PHASES

PSU

First-principles calculations of diffusion coefficients in magnetic systems: Ni, Cr, and Ni-X alloys

Chelsey Zacherl, Shun-Li Shang, and Zi-Kui Liu

NIST Diffusion Workshop

May 4th, 2012

Acknowledgement: Office of Naval Research (ONR) under contract No. N0014-07-1-0638 and the Center for Computational Materials Design (CCMD), a joint National Science Foundation (NSF) Industry/University Cooperative Research Center at Penn State (IIP-1034965) and Georgia Tech (IIP-1034968).

PENNSTATE

1855

Outline

- Current challenges in diffusion by first-principles
- Ni self-diffusion (fcc)
  - Ferromagnetic calculations
- Cr self-diffusion (bcc)
  - Anti-ferromagnetic calculations
- Impurity diffusion in Ni-X binary alloys
  - 26 Ni-X systems
- Non-dilute diffusion in Ni-Al fcc system
- Summary and future work

Current challenges in calculating diffusion by first-principles

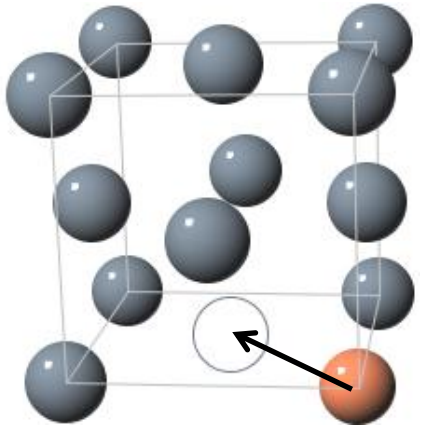
- Vibrational properties at the saddle point
  - SOLUTION: Eyring's reaction rate theory and Nudged-Elastic Band (NEB) method
- Experimental self-diffusion data for Ni, Cr exists above magnetic transition temperature
  - Calculations performed with magnetic ordering
- Effect of magnetic ordering and disordering such as in Ni and Ni alloys
  - Empirical magnetic terms
  - Partition function/quantum Monte Carlo approach

Self-diffusion in cubic systems

$$D = fa^2 C_V w$$

- Vacancy-mediated

  f – jump correlation factor
  a^2 – lattice parameter
  C – vacancy concentration
  w – atom jump frequency

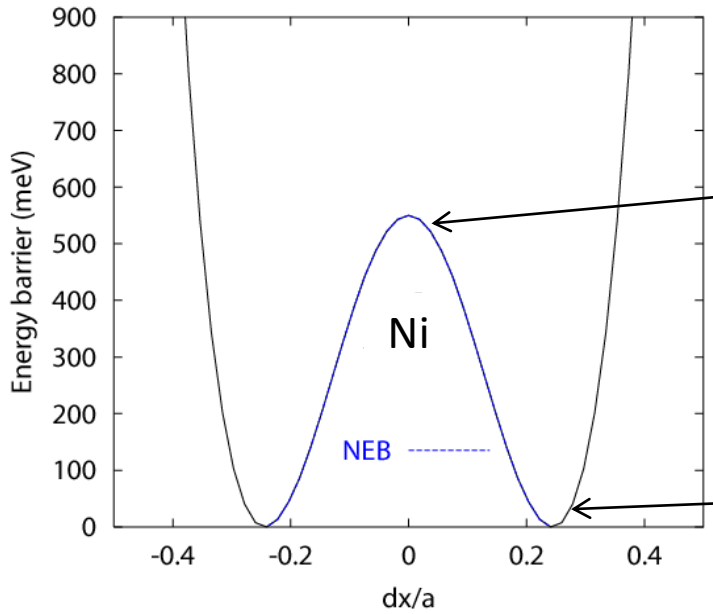


- In Arrhenius form: $D = D_0 \exp(-Q / k_B T)$

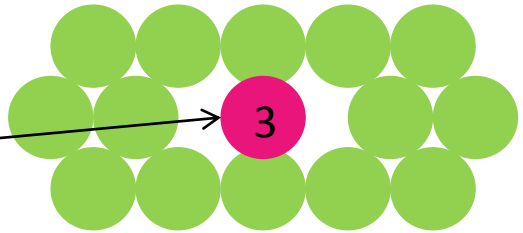
  D_0 – diffusion prefactor (intercept)
  Q – activation energy (slope)
  k_B – Boltzmann's constant

Mehrer, *Diffusion in Solids*, 2007

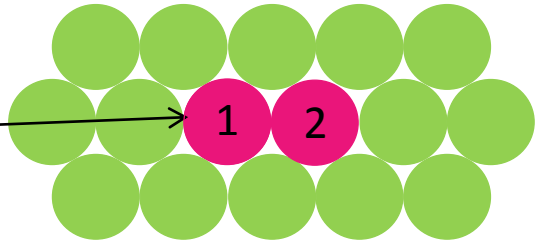
Vacancy mediated self-diffusion in fcc Ni: calculating the least energy diffusion path within Eyring's reaction rate theory



Saddle configuration



Initial vacancy configuration



Vacancy formation and migration:

$$C_V = exp\left(\frac{\Delta_f S}{k_B}\right) exp\left(-\frac{\Delta_f H}{k_B T}\right) \qquad w = \frac{k_B T}{h} exp\left(\frac{\Delta S_m}{k_B}\right) exp\left(\frac{\Delta H_m}{k_B T}\right)$$

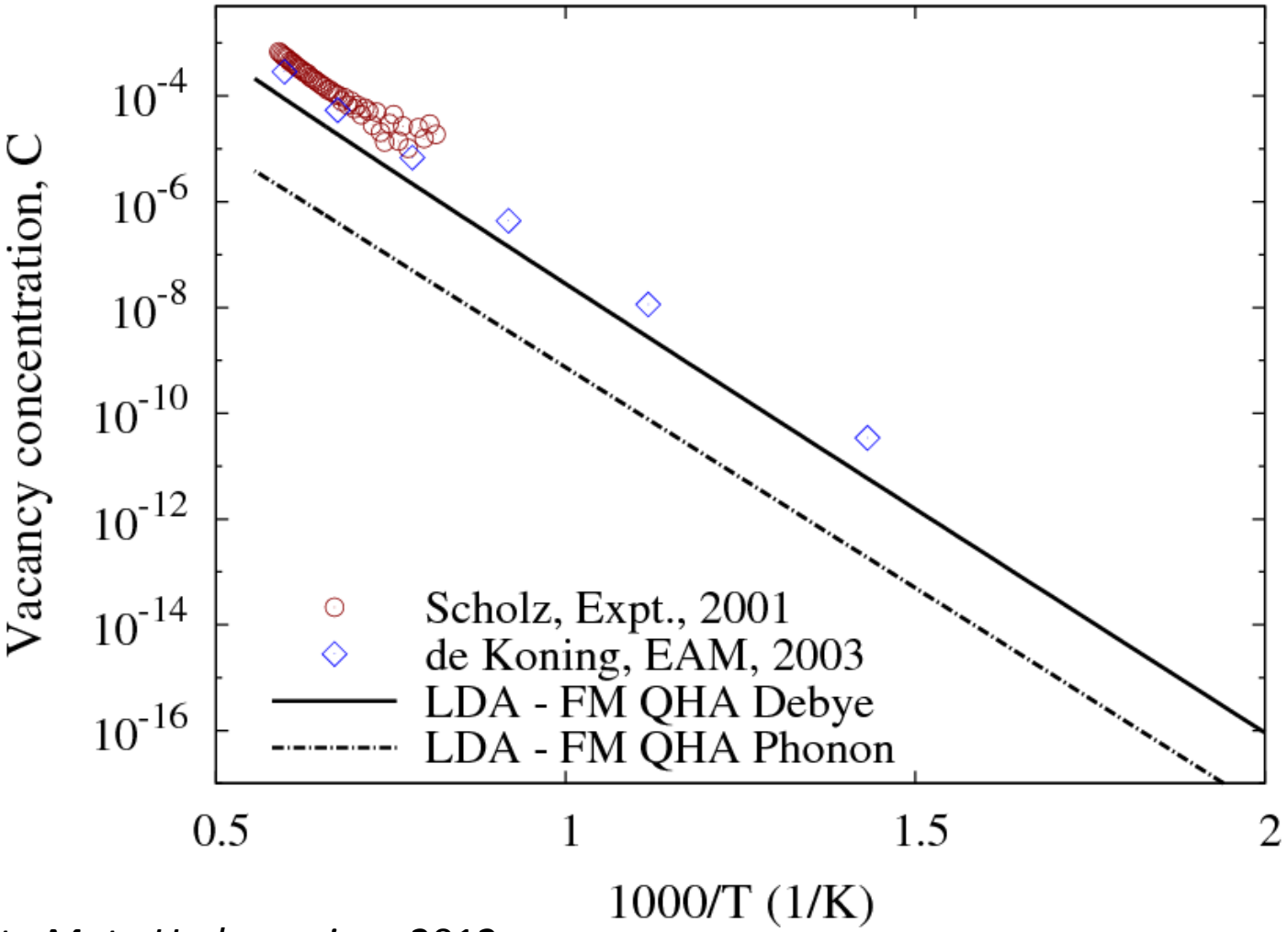
Mantina, PSU Dissertation, 2008

Eyring, *J. Chem. Phys.* 1935

Fcc Ni self-diffusion coefficients calculation input details

- Vienna *ab-inito* Simulation Package (VASP)
- Automated Theoretical Alloy Toolkit (ATAT) or Debye-Grüneisen model for finite temperature vibrational contribution
- 32-atom Ni supercell (2 x 2 x 2)
- Ferromagnetic spin on all atoms
- PAW-LDA
- Full relaxation of perfect and equilibrium vacancy configurations
- Nudged-Elastic Band (NEB) method for saddle point configurations
- No surface corrections used

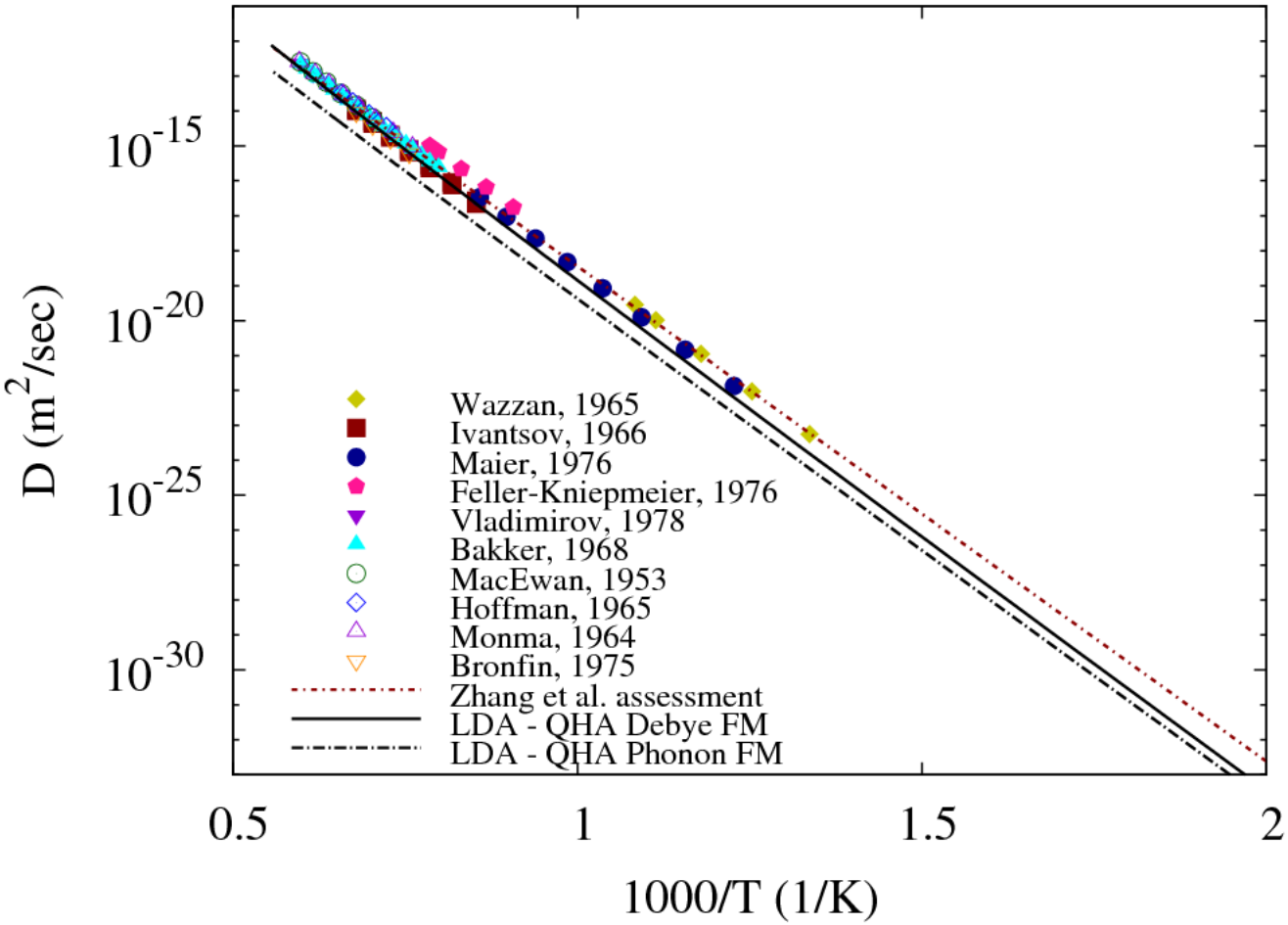
Underestimation of diffusion parameters compared to experiments is a consistent trend in the present work



