# Tracer Diffusivities by First-principles

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# OUTLINE

- Self-diffusion
- Exclusively first-principles
- Impurity diffusion coefficient in fcc
- Self-diffusion in hcp
- Entropy of migration
- Summary

# NO IMPURITY

- Vacancy-mediated diffusion in a cubic system

$$D_0 = f_0 c_0 w_0 a^2$$

$f_0$ – correlation factor

$a$ – lattice parameter

$c_0$ – vacancy concentration

$w_0$ – successful atom jump frequency

# SELF-DIFFUSION

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

$\Delta_f H$- enthalpy of vacancy formation

$\Delta_f S$ - vibrational entropy of vacancy formation

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

$\Delta_m H$ - enthalpy of migration

$\Delta_m S$ - vibrational entropy of migration

$\tilde{\nu}$ - characteristic vibrational frequency in the diffusion direction

# JUMP FREQUENCY

- Eyring's reaction rate theory [1]

$$w = \frac{k_B T}{h} \frac{Z^*_{tr}}{Z_{in}}$$

* represents not including the contribution of the unstable phonon mode

Partition function $\quad Z = \exp(-\frac{G}{k_B T})$

$$w = \frac{k_B T}{h} \exp(\frac{S^*_{tr} - S_{in}}{k_B}) \exp(-\frac{(H^*_{tr} - H_{in})}{k_B T})$$

NO NEED TO CALCULATE THE MIGRATION PROPERTIES

[1] Eyring, H., J. Chem. Phys. **3** (1935) 107

# FIRST-PRINCIPLES

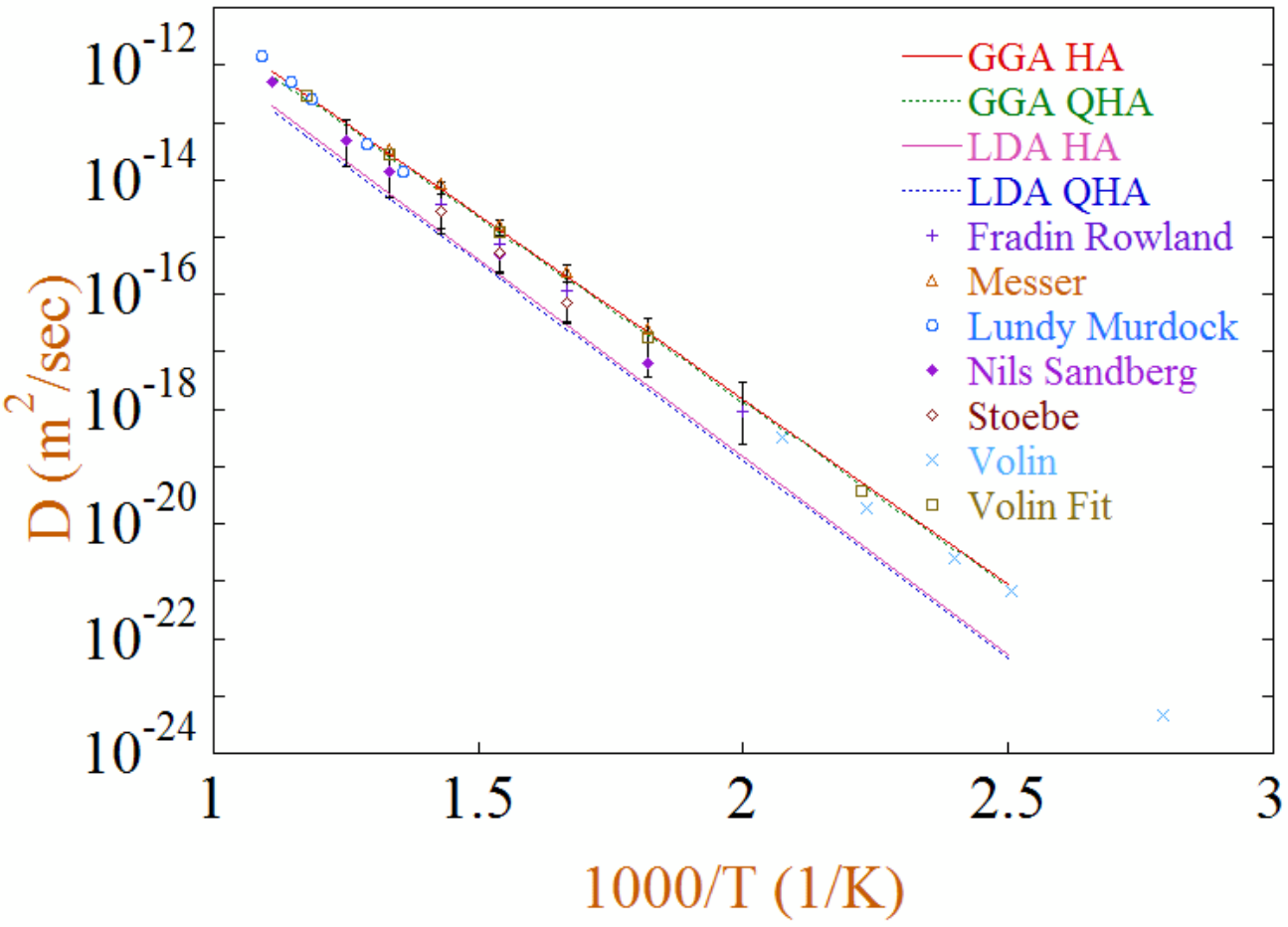
- VASP – PAW
  - System size – 32 lattice sites
- Fully relaxed perfect and equilibrium configurations
  - Volume, shape and atomic positions relaxed
- Saddle point and minimum energy saddle configuration
  - Nudged elastic band method (NEB)
- Phonon frequencies for the normal modes are determined using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

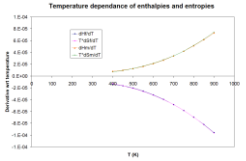
[Van de Walle et al, CALPHAD, **26**, 539 (2002)]

# ENERGY CORRECTION

- Single vacancy in Al [Carling et al, PRL 85, 3862 (2000)]
  - Correction term: 0.15eV for GGA, 0.06eV for LDA
- Two partial vacancies in Al
  - Additional correction term: 0.05eV for GGA, 0.02eV for LDA [Sandberg, et al, PRL 89, 065901 (2002)]

# ALUMINUM SELF-DIFFUSION



- Anharmonic effects from temperature dependences are seen to be negligible.

