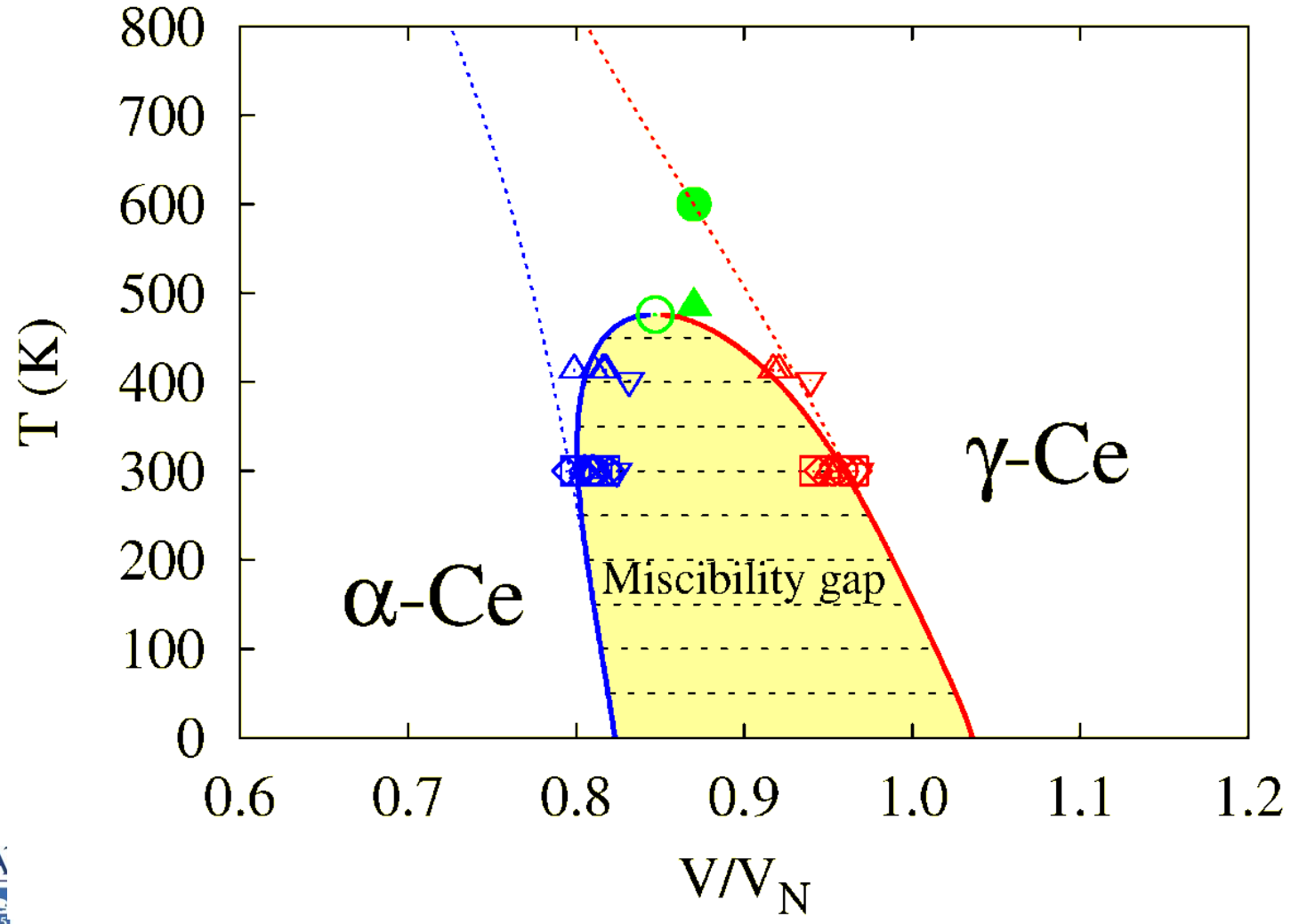
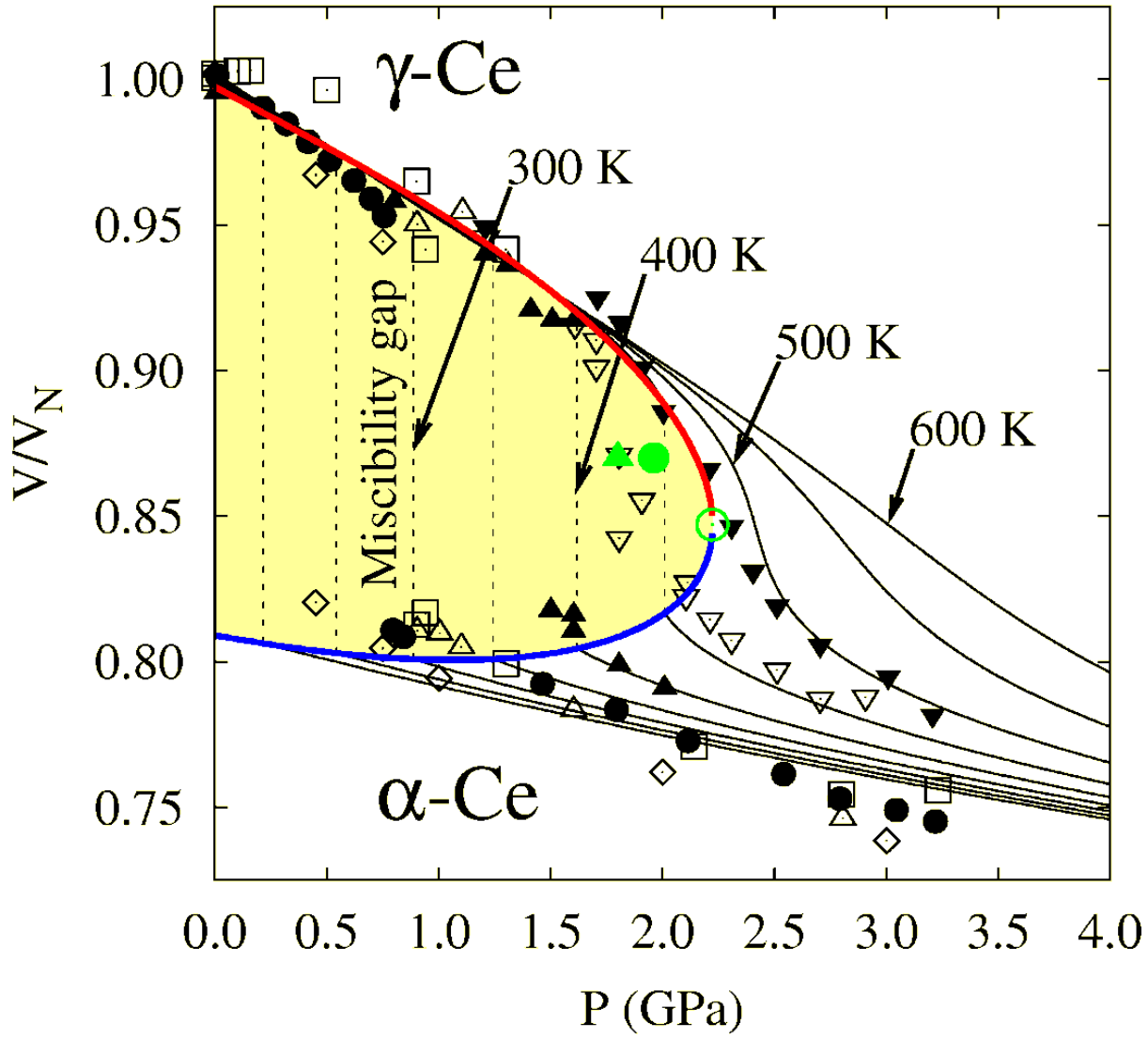
Predicted temperature-volume phase diagram



