PENNSTATE

Tracer Diffusivities from First-principles

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OUTLINE

- Tracer diffusion in cubic systems
  - Theory
  - Diffusion results in fcc and bcc
- Tracer diffusion in hcp
  - Theory
  - Diffusion results
- Summary

CUBIC SYSTEMS

- Vacancy-mediated tracer (host or impurity) diffusion

$$D = fa^2Cw$$

f – correlation factor

a – lattice parameter

C – vacancy concentration adjacent to tracer

w – atom jump frequency

VACANCY CONCENTRAION

- For self-diffusion:

$$C = \exp(-\frac{\Delta G_f}{k_B T})$$

ΔG_f - free energy of vacancy formation in pure element

- For impurity diffusion:

$$C = \exp(-\frac{\Delta G_f - \Delta G_b}{k_B T})$$

ΔG_b - free energy of solute-vacancy binding

ATOM JUMP FREQUENCY

- For host or impurity atom jump

$$w = \frac{k_B T}{h} \exp\left(-\frac{H^*_{TS} - H_{IS}}{k_B T}\right) \exp\left(\frac{S^*_{TS} - S_{IS}}{k_B}\right)$$

X_{IS} - thermodynamic property of initial state before the jump (from all degrees of freedom)

X^*_{TS} - thermodynamic property of transition state after ignoring the unstable vibrational mode

CORRELATION FACTOR

- Pure element: single jump frequency - constant value - determined by Compaan and Haven [1] .
- With impurity – definition in terms of the different jump frequencies, given by Manning [2] based on five-frequency model
- eg: for solute diffusion in fcc $f = \dfrac{1+3.5F(w_4/w_0)(w_3/w_1)}{1+(w_2/w_1)+3.5F(w_4/w_0)(w_3/w_1)}$

$$F(x) = 1 - \frac{1}{7}\frac{10x^4 + 180.5x^3 + 927x^2 + 1341}{2x^4 + 40.2x^3 + 254x^2 + 597x + 435} \quad \text{where } x = \frac{w_4}{w_0}$$

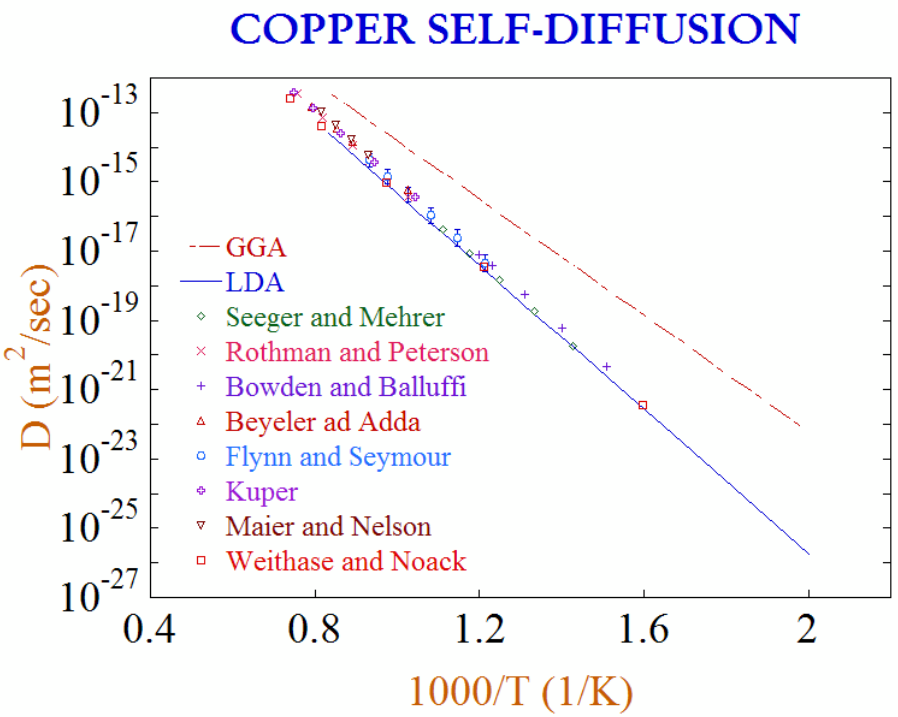
[1] Compaan, K., Haven, Y., *Trans. Faraday Soc.* **52,** 786 (1956)