# WITH IMPURITY

- Impurity diffusion coefficient in cubic system

$$D_2 = f_2 w_2 c_2 a^2$$

$f_2$ – impurity correlation factor

$a$ – lattice parameter

$c_2$ – vacancy concentration adjacent to impurity

$w_2$ – successful impurity jump frequency

# IMPURITY DIFFUSION

- Five-frequency model[2] best suited for diffusion in dilute fcc alloys

$$f_2 = \frac{1+3.5(w_3/w_1)}{1+(w_2/w_1)+3.5(w_3/w_1)}$$

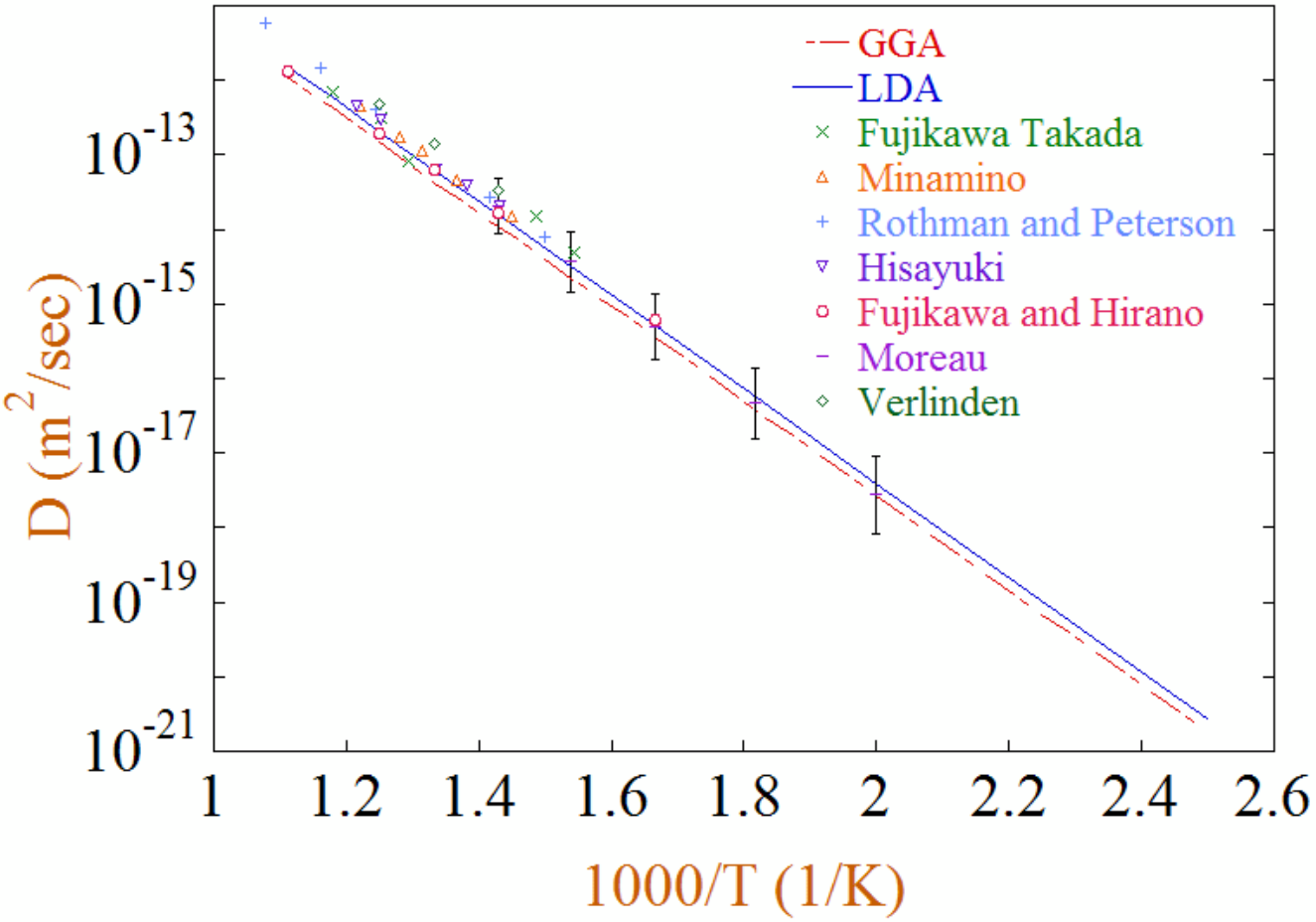
$$\frac{D_2}{D_0} = \frac{f_2}{f_0}\frac{w_2}{w_0}\frac{w_4}{w_3}$$

- Considering $w_4$ and $w_3$ are reverse jumps of each other we have

$$\frac{c_2}{c_0} = \exp\left(-\frac{\Delta G_b}{k_B T}\right) = \frac{w_4}{w_3}$$

[2] Le Claire, A.D., Journal of Nuclear Materials **69-70** (1978) 70

# Mg DIFFUSIVITY IN Al




- No correction term - different jumps need different corrections

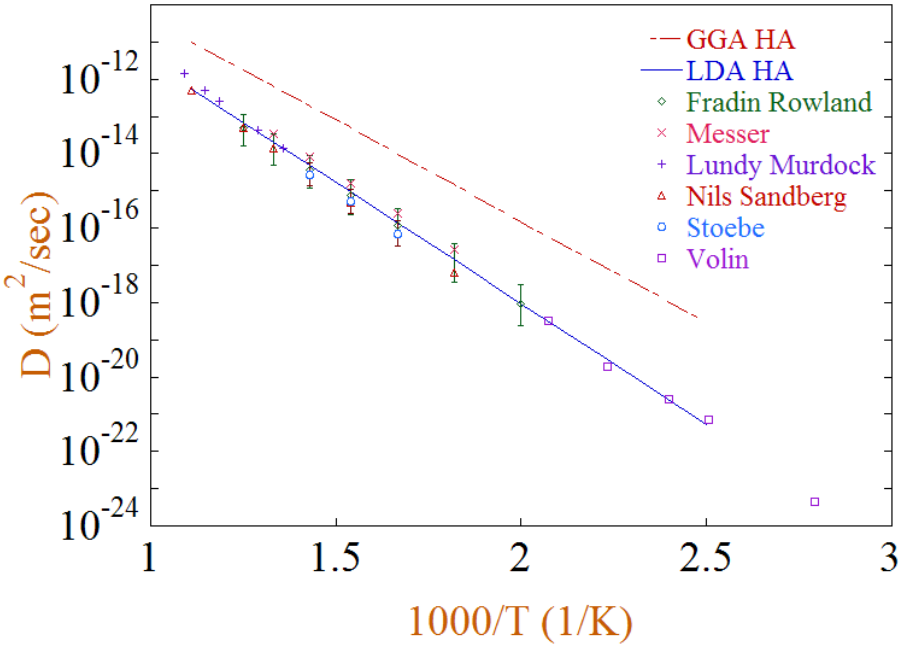
# PAW LDA – NO CORRECTION

- LDA - cancellation of errors between the exchange and correlation energies [4] making it more suitable for surface calculations.
- Energy calculation of the surface due to vacancy from LDA is reasonable.
- In diffusion calculation - errors due to over-binding from LDA get canceled.

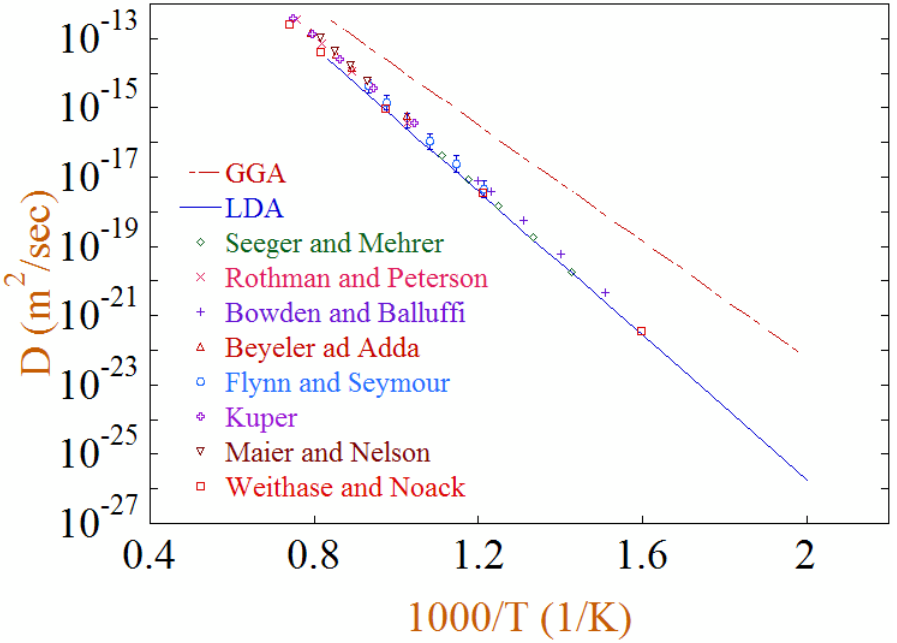
[4] Vitos, L., Surface Science **411** (1998) 186