Zacherl, *Acta Mat., Under review*, 2012

QHA Debye model approach yields better agreement with experiments than QHA phonon method

$$D = D_0 \exp(-Q / k_B T)$$



**Filled data points: Single-crystal

**Open data points: Poly-crystal

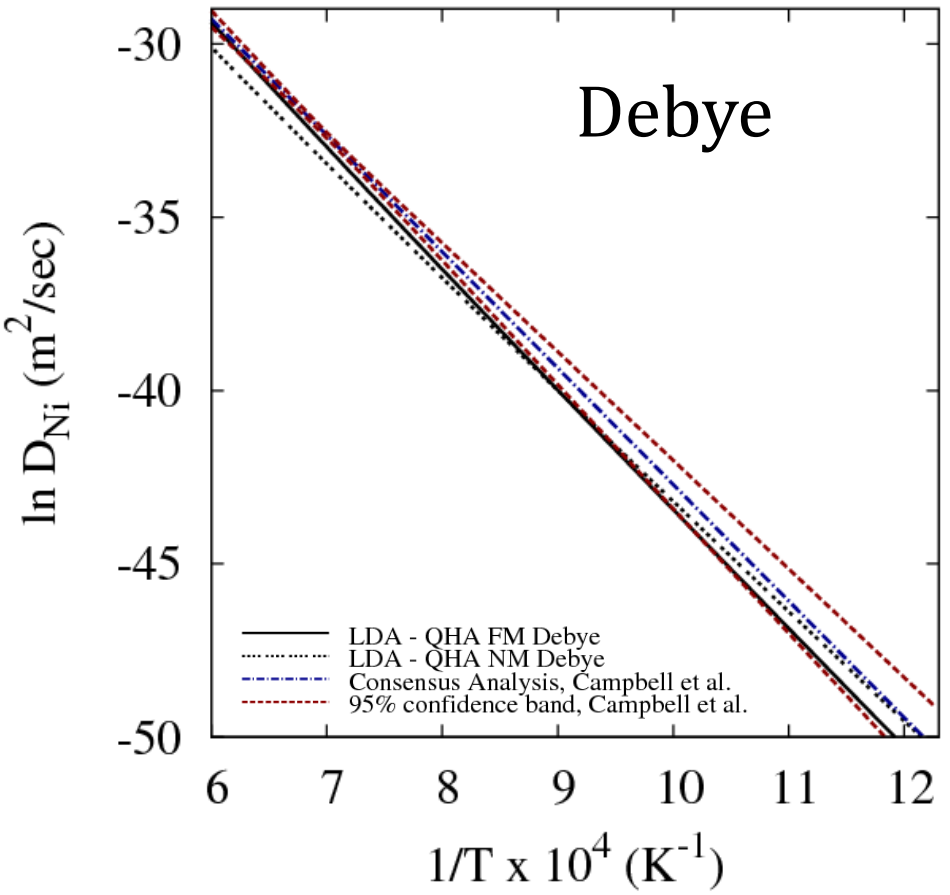
Zacherl, *Acta Mat., Under review*, 2012

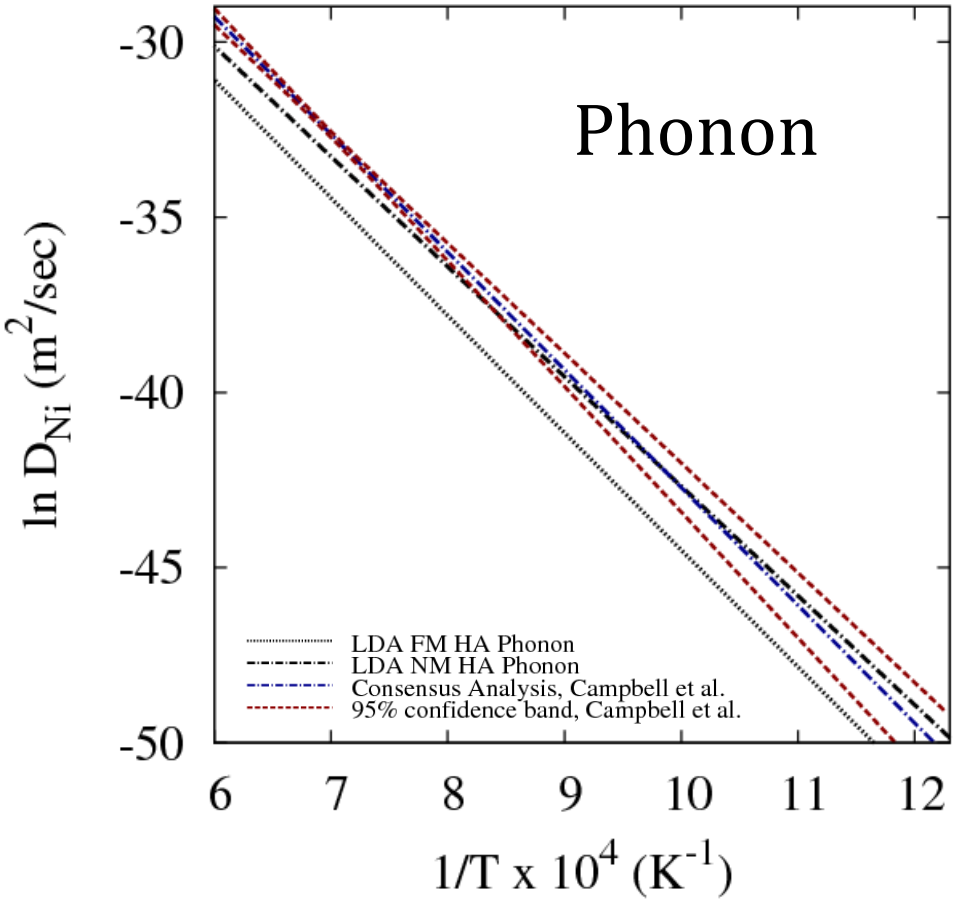
Tabulated data yields same results regarding QHA Debye vs QHA Phonon

Method	References	D_0 (m^2/sec)	Q (eV)	T (K)
DFT LDA QHA Debye (FM)	The present work	1.99×10^{-5} – 2.14×10^{-4}	2.85 – 3.03	700 - 1700
DFT LDA Debye QHA (NM)	The present work	5.27×10^{-6} – 3.92×10^{-5}	2.64 – 2.69	700 - 1700
DFT LDA QHA Phonon (FM)	The present work	3.90×10^{-6} – 8.98×10^{-6}	2.80 - 2.79	700 - 1700
DFT LDA HA Phonon (NM)	Mantina	7.00×10^{-6} – 7.09×10^{-6}	2.65 – 2.66	700 - 1700
Expt. (SC)	Bakker	1.77×10^{-4}	2.995	1253 - 1670
Expt. (SC)	Vladimirov	0.85×10^{-4}	2.87	1326 - 1673
Expt. (SC)	Maier	1.33×10^{-4}	2.91	815 - 1195

Zacherl, *Acta Mat., Under review*, 2012

Non-magnetic calculations show worse results than ferromagnetic calculations for both methods





Campbell, *Acta Materialia,* 2011

Thermodynamic properties of QHA FM LDA Debye compare well with experimental data

PHASES

PSU

Ferromagnetic

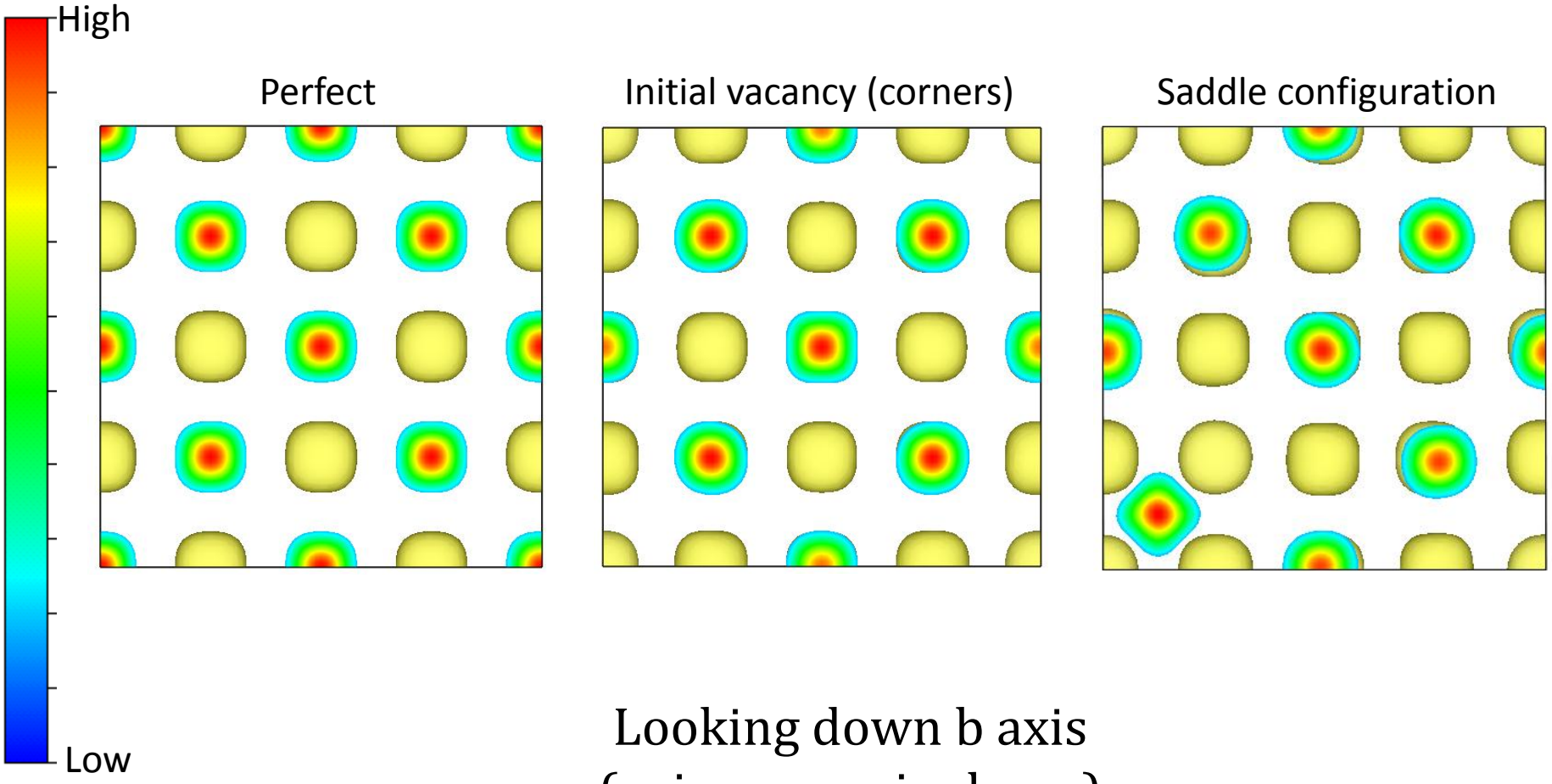
Thermodynamic Property	The present work, FM		The present work, NM		Other DFT study	Experiment
Temperature	700 K	1700 K	700 K	1700 K	0 K	1200 – 1650 K
ΔH_f (eV)	1.70	1.87	1.63	1.73	1.66 [57] 1.67 [58]	1.73[37] 1.79[54]
ΔS_f (k_B)	3.36	4.99	1.19	2.16	1.82 [11]	3.3 ± 0.05 [35]
ΔH_m (eV)	1.15	1.14	1.01	1.15	1.48 [57]	1.04 [37]