Volume-pressure property diagram



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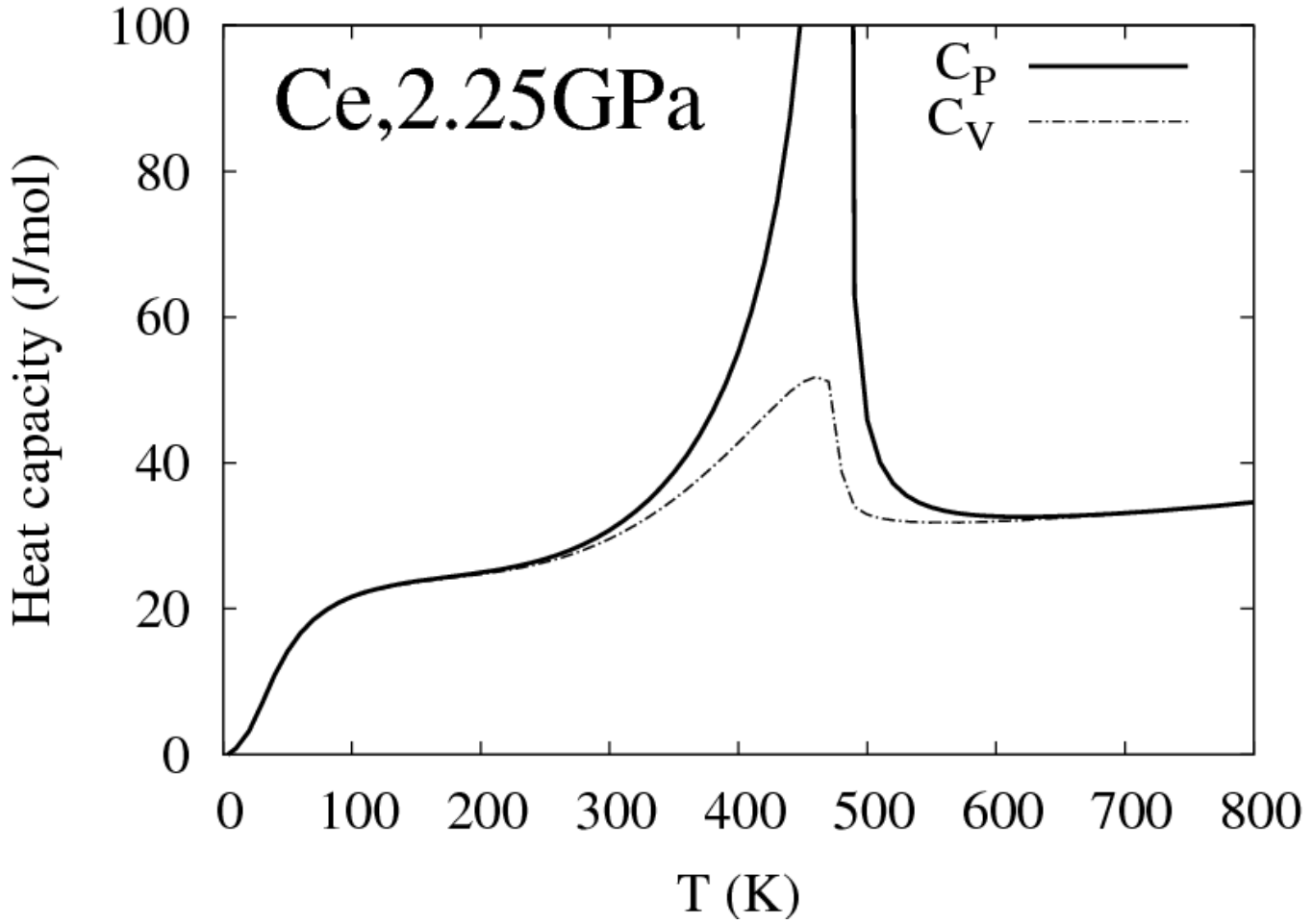
Predicted heat capacity for second-order magnetic transition