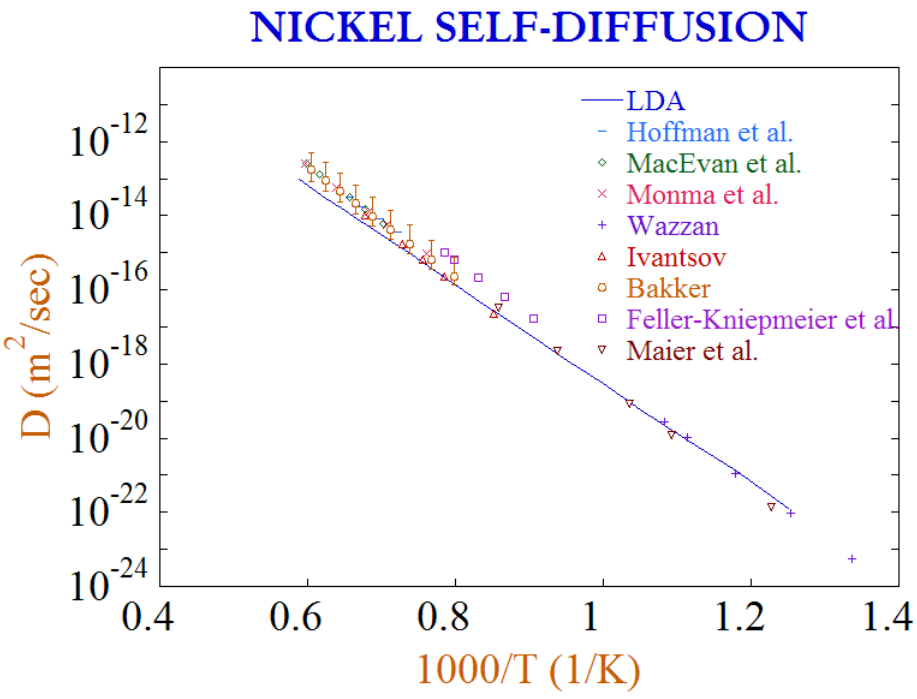
[2] Manning, J.R., *Phys Rev.* **136** A1758 (1964)

FIRST-PRINCIPLES

- VASP – PAW
  - System size – 32 lattice sites
- Fully relaxed perfect and equilibrium configurations
  - Volume, shape and atomic positions relaxed
- Saddle point and minimum energy saddle configuration
  - Nudged elastic band method (NEB)
- Phonon frequencies for the normal modes are determined using Supercell method (ATAT)