# SELF-DIFFUSION RESULTS

## ALUMINUM SELF-DIFFUSION

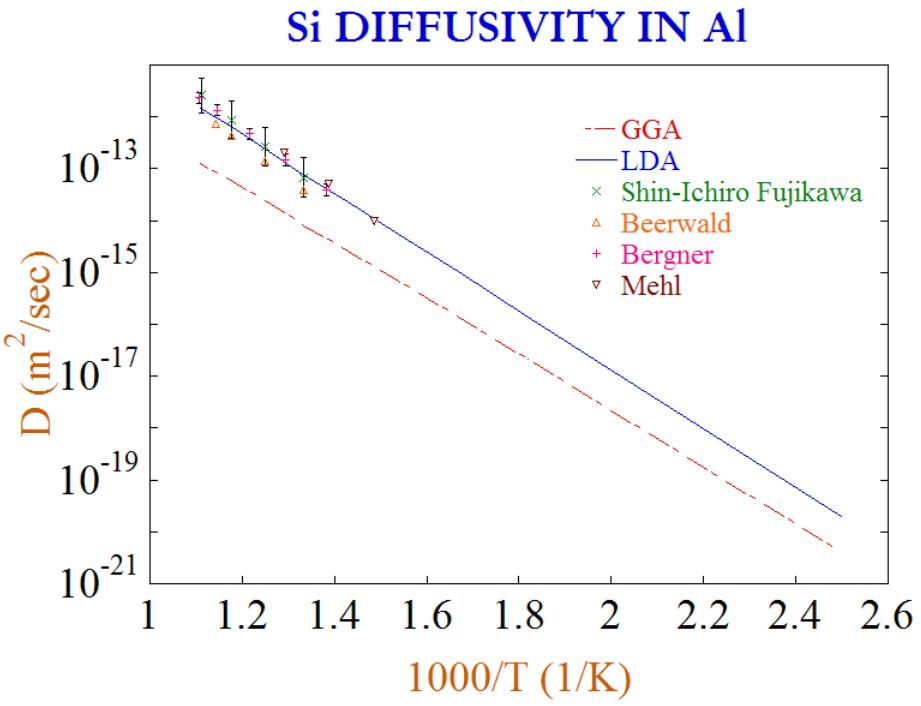


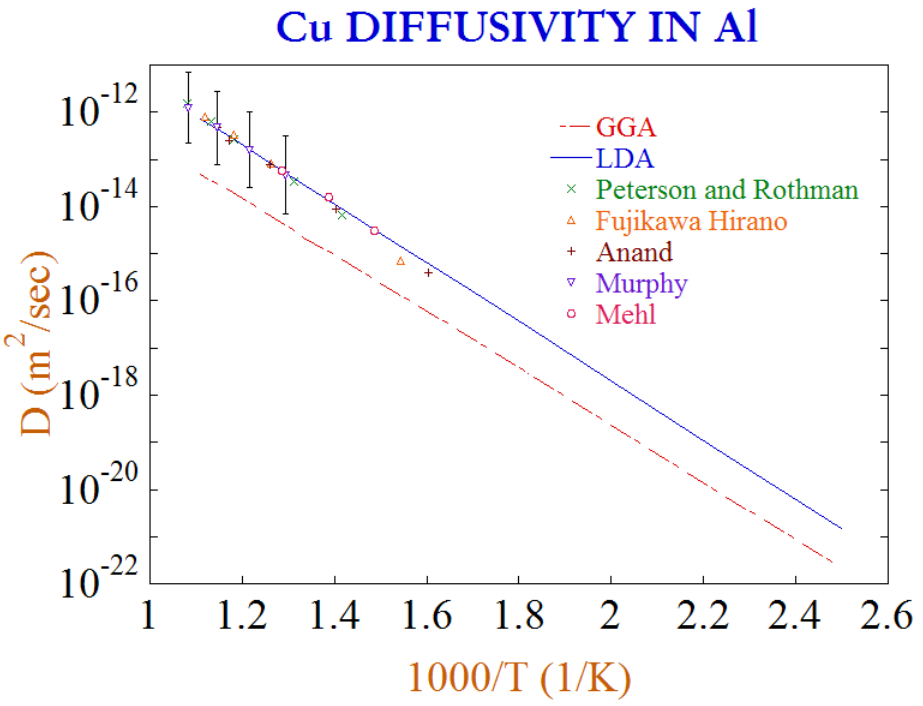

## COPPER SELF-DIFFUSION




**NO CORRECTION**

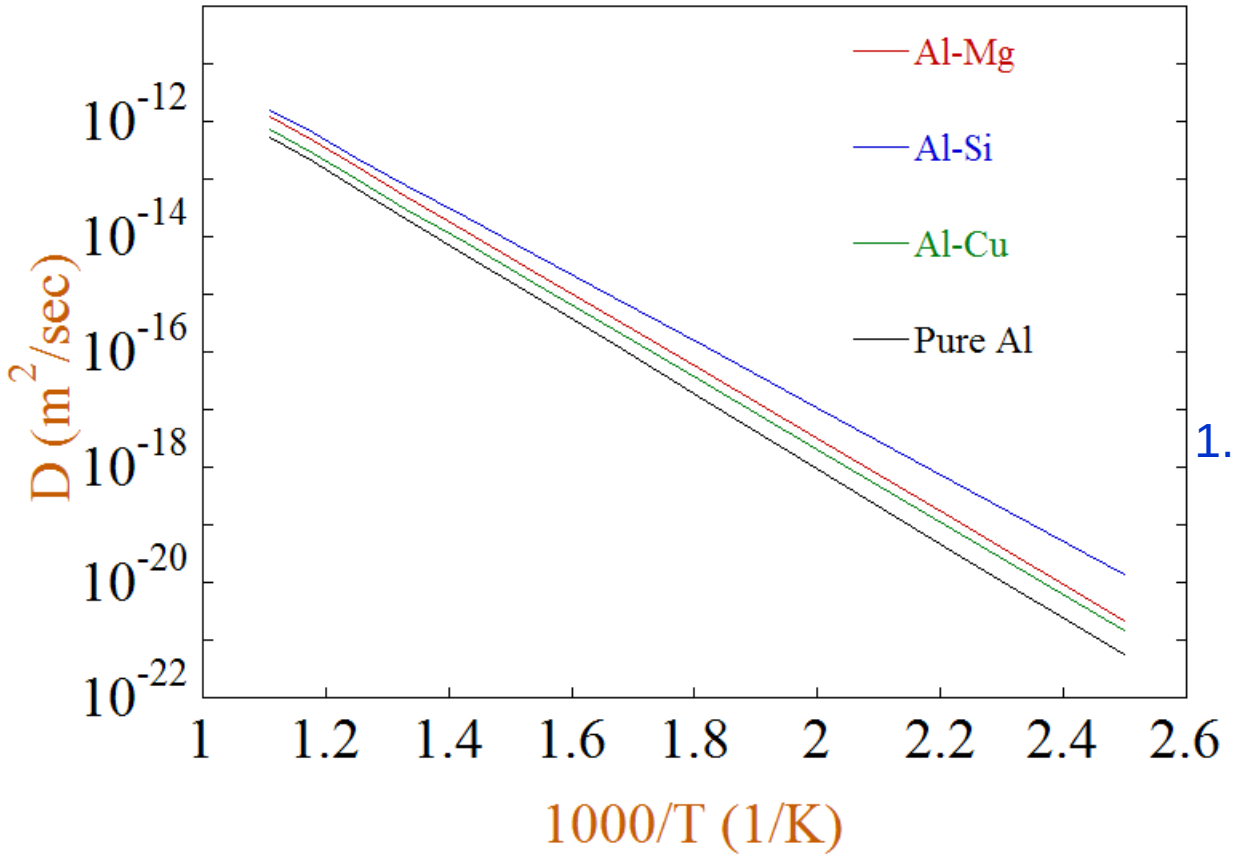
# IMPURITY DIFFUSION RESULTS




**NO CORRECTION**

# OBSERVATION




$r_{Mg} > r_{Al} > r_{Si} > r_{Cu}$ [5]