Wang, *unpublished*

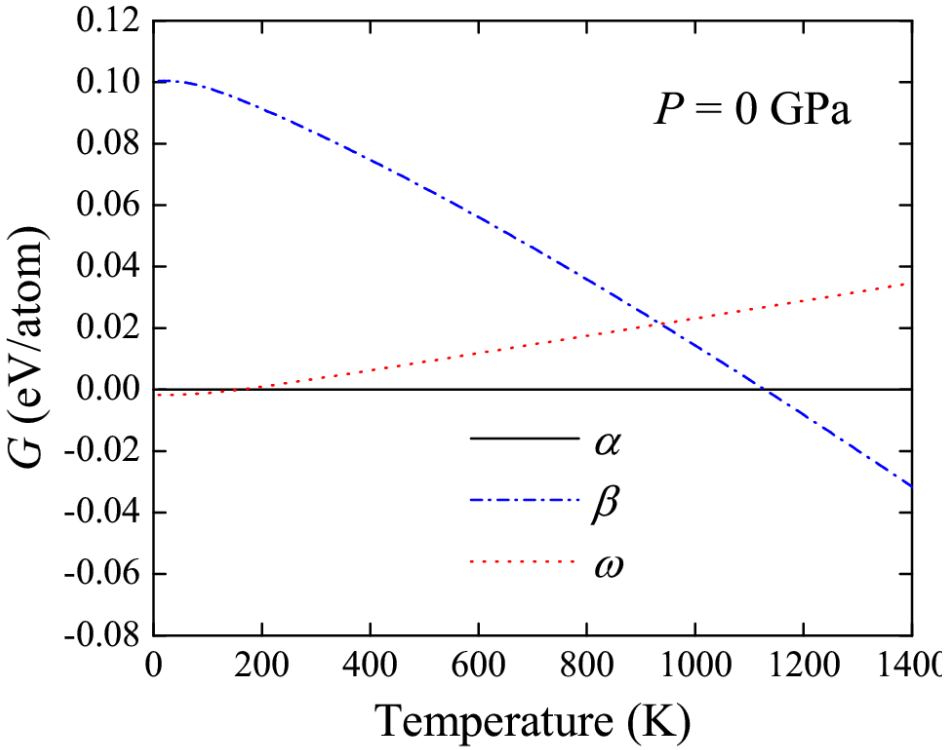
Unstable states

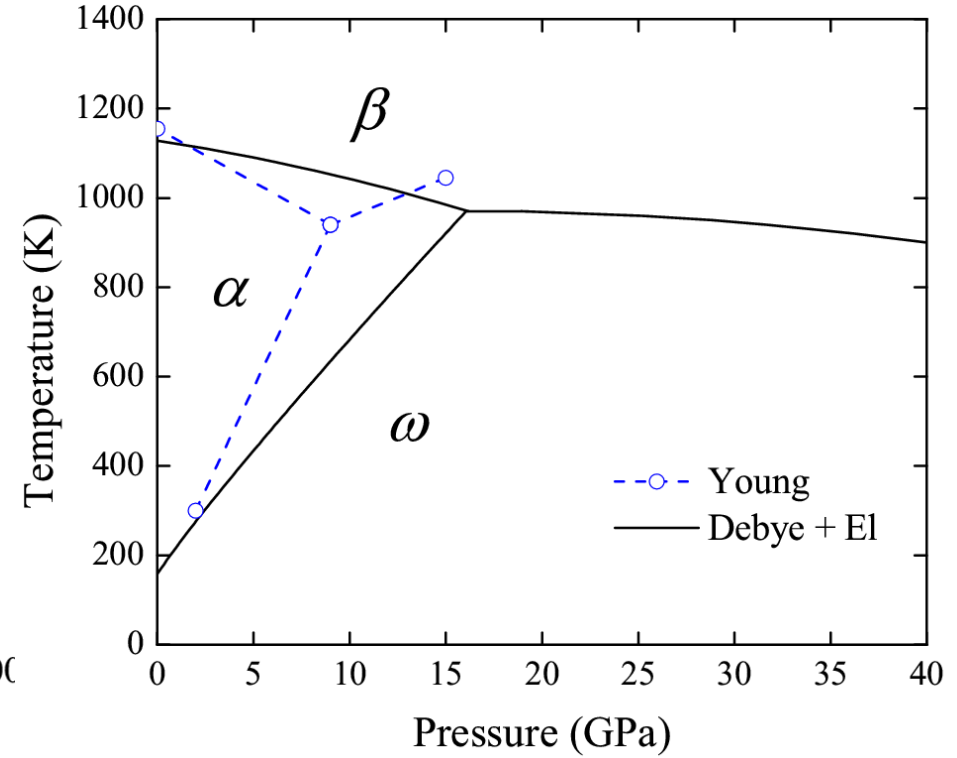
- **Two cases**
  - **the transition state (saddle point)**
  - **zero Kelvin**
- **Phonon approach is not applicable due to imaginary frequencies, soft modes.**
- **Debye model to obtain free energy**
  - **Testing system: Ti**

Debye model for Ti

$$\Theta_D = sAV_0^{1/6}\left(\frac{B_0}{M}\right)^{1/2}\left(\frac{V_0}{V}\right)^{\gamma}$$

$$F_{vib}(V,T) = \frac{9}{8}k_B\Theta_D + k_BT\left\{3\ln\left[1-\exp\left(-\frac{\Theta_D}{T}\right)\right] - D\left(-\frac{\Theta_D}{T}\right)\right\}$$





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Mei, to be published, Penn State, 2009

Future work on magnetic and unstable states

- First-principles calculations for various magnetic states with and without vacancy and at the saddle point
- Debye model for states with soft modes
- Free energy functions for all states
- Nonmagnetic elements: free energy difference between the saddle point and equilibrium state without vacancy
- Magnetic elements
  - Partition function to get free energy of the system as a function of temperature
  - Free energy difference at the saddle point and equilibrium state without vacancy