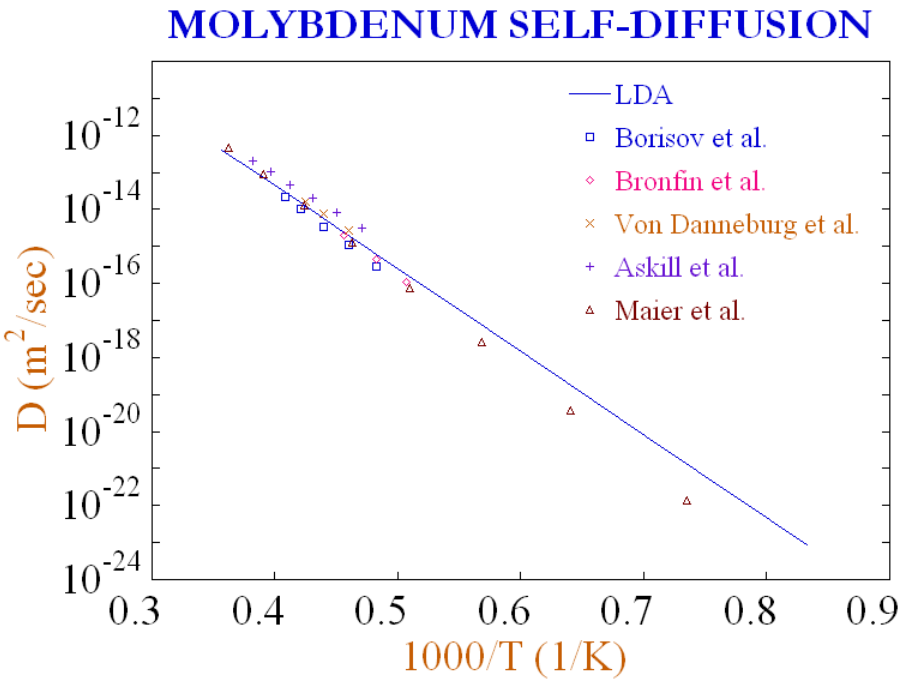
SELF-DIFFUSION IN FCC

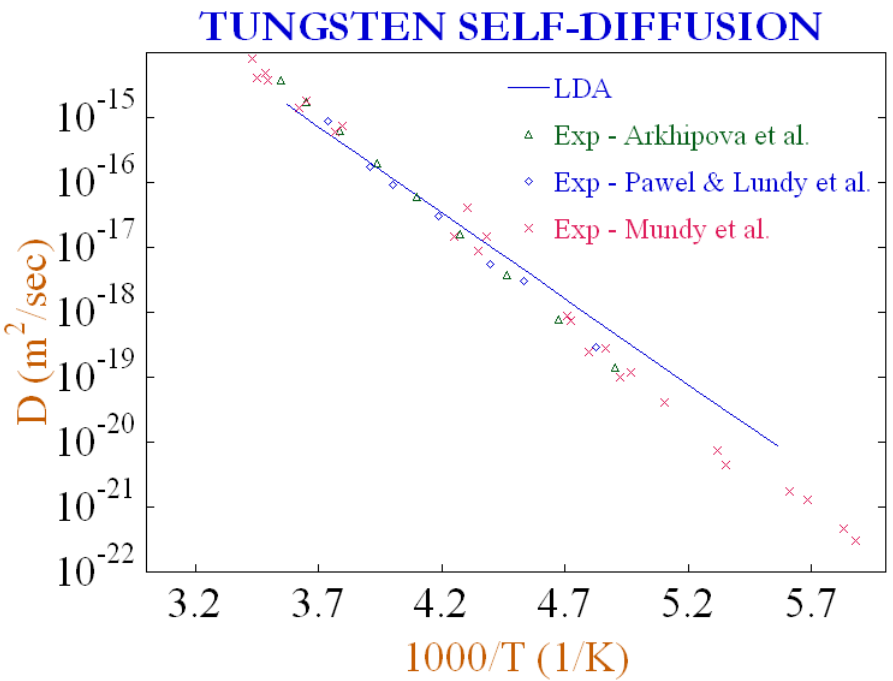




- LDA (without surface correction) yields diffusion results in good agreement with measurements.

SELF-DIFFUSION IN BCC

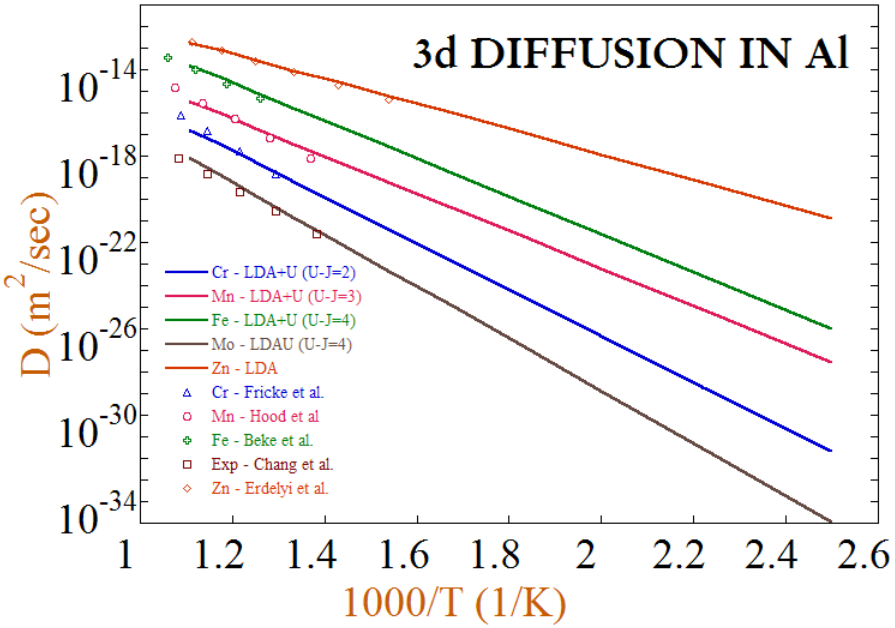




- Possible di-vacancy contributions to diffusion. Diffusion from di-vacancies being determined.

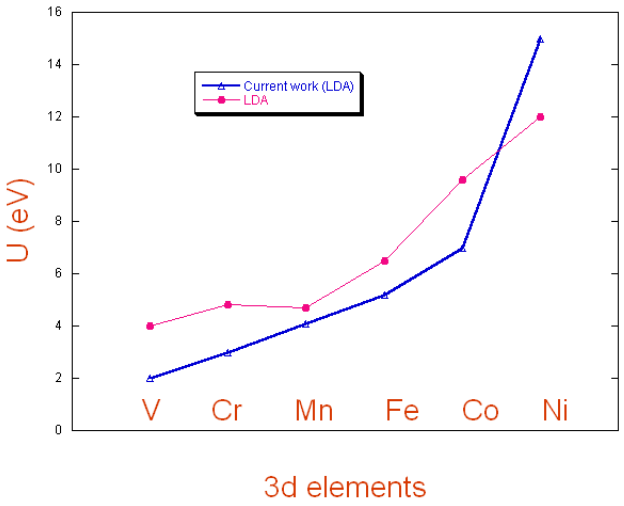
IMPURITY DIFFUSION IN FCC

- 3d transition metals diffusion in Al – LDA+U
- U parameter determined from diffusion results matching with reliable experimental data