Nonmagnetic

Thermodynamic Property	The present work		Other DFT study	Experiment
Temperature	700 K	1700 K	0 K	1200 – 1650 K
ΔH_f (eV)	1.63	1.70	1.66 [48] 1.67 [49]	1.73 [35] 1.79 [46]
ΔS_f (k_B)	1.85	2.48	1.82 [10]	3.3 ± 0.05 [47]
ΔH_m (eV)	1.02	0.99	1.48 [48]	1.04 [35]

Zacherl, *Acta Mat., Under review*, 2012

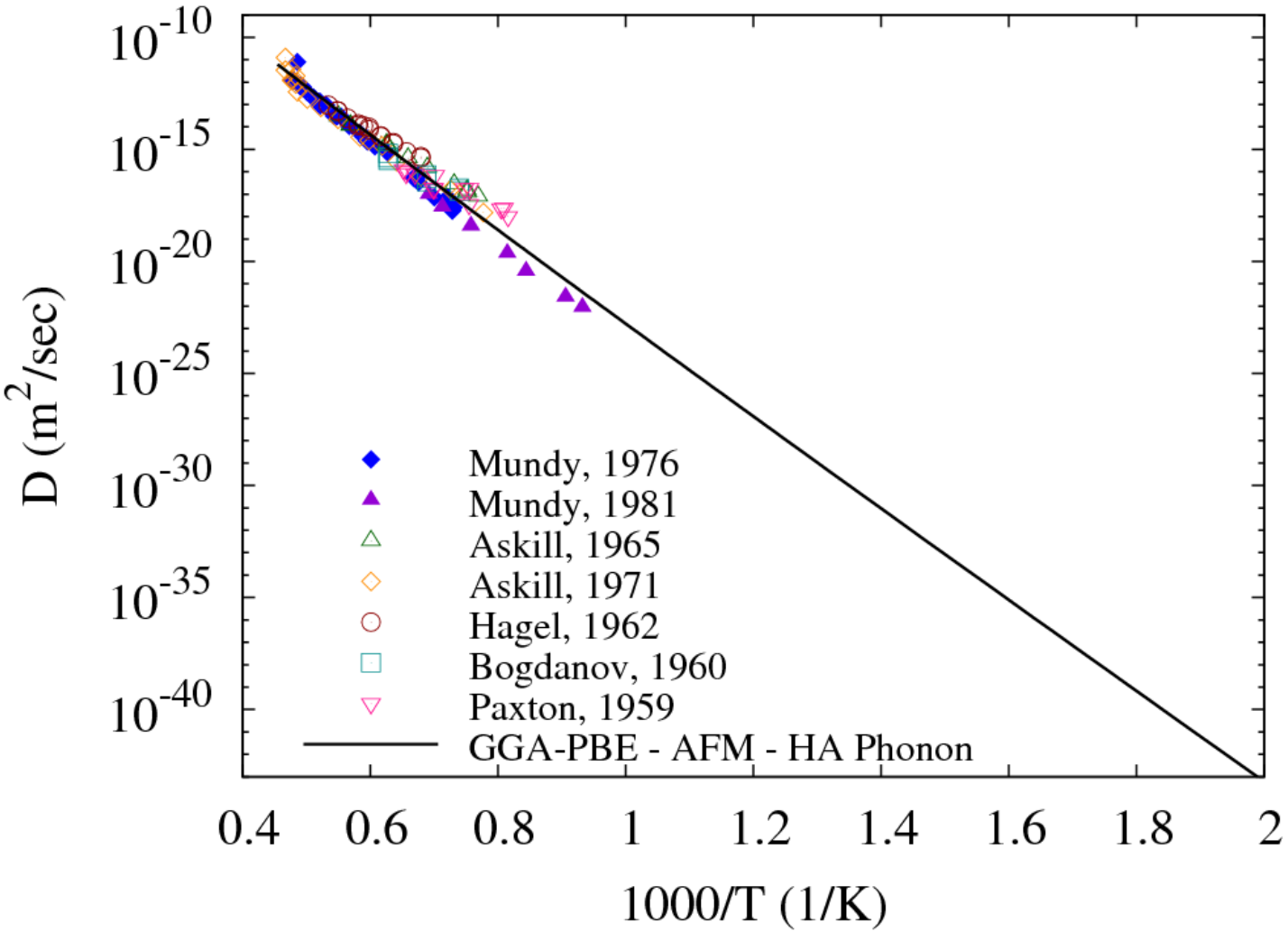
Magnetization charge density shows magnetic influence on thermodynamic properties



Looking down b axis
(spin up – spin down)

Zacherl, *Acta Mat., Under review*, 2012

Diffusion of bcc AFM Cr shows good agreement with single-crystal data



**Filled data points: Single-crystal

**Open data points: Poly-crystal

Arrhenius parameters of Cr self-diffusion

Method	References	$D_0 * 10^4$ (m^2/sec)	Q (eV)	T (K)
DFT PBE HA Phonon	The present work	41.20	4.05	1000
		145.8	4.11	2000
Expt: Single crystal	Mundy, 1976	970	4.51	1369-2093
Expt: Single crystal	Mundy, 1981	40	4.58	1073-1446

Conclusions from self-diffusion work in magnetic systems

- Magnetic effects are far reaching throughout supercell and affect thermodynamic properties
- Overestimation of energy of vacancy regardless of X-C functional used
  - Surface effect magnified by magnetic properties of fcc Ni
- Empiricism of the Debye model makes up for magnetic effects phonon is not representing
  - "double correction"

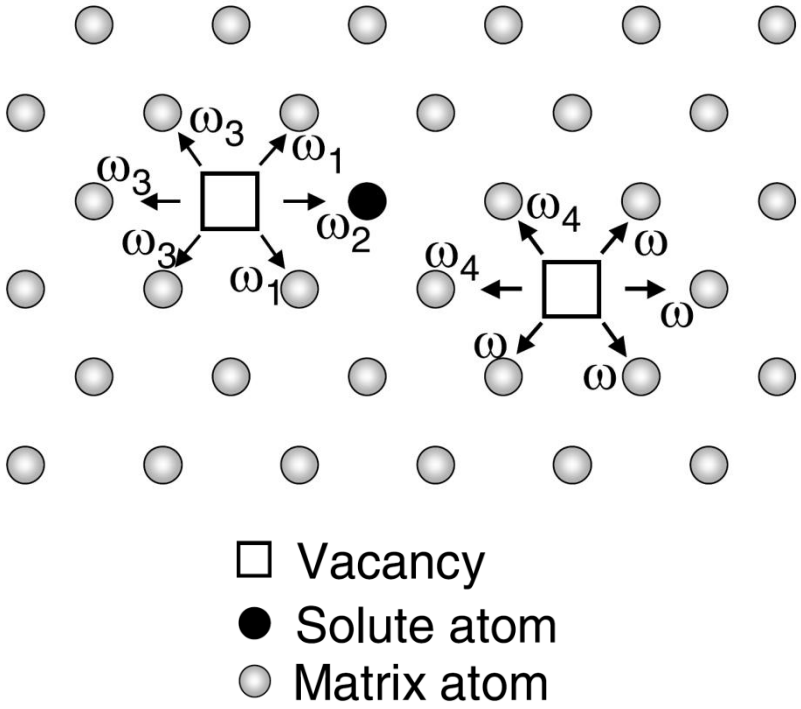
Dilute impurity diffusion in fcc ferromagnetic Ni-X alloys

										Al* 13	**Si*** 14
Sc 21	**Ti*** 22	**V*** 23	**Cr*** 24	**Mn*** 25	**Fe*** 26	**Co*** 27	**Ni** 28	**Cu*** 29	**Zn** 30		
Y 39	**Zr*** 40	**Nb*** 41	**Mo*** 42	**Tc** 43	**Ru** 44	**Rh** 45	**Pd** 46				
	Hf* 72	**Ta*** 73	**W*** 74	**Re** 75	**Os** 76	**Ir** 77	**Pt** 78				

* Experimental dilute impurity diffusion data

Approach: impurity diffusion in Ni-X determined from jump frequency of the impurity atom, w_2

- LeClaire and Lidiard's five frequency model



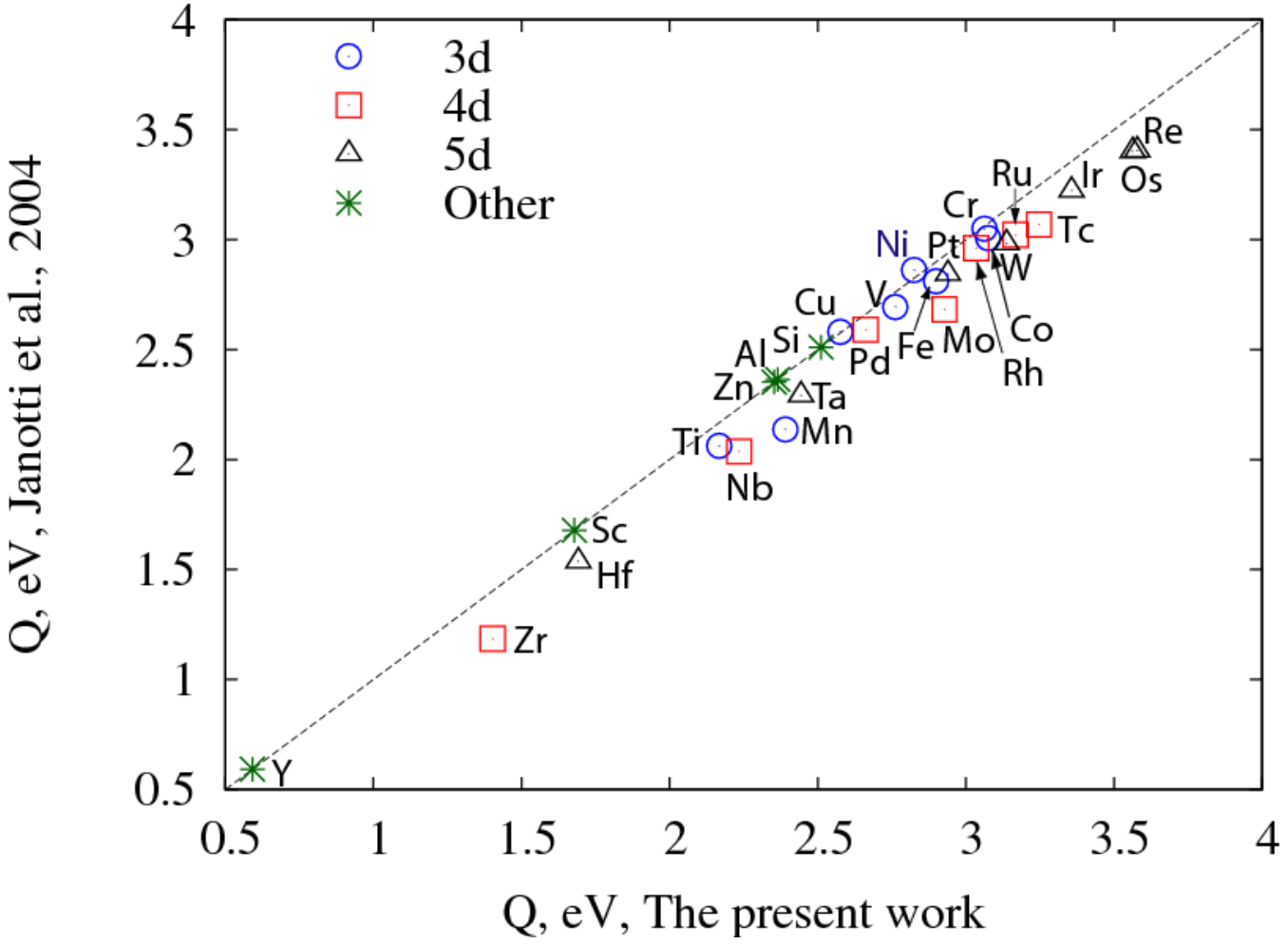
$$\frac{D_2}{D_0} = \frac{f_2}{f_0}\frac{w_2}{w_0}\frac{w_4}{w_3}$$