1.597 > 1.431 > 1.392 > 1.284

- Impurity diffusivities do not follow the trend of their size

[5] Y. Wang et.al., CALPHAD, **28** (2004) 79-90

# SELF-DIFFUSION IN HCP

- Diffusion in hexagonal cubic system

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

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

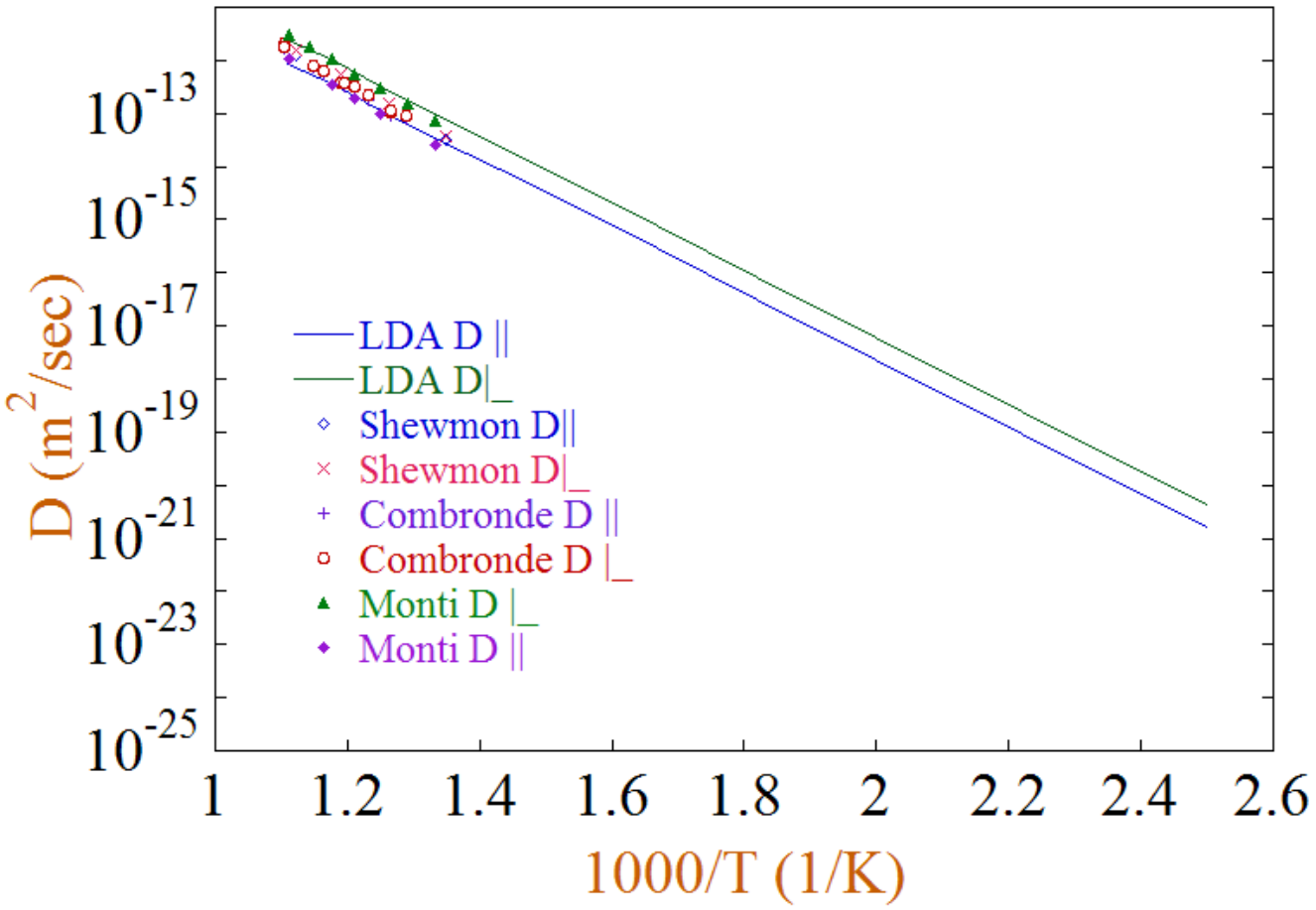
$f_{ij}$ – correlation factors function of $w_A / w_B$ ratio

$a,c$ – lattice parameters along x,z axes

$C$ – vacancy concentration

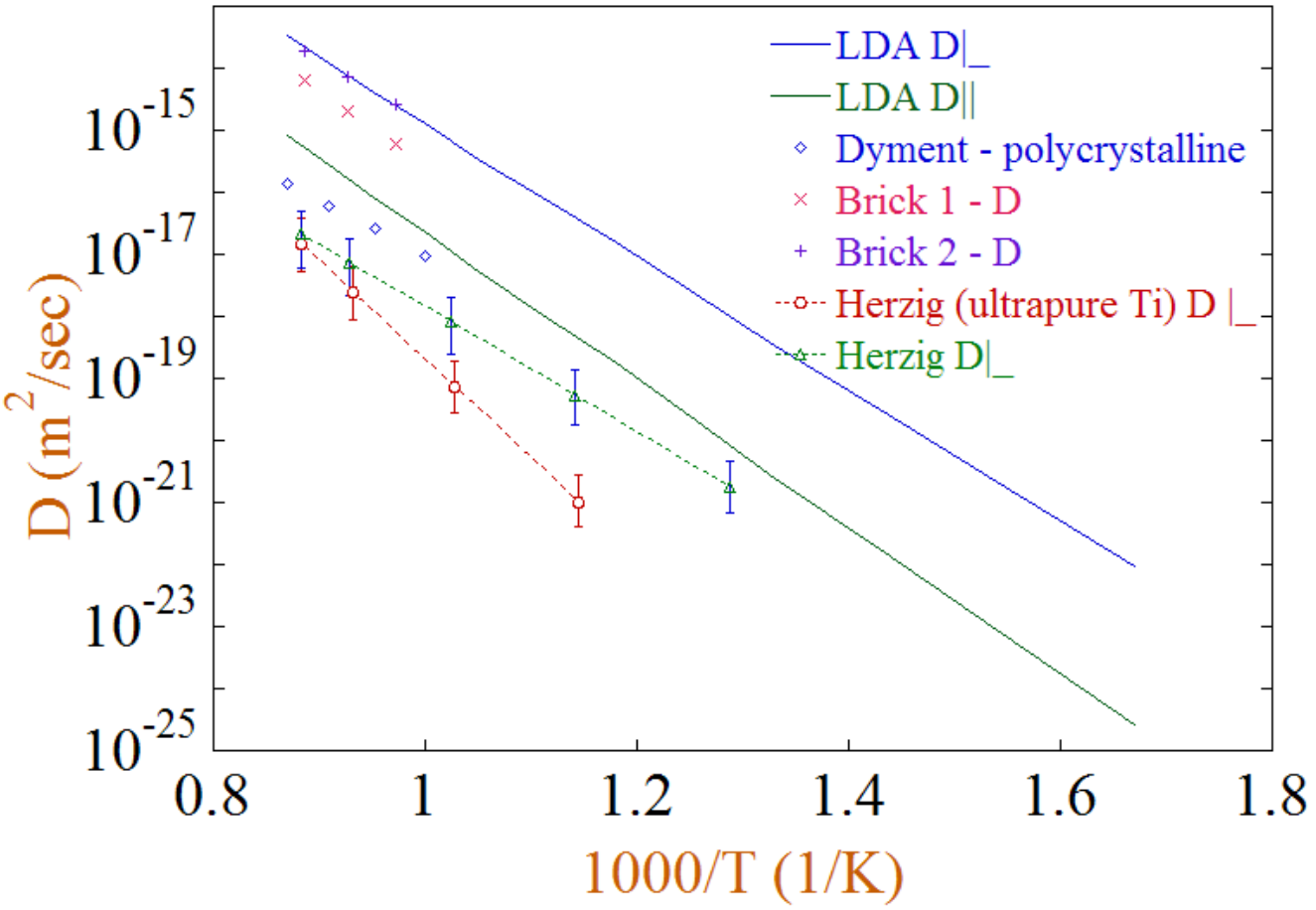
$w_A, w_B$ – successful jump frequency |_ and || to z-axis