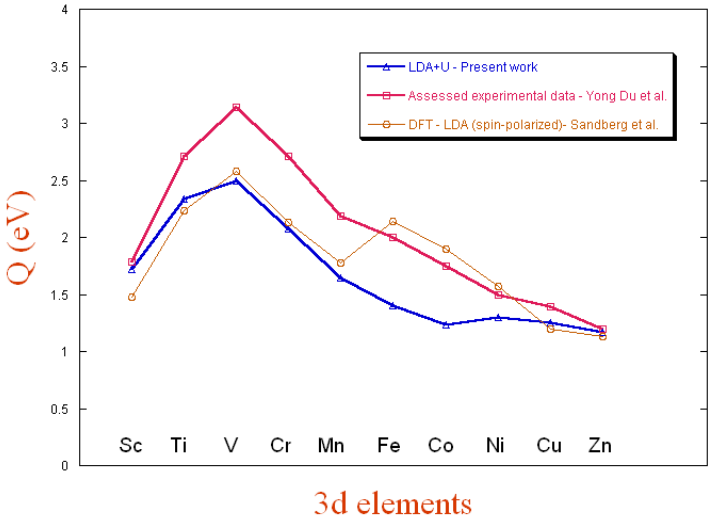


3d DIFFUSION IN FCC Al

U PARAMETERS

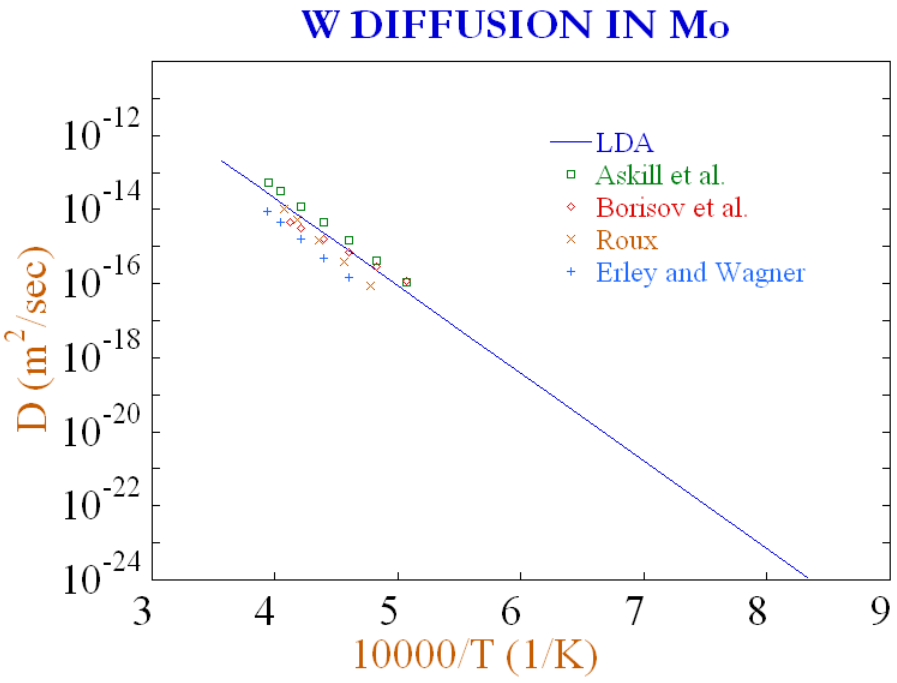


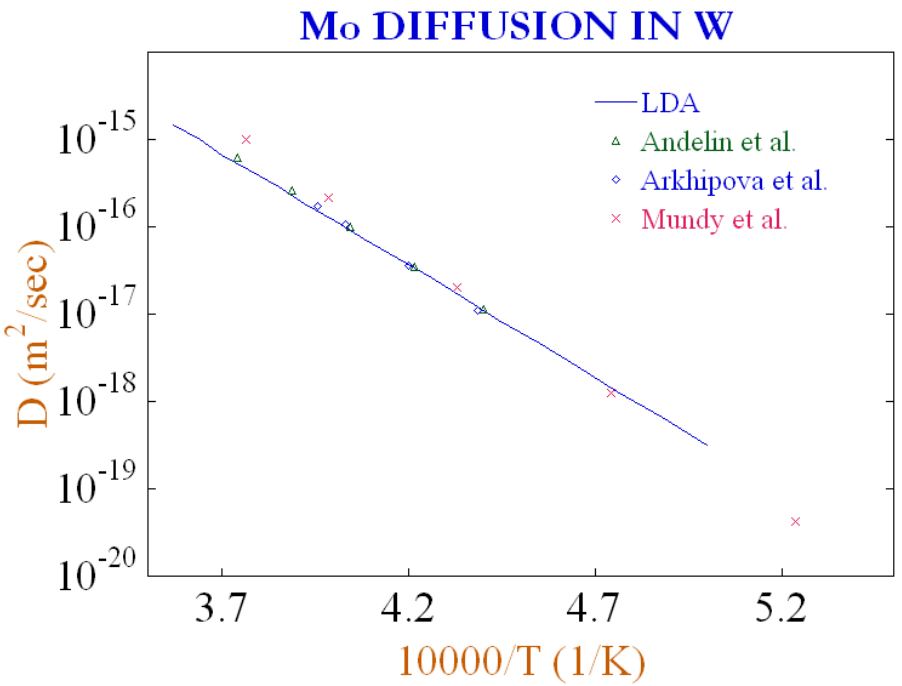
ACTIVATION ENERGY



- Al with Fe, Cr and Mn impurities is magnetic.
- Localization of charges around 3d elements with partially filled d shell causes high activation energies.
- Correlation factor ***f*** = 1 for the partially filled d-shell elements