$$D_2 = f_2 a^2 C_2 w_2$$

Impurity correlation factor

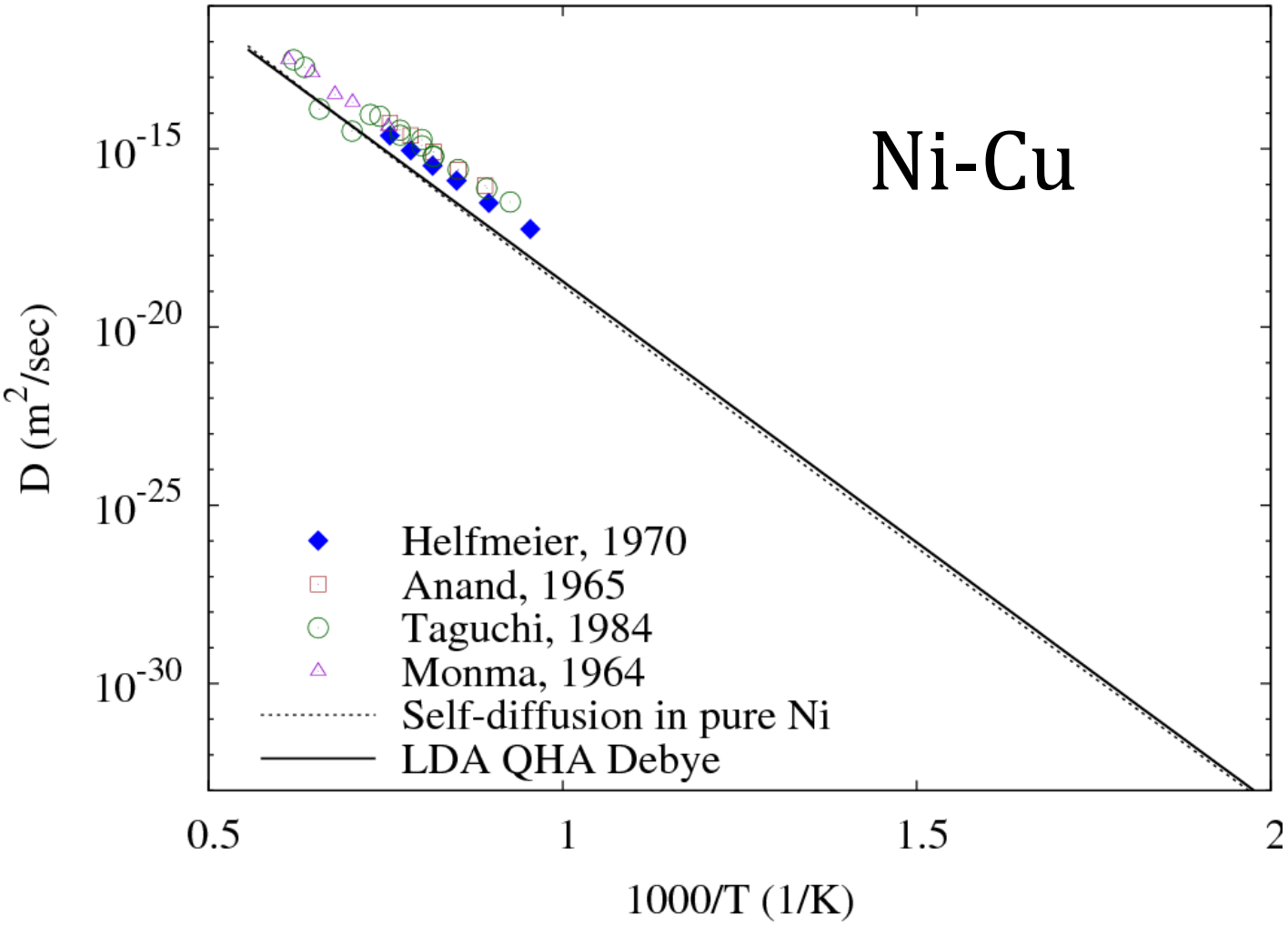
LeClaire, *Phil. Mag.*, 1956
Mehrer, *Diffusion in Solids*, 2007

Validation of methodology by comparing *Q*, activation barrier for diffusion to previous 0 K study



Janotti, *Physical Review Letters*, 2004

Test system: LDA QHA Debye model for vibrational contribution, no electronic used



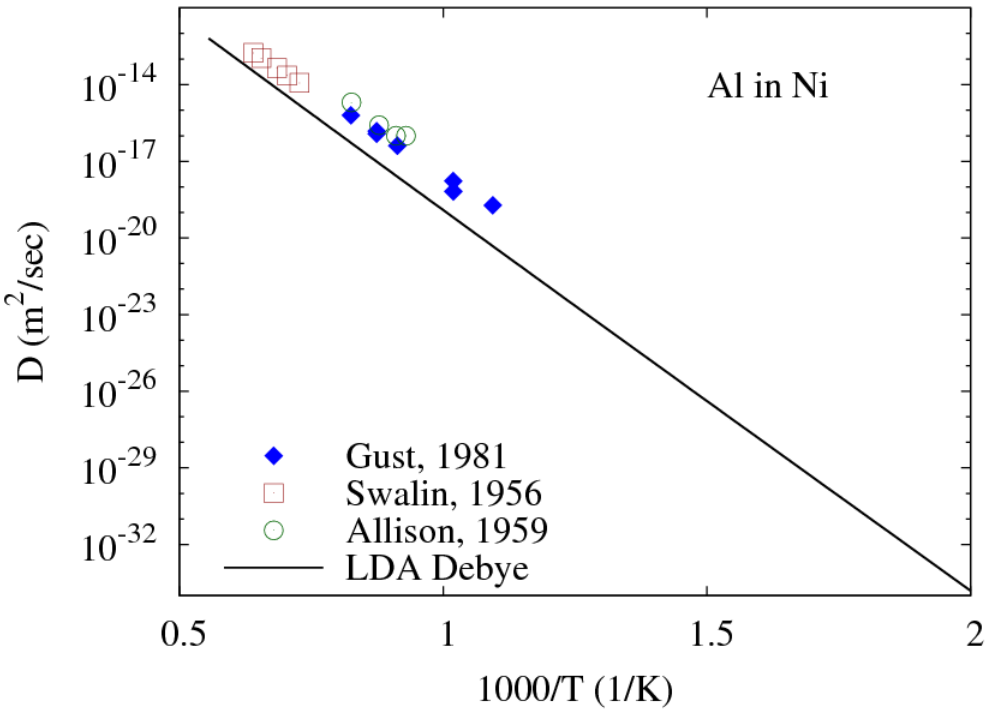
**Filled data points: Single-crystal

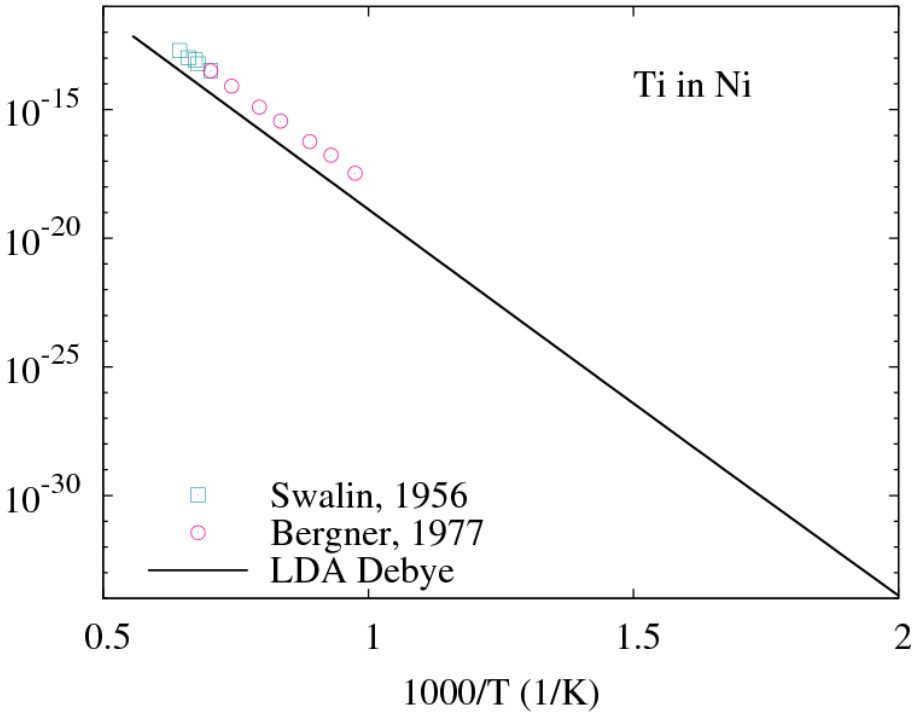
**Open data points: Poly-crystal

Arrhenius parameters including temperature dependence at all temperatures

	D_0 ($10^{-4}m^2/sec$)	Q (eV)	T (K)
This work – LDA Debye	0.004	2.58	700
	0.088	2.58	1700
Expt., Monma, 1964	0.57	2.676	1327 – 1632
Expt., Anand, 1965	0.66	2.645	1123 – 1323
Expt., Helfmeier, 1970	0.27	2.646	1048 – 1323
Expt, Taguchi, 1984	0.61	2.641	1080 – 1613