# MAGNESIUM SELF-DIFFUSION




- Diffusion in the basal plane higher than along z-axis

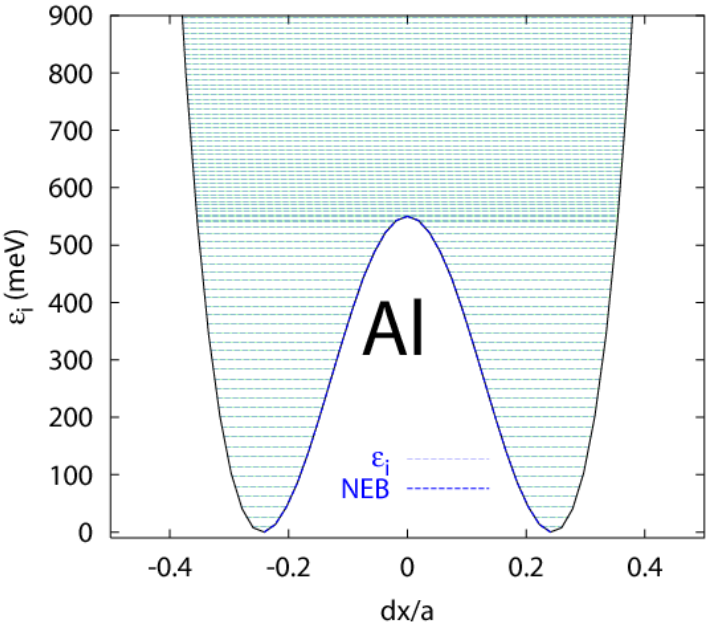
# TITANIUM SELF-DIFFUSION




- High difference in diffusivities between || & |_ directions

# ENTROPY OF MIGRATION

- Entropy of migration is defined as $\Delta S_m = S_{tr} - S_{in}$
- We need to calculate entropy contribution $\tilde{S}$ from the unstable mode.




$$\tilde{Z} = \sum_i \exp\left(\frac{-\varepsilon_i}{k_B T}\right)$$

$$\tilde{\nu} = \frac{k_B T}{h\tilde{Z}}$$

# SUMMARY

- General procedure to calculate atom jump frequencies from static first-principles is presented.
- Accurate tracer diffusivities can be obtained exclusively from first-principles with LDA.
- Anharmonic effects due to temperature dependences of the quantities is minimum – curvature in D mostly due to di-vacancies at high T.
- Solute diffusivities do not follow the trend of their size.
- In hcp, self-diffusion in the basal plane seen to be higher than in normal.
- Calculated entropy of migration and characteristic vibrational frequency.

# THANK YOU FOR LISTENING

# EQUATIONS

$$F = E^* + Nk_BT\int_0^\infty \ln\left[2\sinh\left(\frac{h\nu}{2k_BT}\right)\right]g(\nu)d\nu$$

Simplified high temperature ($T > \theta_D$) form

$$F = E^* + Nk_BT\int_0^\infty \ln\left(\frac{h\nu}{k_BT}\right)g(\nu)d\nu$$

$$= E^* + k_BT\sum_m \ln\left(\frac{h\nu_i}{k_BT}\right)$$

$$S = k_B\int_0^\infty\left[\left(\frac{h\nu}{2k_BT}\right)\coth\left(\frac{h\nu}{2k_BT}\right) - \ln\left[2\sinh\left(\frac{h\nu}{2k_BT}\right)\right]\right]g(\nu)d\nu$$

$$U = E^* + 0.5\int_0^\infty h\nu\coth\left(\frac{h\nu}{2k_BT}\right)g(\nu)d\nu$$

m – vibrational degrees of freedom

$$S = -k_B\sum_m \ln\left(\frac{h\nu_i}{ek_BT}\right) \Rightarrow \tilde{S} = -k_B\ln\left(\frac{h\tilde{\nu}}{ek_BT}\right)$$

$E^*$ is the 0K energy of the system in equilibrium

$\nu$ represents the phonon frequencies of the system

$g(\nu)$ represents the phonon DOS

$$U_{vib} = F_{vib} + TS \qquad \text{where} \qquad F_{vib} = k_BT\sum_m \ln\left(\frac{h\nu_i}{k_BT}\right)$$

$$U_{vib} = k_BT\left(\sum_m \ln\left(\frac{\left(\frac{h\nu_i}{k_BT}\right)}{\left(\frac{h\nu_i}{ek_BT}\right)}\right)\right) = mk_BT \qquad \Rightarrow \tilde{U} = k_BT$$