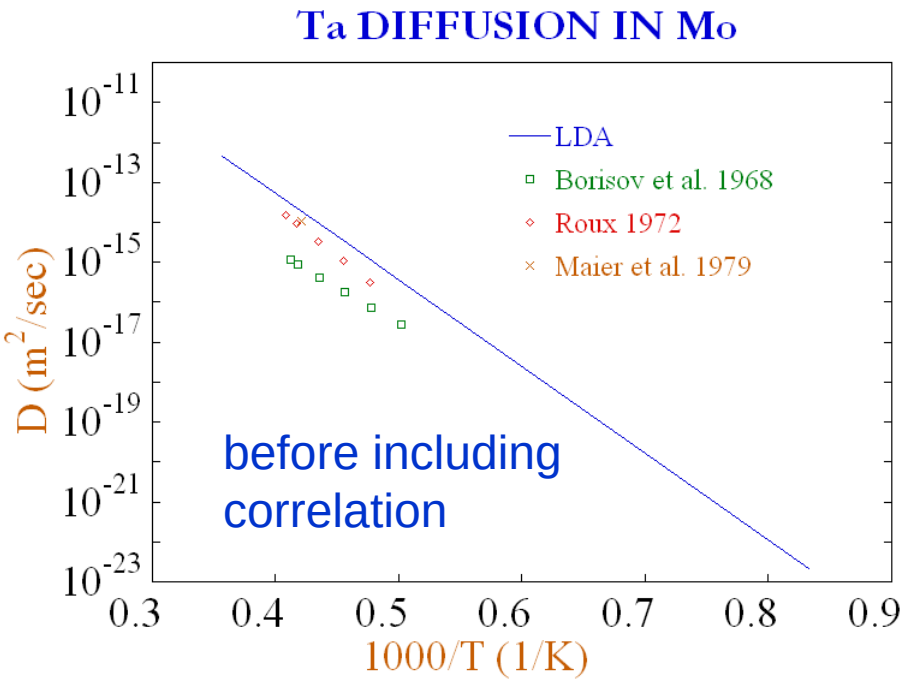
IMPURITY DIFFUSION IN BCC

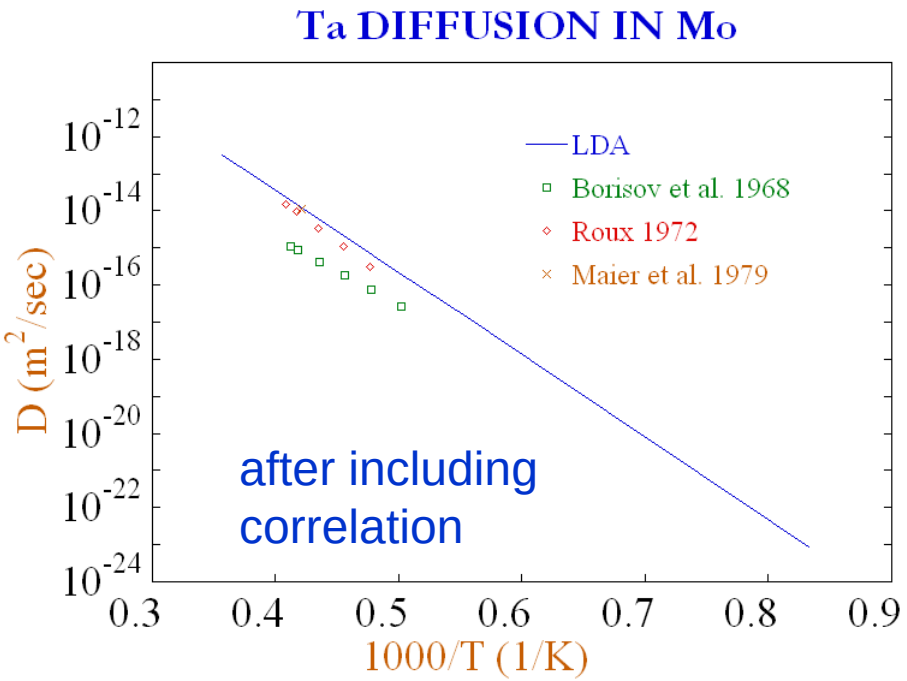




- For the case of these impurity diffusion coefficients correlation factor is expected to be close to unity.

IMPURITY DIFFUSION IN BCC





- Correlation factor for Ta diffusion in Mo calculated and the value is obtained to be 0.4 at room temperature.

ANISOTROPIC SYSTEM - HCP

- Vacancy-mediated diffusion of tracer (host or impurity) in hcp lattice is given by (hexagonal c direction along z-axis)