Results from selected impurity diffusion coefficient calculations

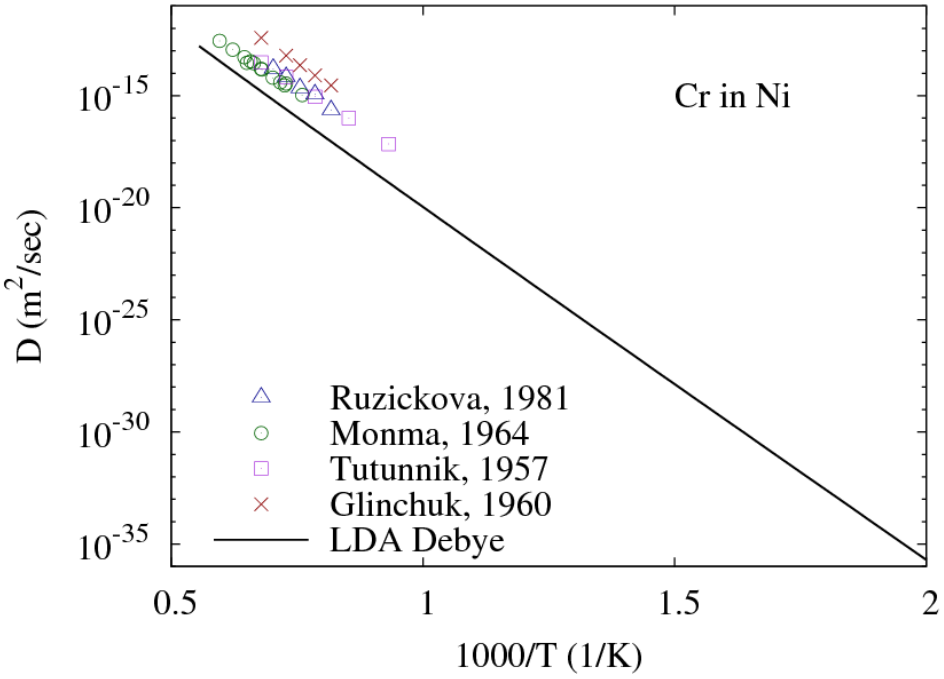


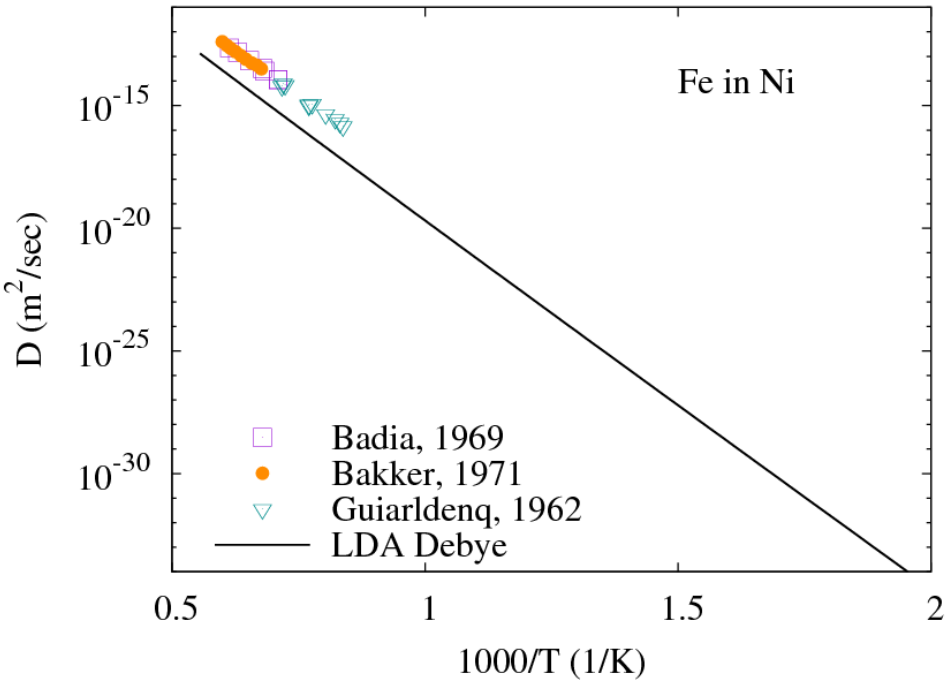


**Filled data points:
Single-crystal

**Open data points:
Poly-crystal

Results from selected impurity diffusion coefficient calculations

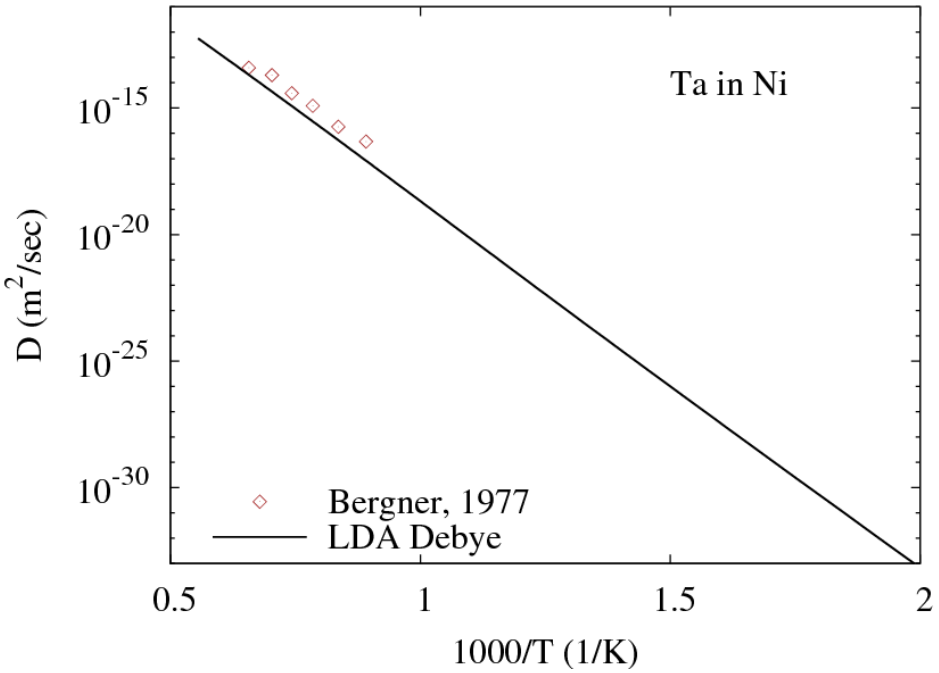


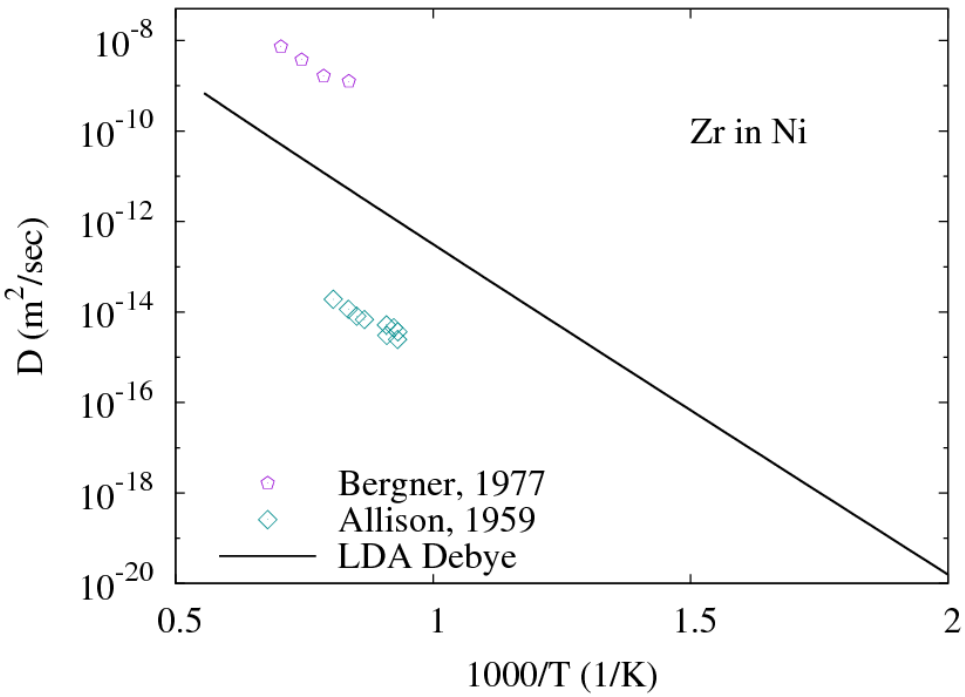


**Filled data points:
Single-crystal

**Open data points:
Poly-crystal

Results from selected impurity diffusion coefficient calculations





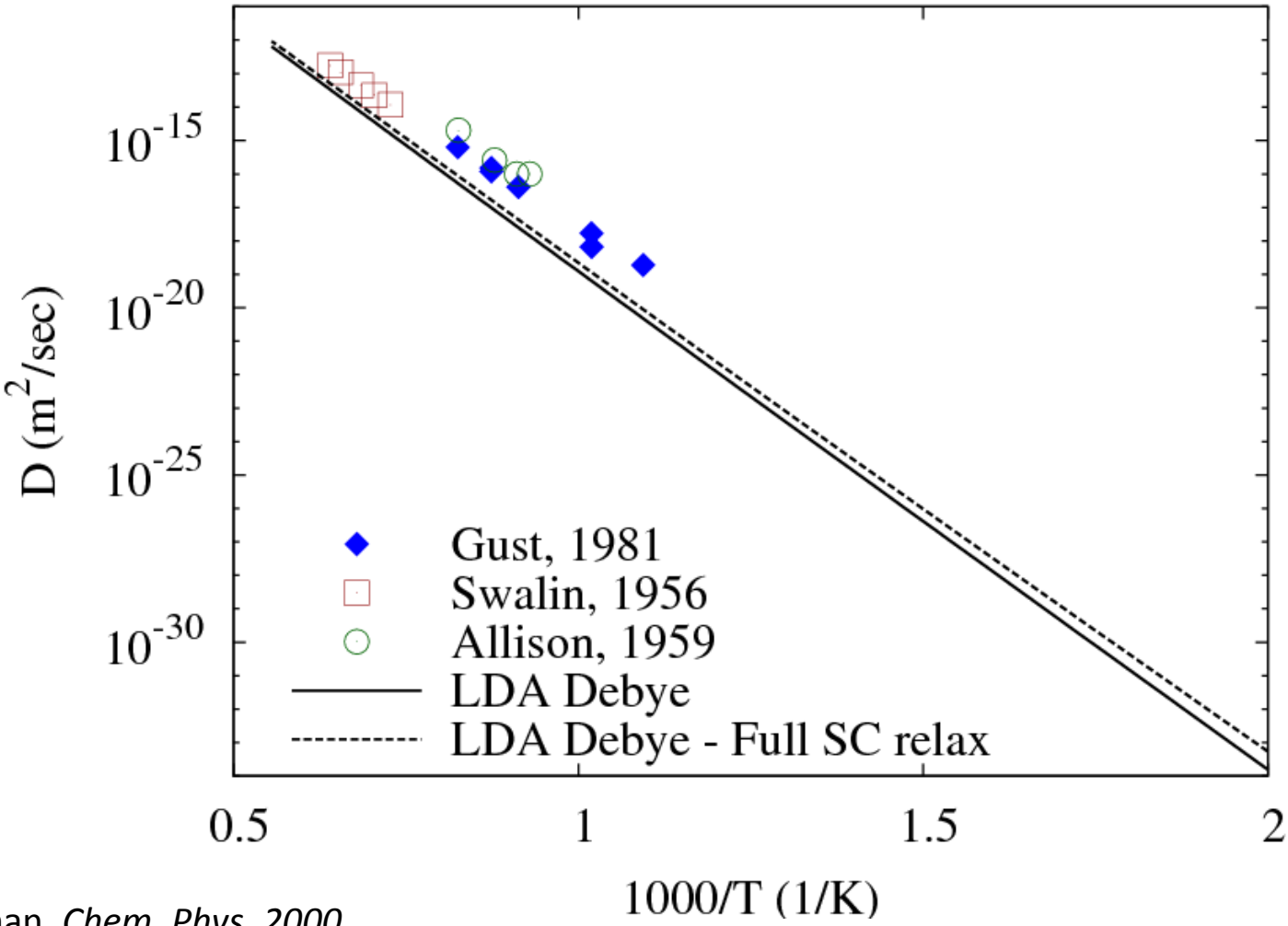
**Filled data points:
Single-crystal

**Open data points:
Poly-crystal

Comments on the Ni-X impurity diffusion results

- Underestimation of one order of magnitude compared to experimental data is consistent for all systems shown
  - Affecting activation barrier for diffusion, Q and diffusion prefactor, D_0
  - Partially attributed to lack of complete relaxation of the three transition states in VASP
- Lingering question:
  - How to analyze data from 26 systems
  - Charge density

Full relaxation in VASP 5 using ss-CINEB TST tools from UT Austin shows slight correction at lower temperatures

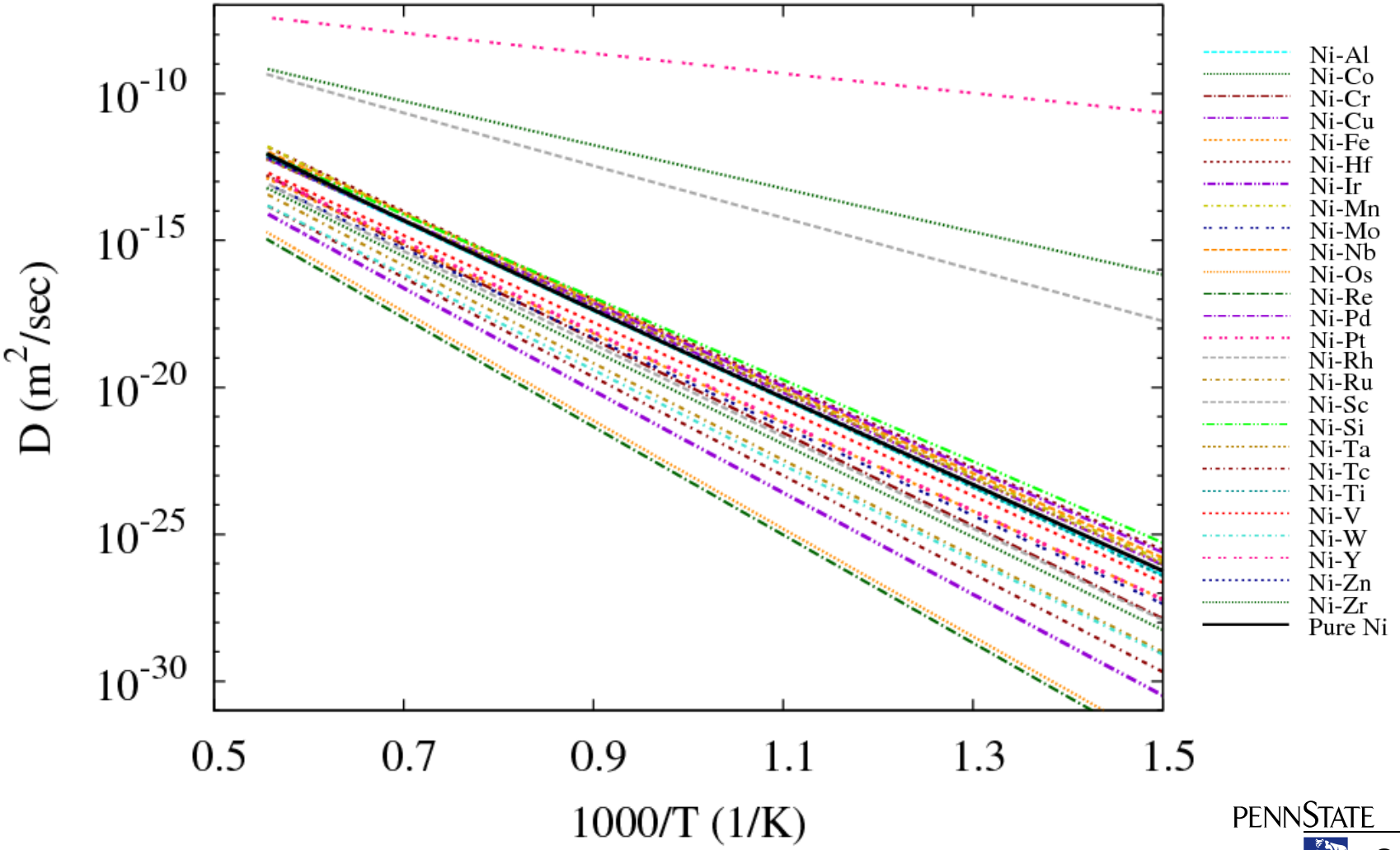


**Filled data points: Single-crystal

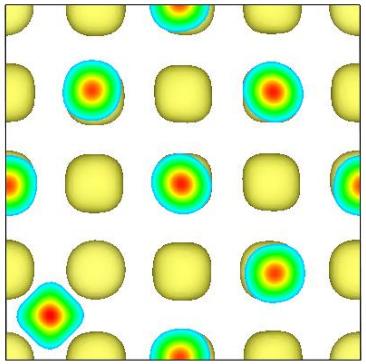
**Open data points: Poly-crystal

Henkelman, *Chem. Phys. 2000*

How can we provide understanding of the effects of each X on the impurity diffusion coefficient?