# HARMONIC THEORY

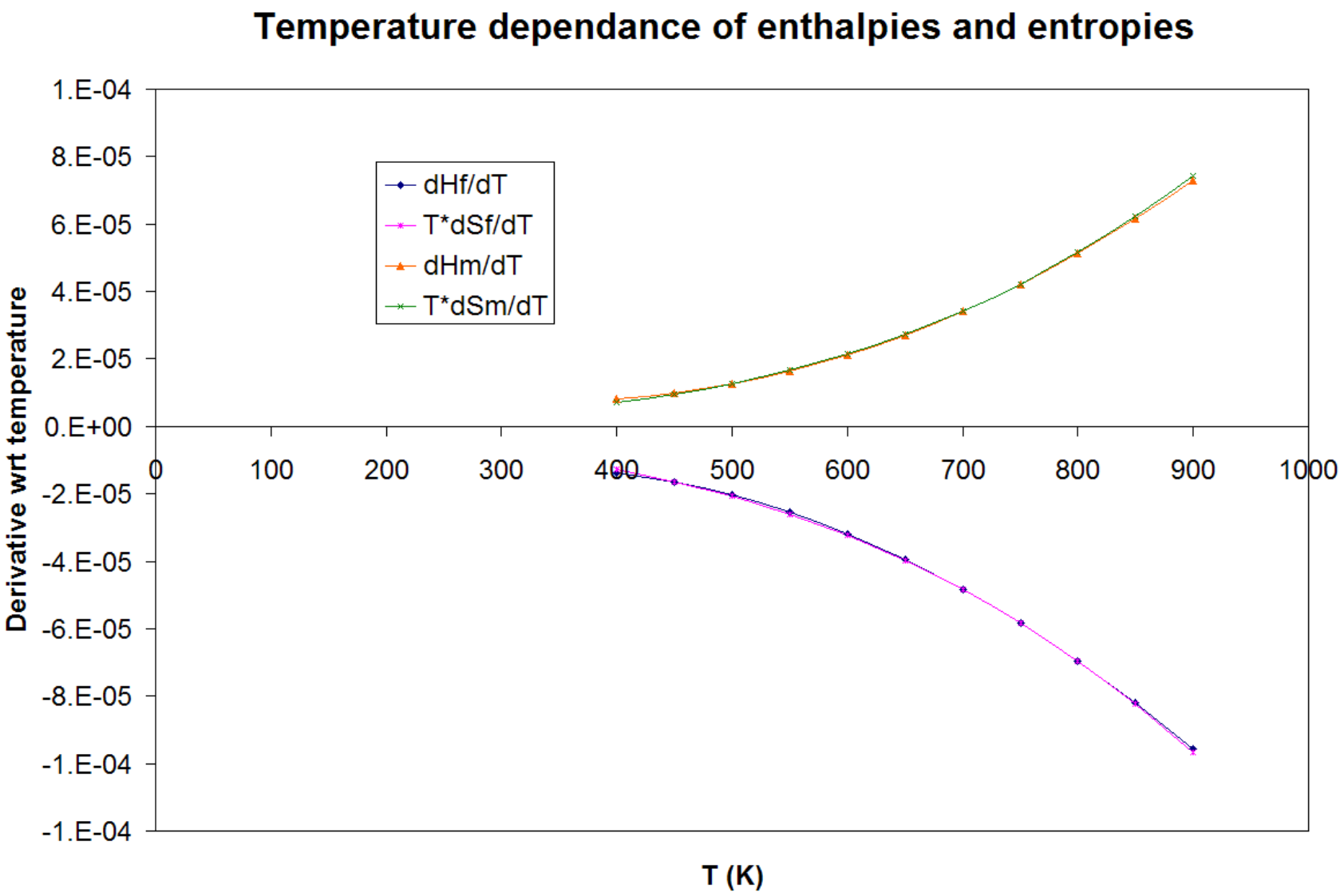
- Equations defining enthalpy and entropy

$$F(V,T) = E(V) + k_B T \sum_j \ln\left[2\sinh\left(\frac{h\nu_j(V)}{2k_B T}\right)\right]$$

$$S(V,T) = k_B \sum_j \left[\left(\frac{h\nu_j(V)}{2k_B T}\right)\coth\left(\frac{h\nu_j(V)}{2k_B T}\right) - \ln\left[2\sinh\left(\frac{h\nu_j(V)}{2k_B T}\right)\right]\right]$$

$$H(V,T) = F(V,T) + TS(V)$$

where the summation *j* is over all the vibrational degrees of freedom (DOF)


Temperature dependance of enthalpies and entropies
1.E-04
8.E-05
6.E-05
4.E-05
2.E-05
0.E+00
-2.E-05
-4.E-05
-6.E-05
-8.E-05
-1.E-04
-1.E-04
0
100
200
300
400
500
600
700
800
900
1000
dHf/dT
T*dSf/dT
dHm/dT
T*dSm/dT
Derivative wrt temperature
T (K)

# IMPURITY DIFFUSION RESULTS

| System | $\Delta H_f$ (eV) | $\Delta S_f$ ($k_B$) | $\Delta H_m$ (eV) | $\Delta S_m$ ($k_B$) | $\tilde{\nu}$ (THz) | $w$ (MHz) | $f$ | $D_0$ ($m^2/s$) | $Q$ (eV) |
|---|---|---|---|---|---|---|---|---|---|
| Pure Al | 0.706 | 1.20 | 0.58 | 2.28 | 2.26 | 1.08 | 0.78 | 8e-6 | 1.286 |
| Al-Mg | 0.743 | 1.57 | 0.42 | 2.74 | 1.54 | 66.6 | 0.17 | 1e-5 | 1.246 |
| Al-Si | 0.627 | 1.03 | 0.55 | 2.59 | 1.41 | 1.24 | 0.67 | 4e-6 | 1.154 |
| Al-Cu | 0.692 | 0.49 | 0.56 | 1.90 | 0.94 | 0.25 | 0.99 | 7e-6 | 1.239 |

- where $\tilde{\nu}$ is the frequency of vibration in the direction of diffusion, $w$ is the successful jump frequency, $f$ is the correlation factor.
- The quantities pertain to the diffusion of Al in the case of pure Al and diffusion of the impurity in the case of impurity-containing systems.
- The values listed are for T=400K

# PHYSICAL INTERPRETATION

- Migration barrier is smaller for larger impurity
  - Difference in strain at the initial and transition states is small for a large impurity [3]
- Activation barrier in the case of impurity diffusion also includes the term $d\ln f_2/dT$ ( $Q \neq \Delta H_f + \Delta H_m$ )

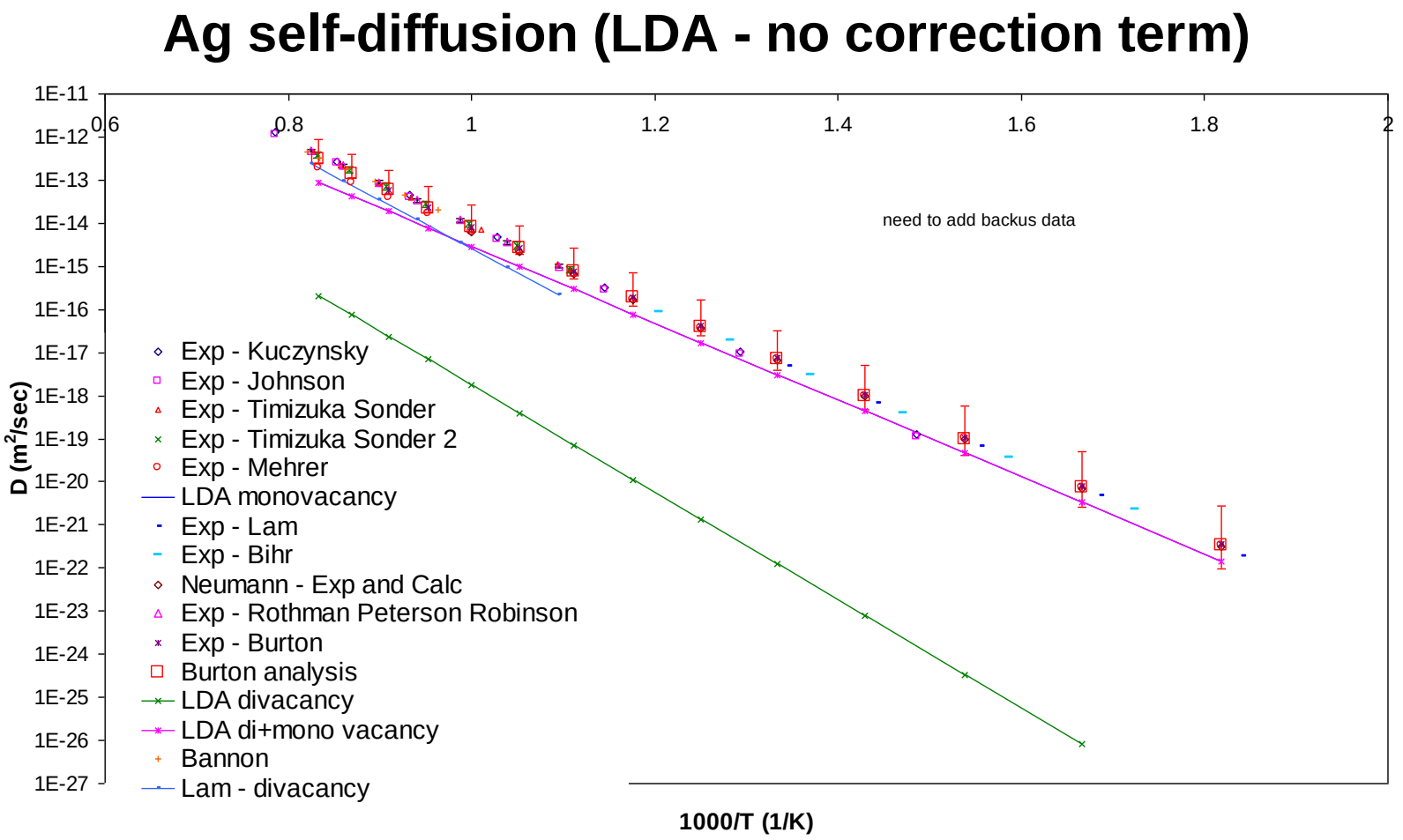
| System | $Q$ (eV) | $\Delta H_f + \Delta H_m$ | $d \ln f_2 / dT$ | $D_0$ ($m^2/s$) |
|---|---|---|---|---|
| Pure Al | 1.285 | 1.286 | 0 | 8e-6 |
| Al-Mg | 1.246 | 1.165 | 0.081 | 1e-5 |
| Al-Si | 1.154 | 1.178 | -0.024 | 4e-6 |
| Al-Cu | 1.239 | 1.252 | -0.013 | 7e-6 |