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

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

f_{ij} – partial correlation factors

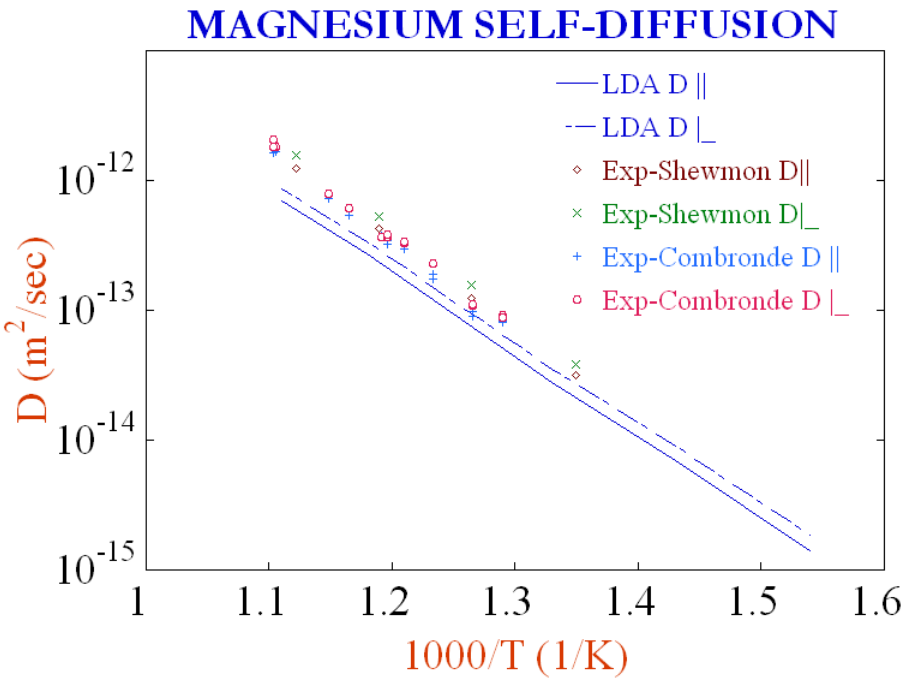
a,c – lattice parameters

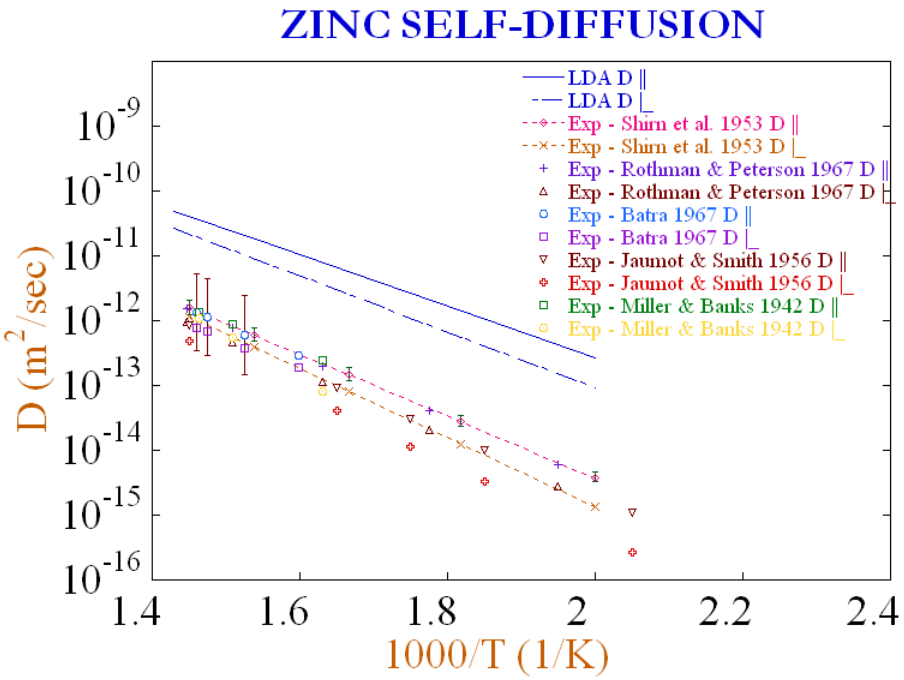
C – vacancy concentration

w_A – frequency for jump within a basal plane

w_B –frequency for jump between adjacent basal planes

SELF-DIFFUSION IN HCP

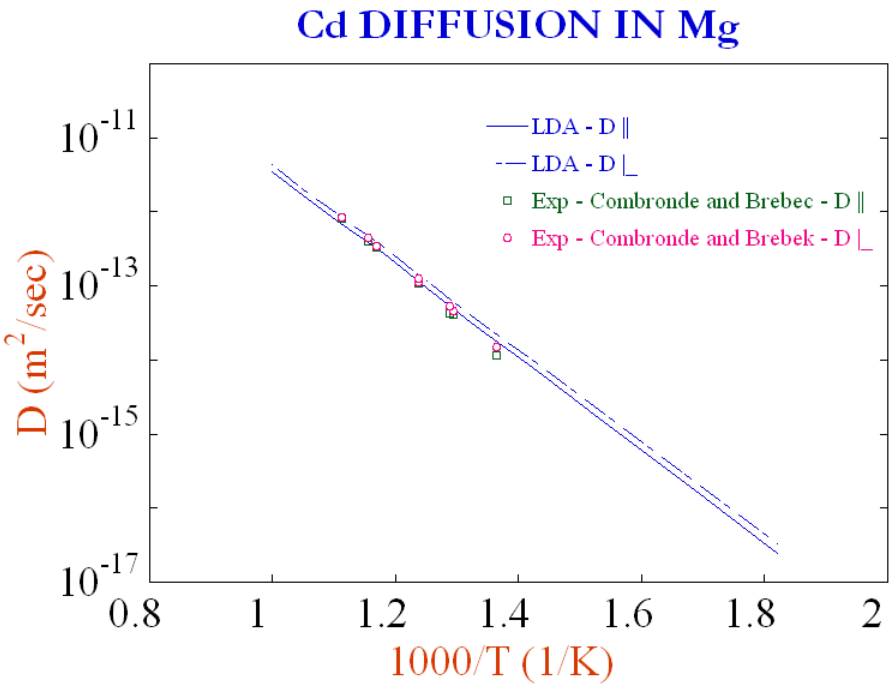