Relative charge density analysis of Ni-Re compared to that of pure Ni



Pure Ni: Saddle configuration

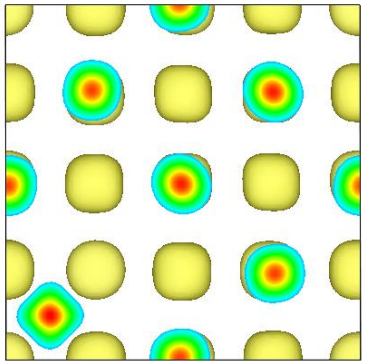
a axis

b axis

c axis

(spin up – spin down)

Relative charge density analysis of Ni-Y compared to that of pure Ni



Pure Ni: Saddle configuration

a axis

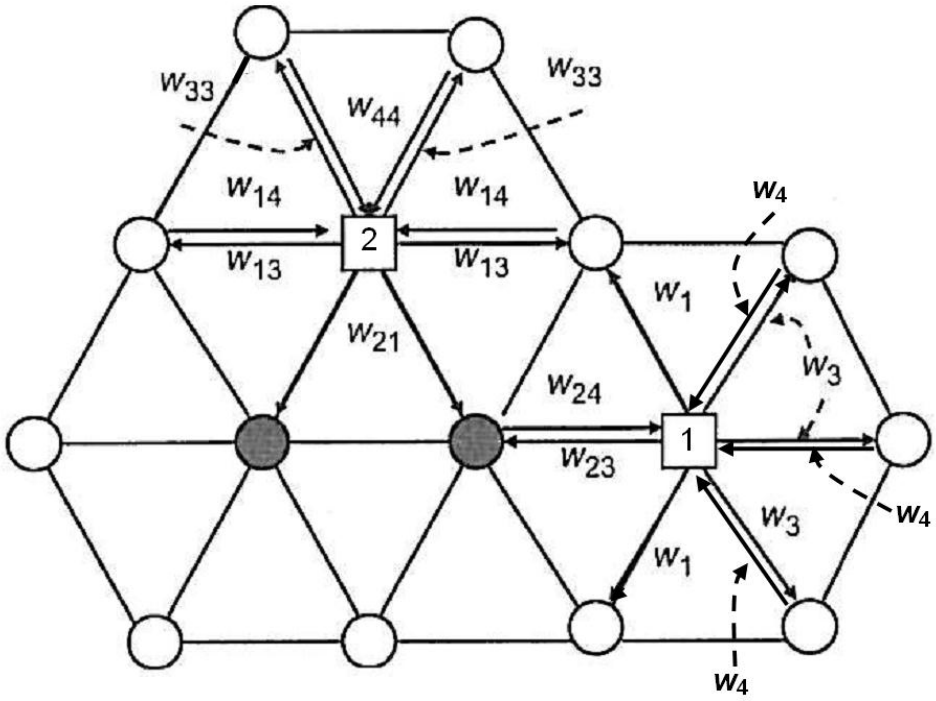
b axis

c axis

(spin up – spin down)

Additional challenge: non-dilute impurity diffusion of Al in fcc FM Ni

- Bocquet's 14 frequency model to predict all possible vacancy interactions with lone or paired solute atoms
- LeClaire's 5 frequency model for lone solute atom – vacancy interactions



Open circle: solvent
Filled circle: solute
Square: vacancy

Bocquet, Report: CEA-R-4292, 1972
Le Claire, J. Nuclear Mater. 69-70(1978) 70

14 Frequency model

- Calculations completed for Ni-Al system
  - 30 Ni atoms and 2 Al atoms
  - Solvent enhancement factor, b_1
  - Solute enhancement factor, B_1
  - Isotope effect measurement, E

$$b_1 = -18 + \frac{w_4}{w}\left[4\frac{c_1}{f}\frac{w_1}{w_3} + 14\frac{c_2}{f}\right]$$

$$B_1 = -6 - 12\exp\left(-\frac{\Delta g_p}{kT}\right) + \left[4\frac{w_{21}}{w_2}\exp\left(-\frac{\Delta g_p}{kT}\right) + 14\frac{w_{23}}{w_2}\right]\exp\left(-\frac{\Delta g_1}{kT}\right)$$

$$E = \frac{\left(D^a / D^b\right) - 1}{\left(m^b / m^a\right)^{1/2} - 1}$$

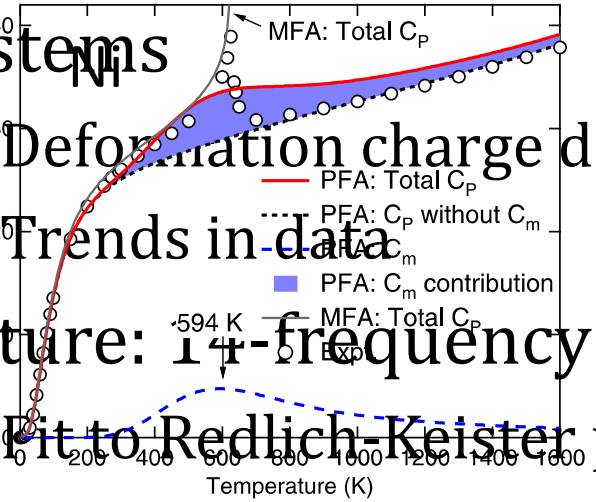
- Current progress:
  - Empirical relation for impurity diffusion coefficient dependent on concentration:

$$D_2(c) = D_0(c)(1 + B_1 c + B_2 c^2 + \ldots)$$

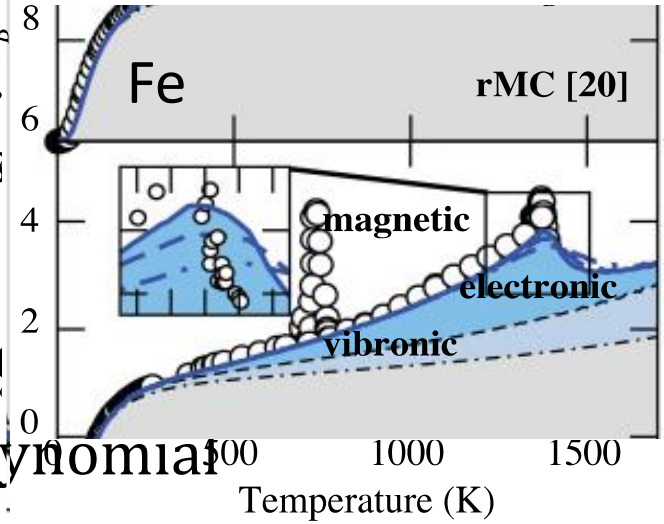
LeClaire, *Journal of Nuclear Materials*, 1978

Conclusions and future work for this project

- All calculations: limitations of magnetic model in comparison to experimental data
  - Did not include transition effects; shown to be less for Ni than other elements like Co or Fe
  - Debye vs. Phonon methods
- Impurity diffusion coefficient for 26 FM Ni-X alloy systems
  - Deformation charge dens
  - Trends in data
- Future: 14-frequency m
  - Fit to Redlich-Keister polynomial



Shang, *J. Appl. Phys.*, 2010



Kormann, *PRB*, 2011

PHASES

PSU

Thank you!

															Al 3.87	Si 3.32	
Sc 29.2	Ti 6.15	V 1.80	Cr 6.04	Mn 4.45	Fe 4.52	Co 7.97	Ni 0.00	Cu 2.14	Zn 4.68								
Y 54.0	Zr 34.1	Nb 9.96	Mo 5.16	Tc 13.2	Ru 10.5	Rh 6.67	Pd 2.74										
	Hf 18.2	Ta 5.84	W 11.6	Re 23.0	Os 21.9	Ir 15.9	Pt 4.19										

Phonon calculations

- Based on the partition function of lattice vibrations, we have the phonon frequency as a function, $g(\omega)$

$$F_{vib}(V,T) = k_B T \int_0^{\infty} \ln\left[2\sinh \frac{\hbar\omega}{2k_B T} \right] g(\omega) d\omega$$

Phonon frequency

Phonon density of states

Shang, Acta. Mat., 2005

Wang, Acta. Mat., 2004

Debye-Grüneisen Model

- Speed of sound is constant in a material
- Linear density of states

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

Zero-point energy from lattice vibrations

Debye function:

$$D(x) = \frac{3}{x^3}\int_0^x \frac{z^3 dz}{e^z - 1}$$

Debye - Grüneisen model for finding $\theta(D)$ and solving above equation:

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

Grüneisen constant

$$\gamma = \frac{1}{2}(1 + B_0') - x$$

Shang, Comp. Mat. Sci., 2010

Moruzzi, Phys. Rev. B., 1988

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

35

Fcc Ni self-diffusion coefficients calculation input details

- Vienna *ab-inito* Simulation Package (VASP)
- Automated Theoretical Alloy Toolkit (ATAT) or Debye-Grüneisen model for vibrational contribution
- 32-atom Ni supercell (2 x 2 x 2)
- Ferromagnetic spin on all atoms
- PAW-LDA or PAW-PBEsol
- Full relaxation of perfect, and equilibrium vacancy configurations
- Nudged-Elastic Band (NEB) method for saddle point configurations