- From $D_0$ and Q values, we obtain $D_{Al\text{-}Si} > D_{Al\text{-}Mg} > D_{Al\text{-}Cu}$

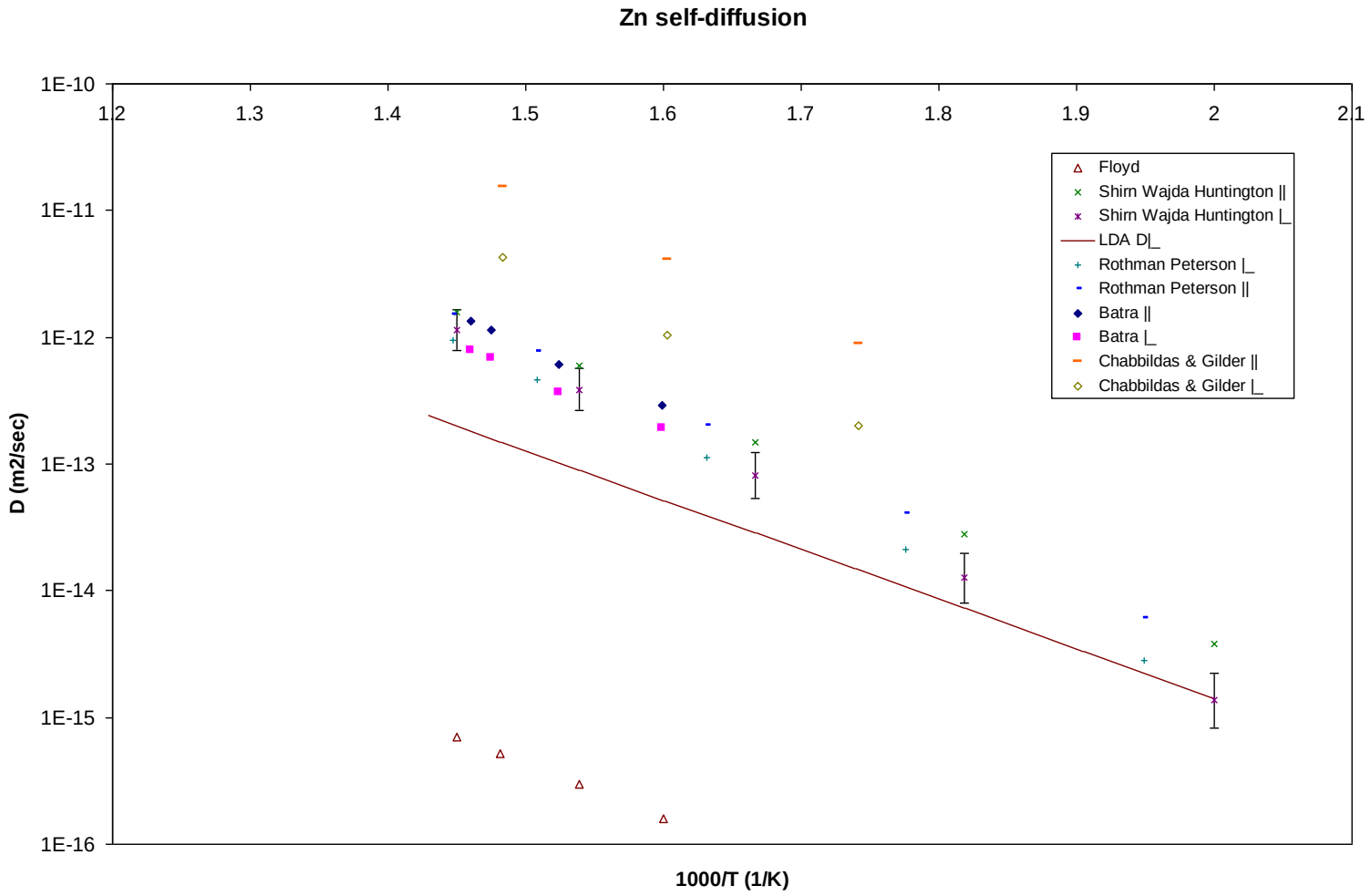
# PHYSICAL INTERPRETATION

- Interpretation of trends of the quantities involved in $D_0$ and Q for different diffusing species can be explained based on
  - Valency
  - Unscreened nuclear charge
  - Mass
  - Size