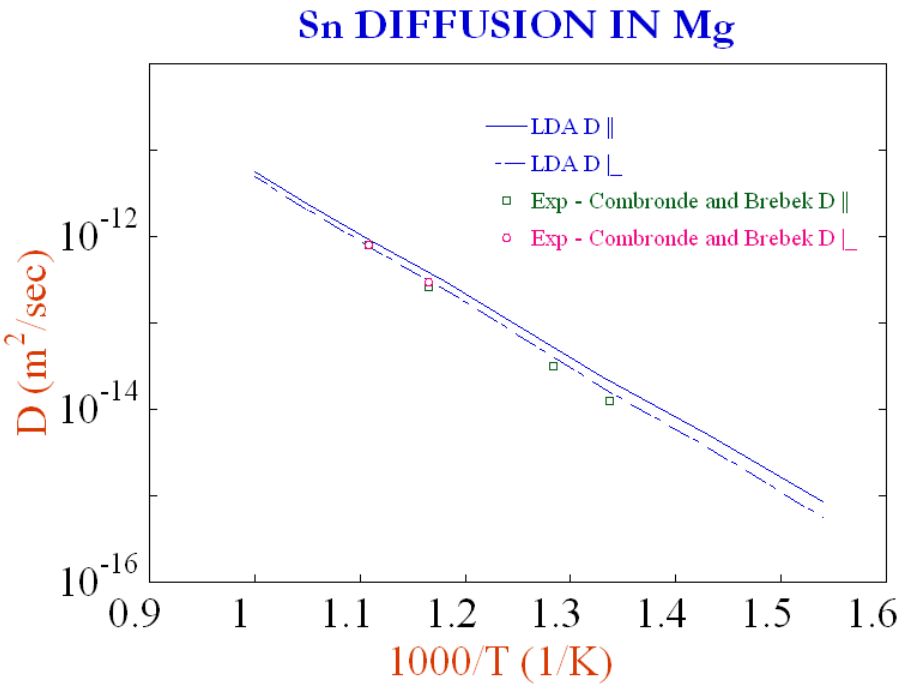


- Correlation factor in pure hcp – function of ratio of the two jump frequencies – tables given by Mullen [3]

[3] Mullen, J.G., *Phys Rev.* **124** 1723 (1961)

IMPURITY DIFFUSION IN HCP





- Correlation factors for impurity diffusion in hcp Mg expected to be ~ 1.

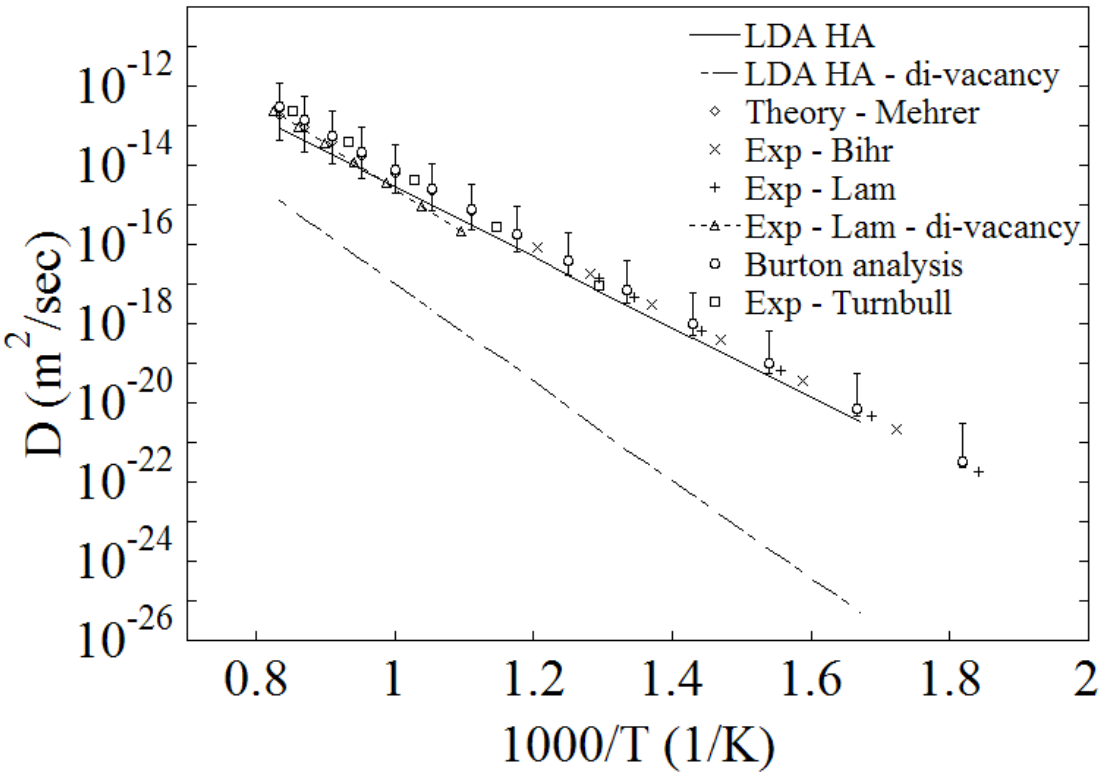
SUMMARY

- First-principles procedure to calculate self-diffusion coefficient [4] extended to fcc, bcc, hcp crystal systems.
- Impurity diffusion coefficients calculated including their correlation factors.
- Physical understanding of the low diffusivities of 3d elements in Al obtained from the +U calculations.
- Procedure being extended to di-vacancy mechanism.

[4] Mantina, M., Wang, Y., et al. *Phys Rev Lett.* in press.

THANK YOU ALL FOR LISTENING

SELF-DIFFUSION IN FCC Ag



- Curvature in the diffusion plot is due to di-vacancy contributions at high temperatures
- Include di-vacancy equations