Diffusion coefficient equations

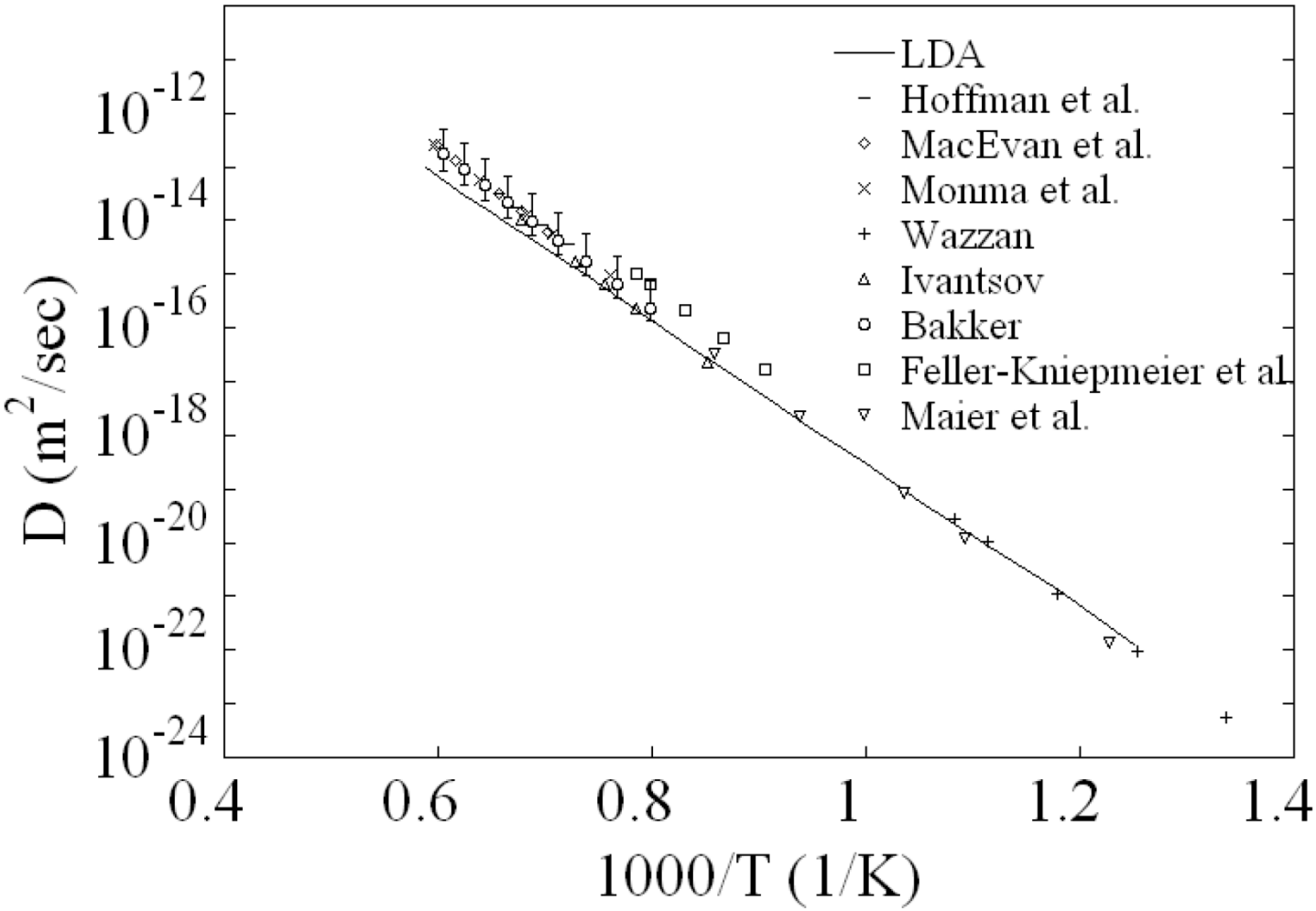
$$D = D_0 \exp(-Q / k_B T)$$

$$D_0 = \frac{k_B T}{h} f a^2 \exp\left(\frac{S^*_{SC} - {}^{31}\!/_{32} S_{PS}}{k_B} \right) \qquad Q = H^*_{SC} - {}^{31}\!/_{32} H_{PS}$$

$$D = f a^2 C_V w$$

Mantina, Defect and Diffusion Forum, 2009

Ni NM diffusion coefficient by harmonic phonon calculations



Mantina, *PhD. Thesis, Penn State University*, 2008

bcc Cr self-diffusion coefficients calculation input details

- Vienna *ab-inito* Simulation Package (VASP)
- Debye-Grüneisen model for vibrational contribution
- 54-atom Cr supercell (2-atom bcc base)
  - Spin of +/- 1.06 μ_B/atom
- Anti-ferromagnetic spin
- PAW-GGA-PBE
- Full relaxation of perfect and equilibrium vacancy configurations
- Nudged-Elastic Band (NEB) method for saddle point configurations
  - Full relaxation

Impurity diffusion coefficient calculation input details

- Vienna *ab-inito* Simulation Package (VASP)
- 32 atom, supercell, N-2 Ni atoms, 1 impurity, 1 vacancy → 8 total configurations
- Ferromagnetic spin on all atoms
- PAW-LDA
- Full relaxation of perfect, and equilibrium vacancy configurations
- NEB or Climbing Image Nudged-Elastic Band (CINEB) method for saddle point configurations
  - Relax only ionic positions
- Debye model for vibrational contribution

Impurity diffusion coefficient determined from the jump frequency of the impurity atom, w_2

- Equation for impurity diffusion is related to tracer diffusion:

$$\frac{D_2}{D_0} = \frac{f_2}{f_0}\frac{w_2}{w_0}\frac{w_4}{w_3} \qquad D_2 = f_2 a^2 C_2 w_2$$

- With vacancy concentration and jump frequency:

$$C_2 = \exp\left(-\frac{\Delta G_f - \Delta G_b}{k_B T}\right) \qquad w_2 = \frac{k_B T}{h}\exp\left(-\frac{\Delta G_{TS}^{w_2} - \Delta G_{IS}^{w_2}}{k_B T}\right)$$

- And the binding energy with impurity, X, and vacancy, V:

$$-\Delta G_b(X-V) = G(Ni_{N-2}X_1V_1) + G(Ni_N) - G(Ni_{N-1}X_1) - G(Ni_{N-1}V_1)$$

LeClaire, *J. Nuclear Matls*, 1978

Wolverton, *Acta Mat.*, 2007

Calculation of the impurity correlation factor, f_2, involves calculating all five jump frequencies

- f_2 is related to the probability of the impurity atom making the reverse jump back to its previous position

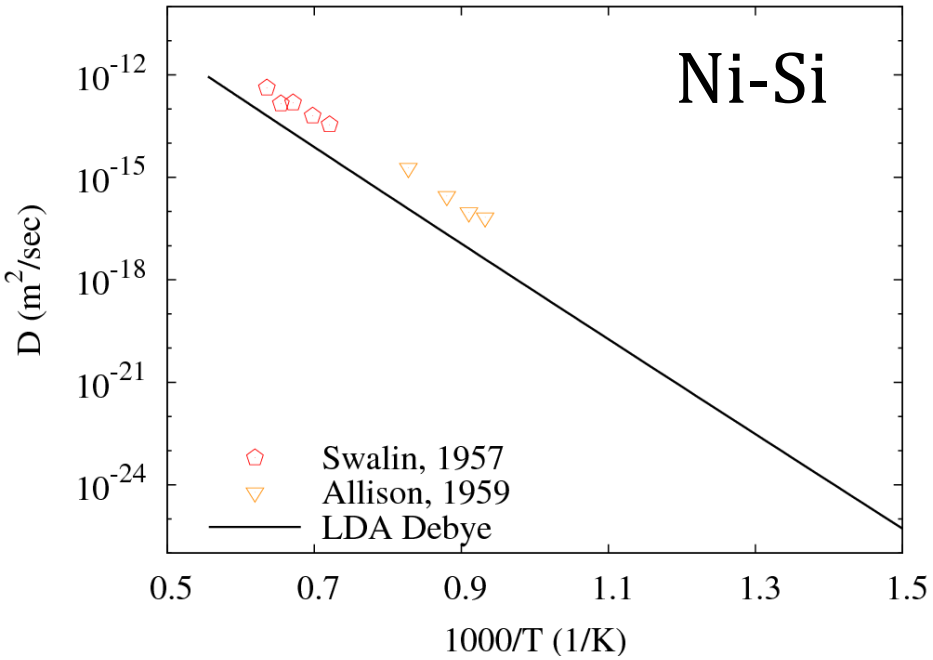
$$f_2 = \frac{1 + 3.5(w_3/w_1)F(w_4/w_0)}{1 + (w_2/w_1) + 3.5(w_3/w_1)F(w_4/w_0)}$$

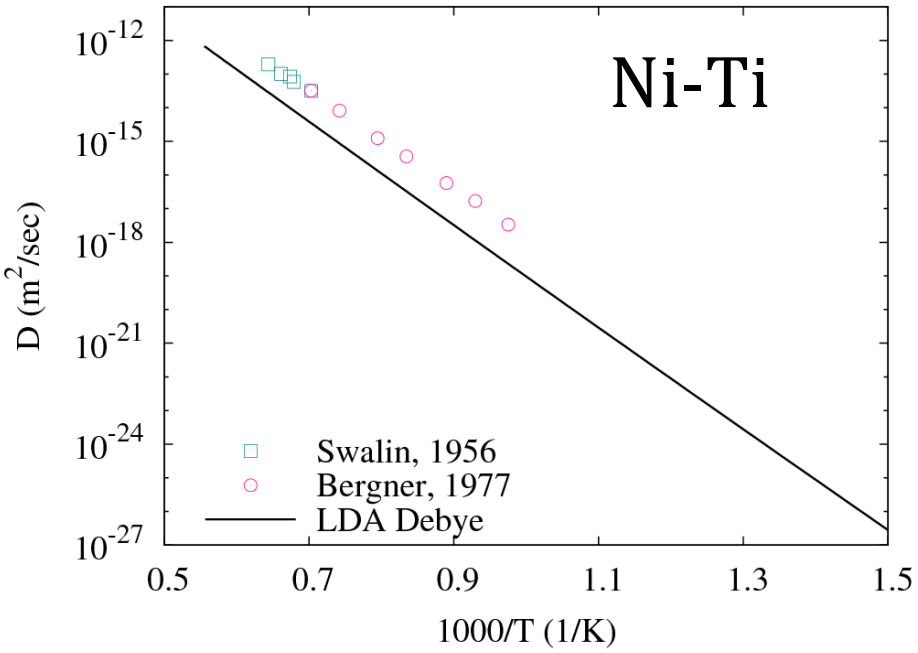
- Where F is the "escape probability" that after a dissociation jump, the vacancy will not return to a first nearest neighbor site of the impurity