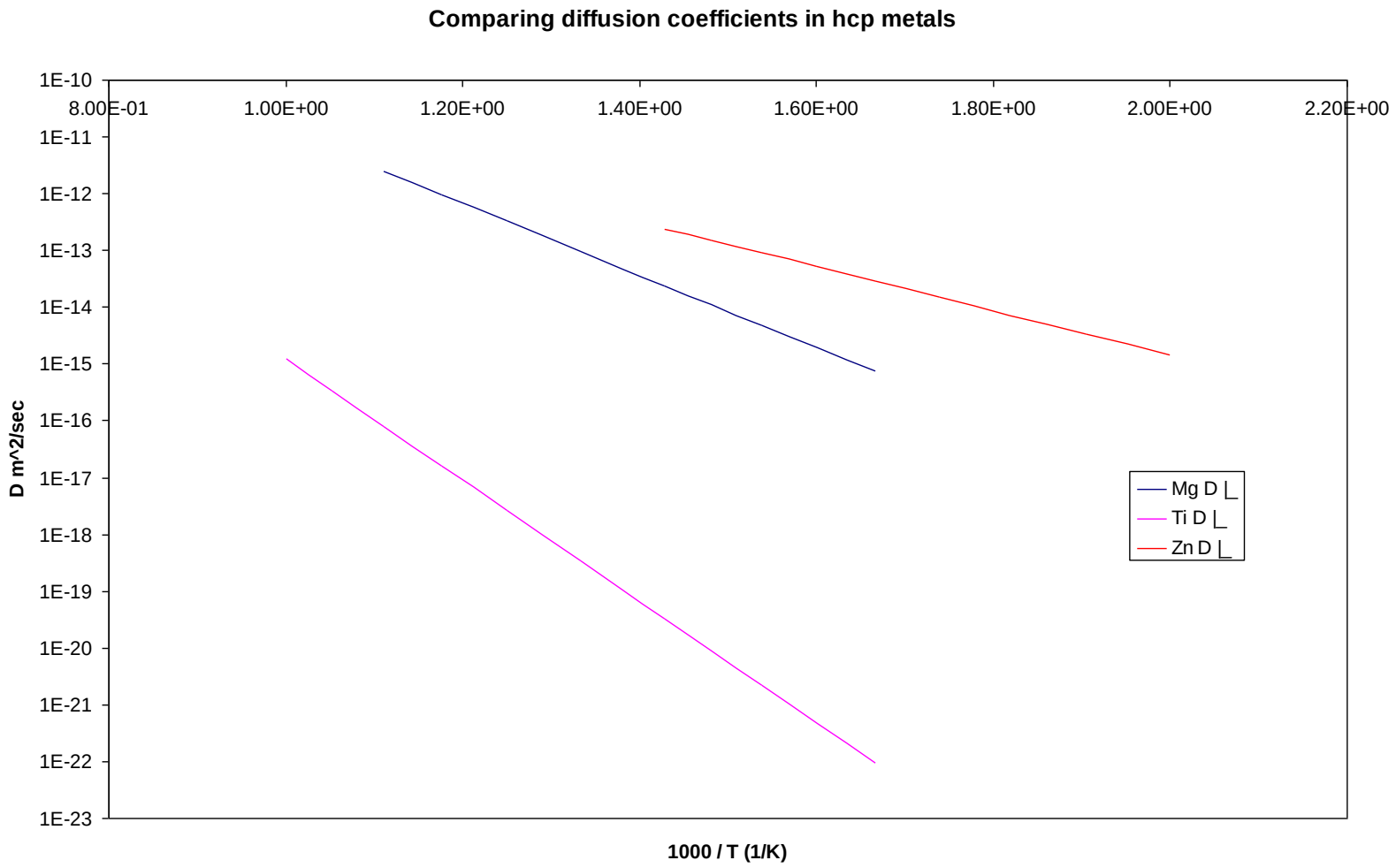
# Ag di-vacancy



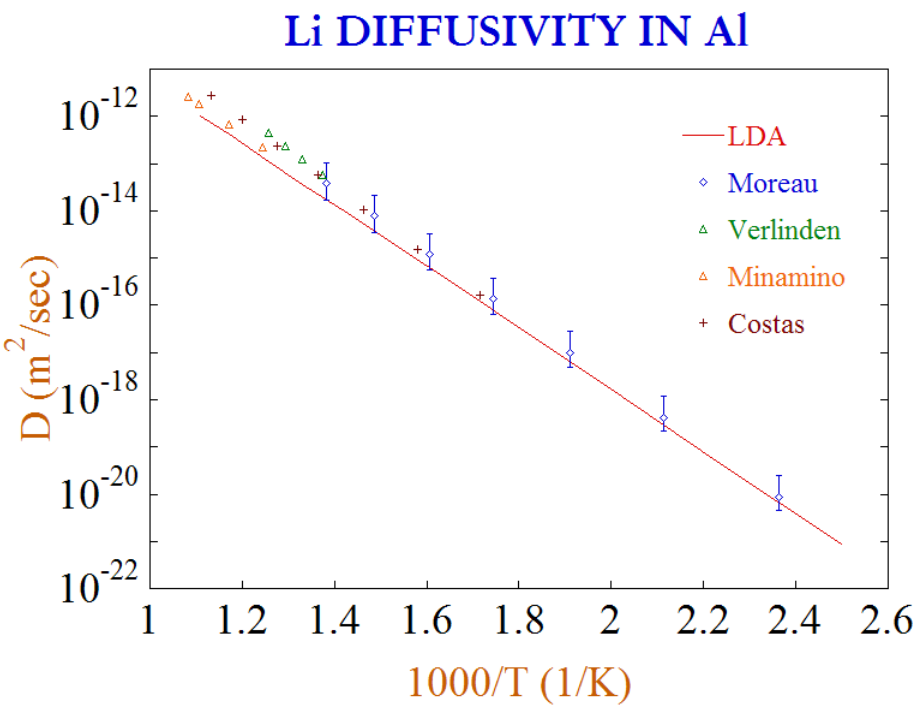
# Zn hcp

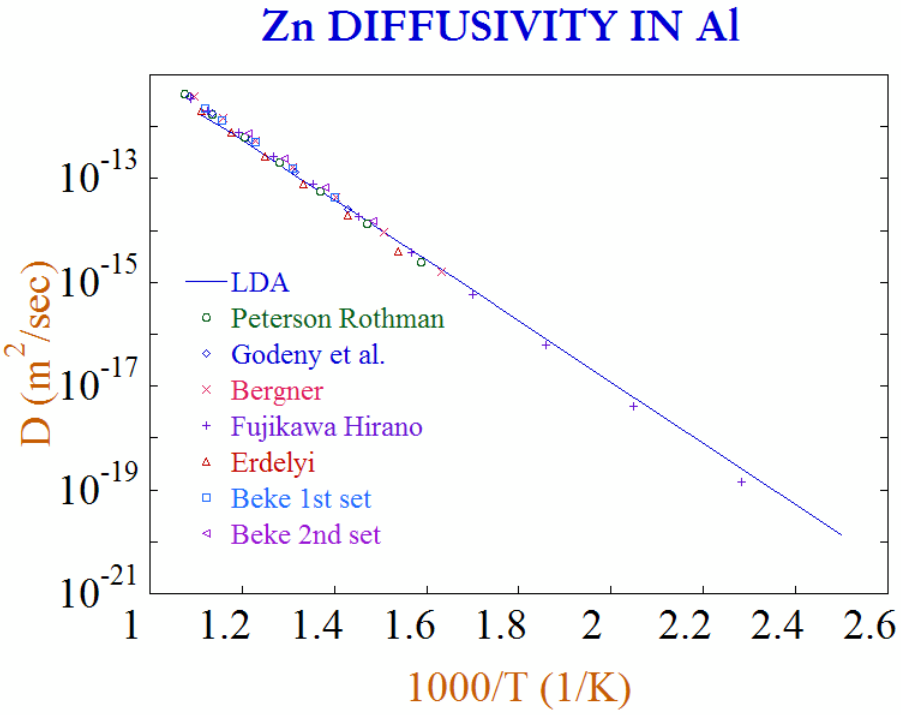

Zn self-diffusion
1E-10
1E-11
1E-12
1E-13
1E-14
1E-15
1E-16
D (m2/sec)
1.2
1.3
1.4
1.5
1.6
1.7
1.8
1.9
2
2.1
1000/T (1/K)
Floyd
Shim Wajda Huntington ||
Shim Wajda Huntington |_
LDA D|_
Rothman Peterson |_
Rothman Peterson ||
Batra ||
Batra |_
Chabbildas & Gilder ||
Chabbildas & Gilder |_

# HCP self-diffusion



# IMPURITY DIFFUSION RESULTS




**NO CORRECTION**