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

Mehrer, *Diffusion in Solids*, 2007
Manning, Physical Review, 1964

Impurity diffusion coefficient for Ni-Si and Ni-Ti systems

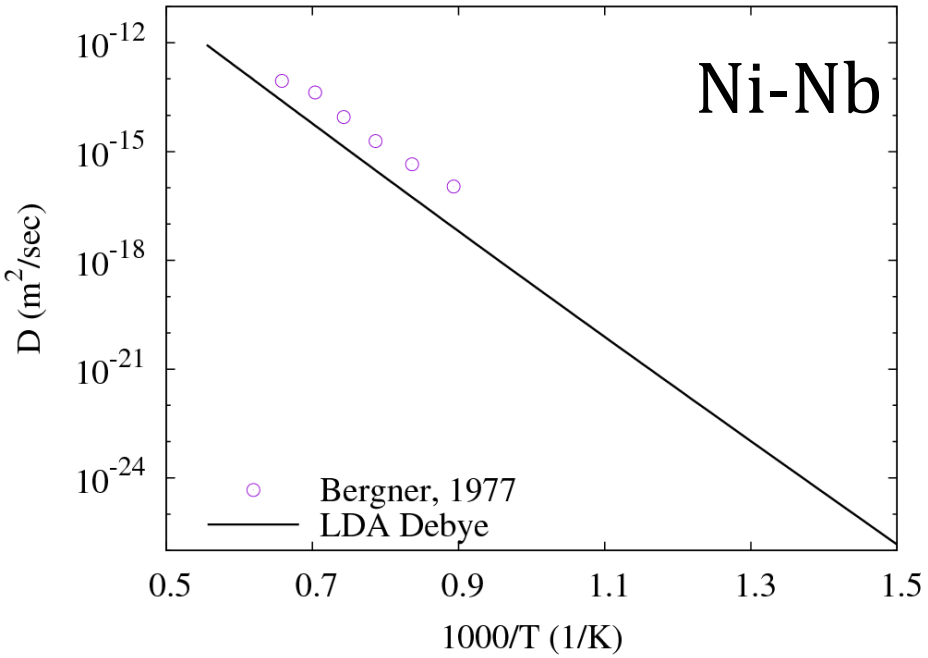


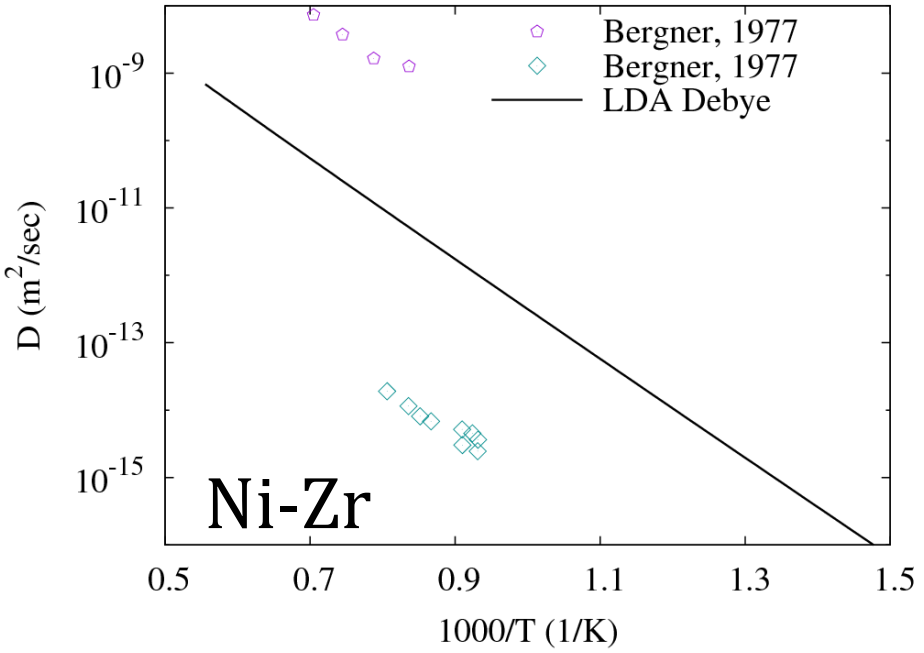


**Filled data points:
Single-crystal

**Open data points:
Poly-crystal

Impurity diffusion coefficient for Ni-Nb and Ni-Zr systems

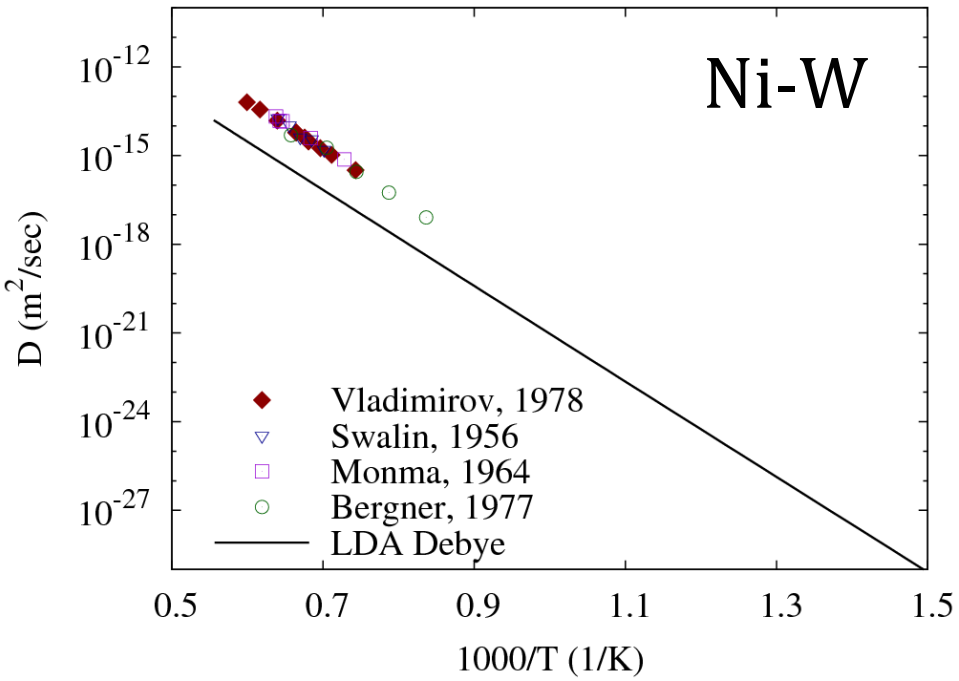


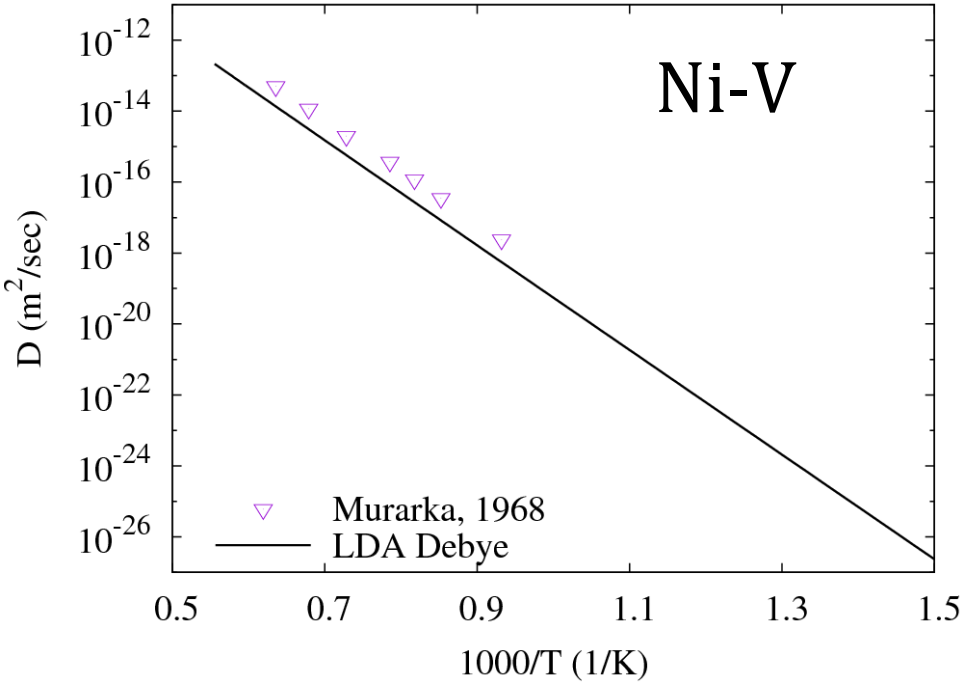


**Filled data points:
Single-crystal

**Open data points:
Poly-crystal

Impurity diffusion coefficient for Ni-W and Ni-V systems

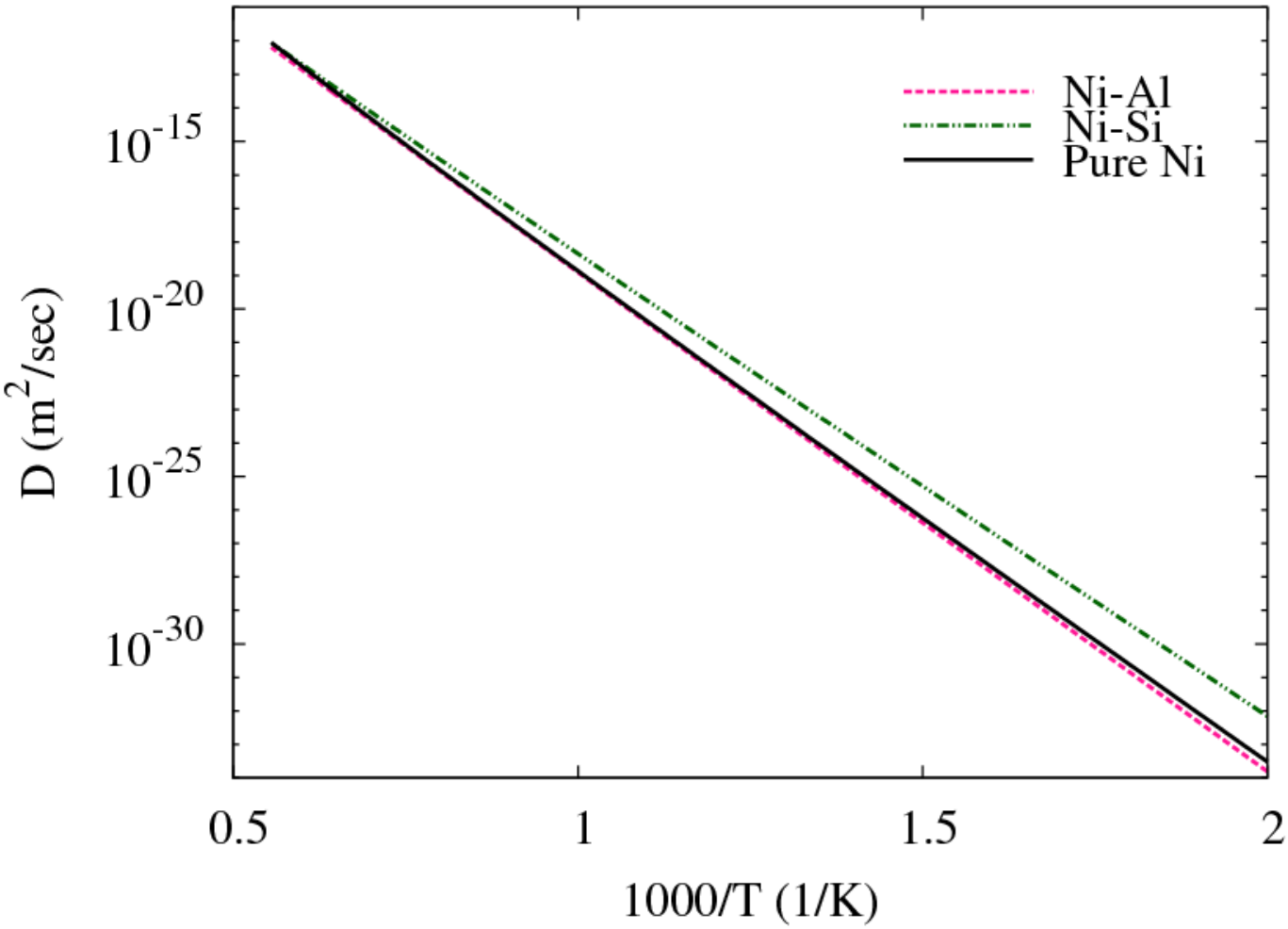




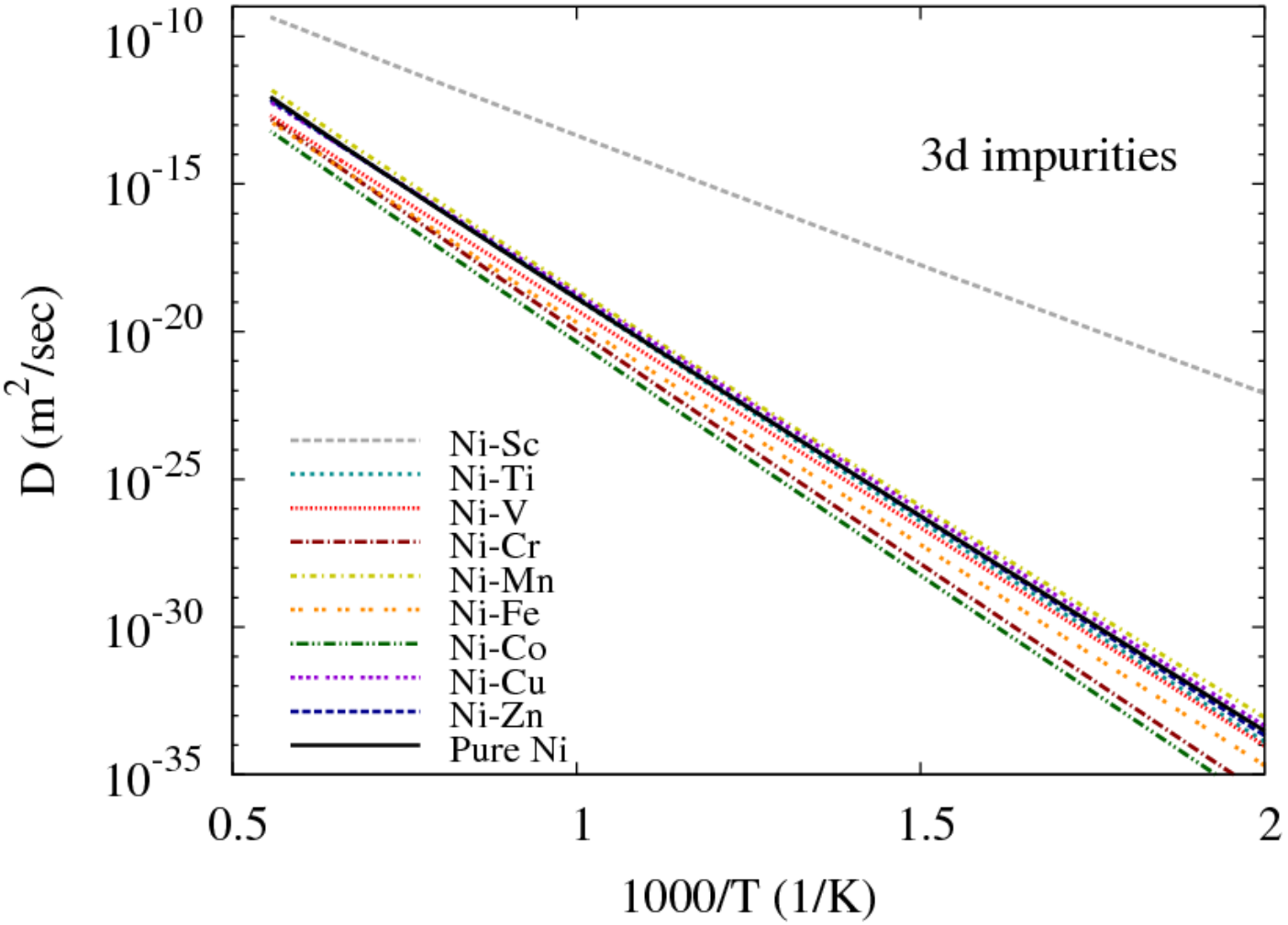
**Filled data points:
Single-crystal

**Open data points:
Poly-crystal

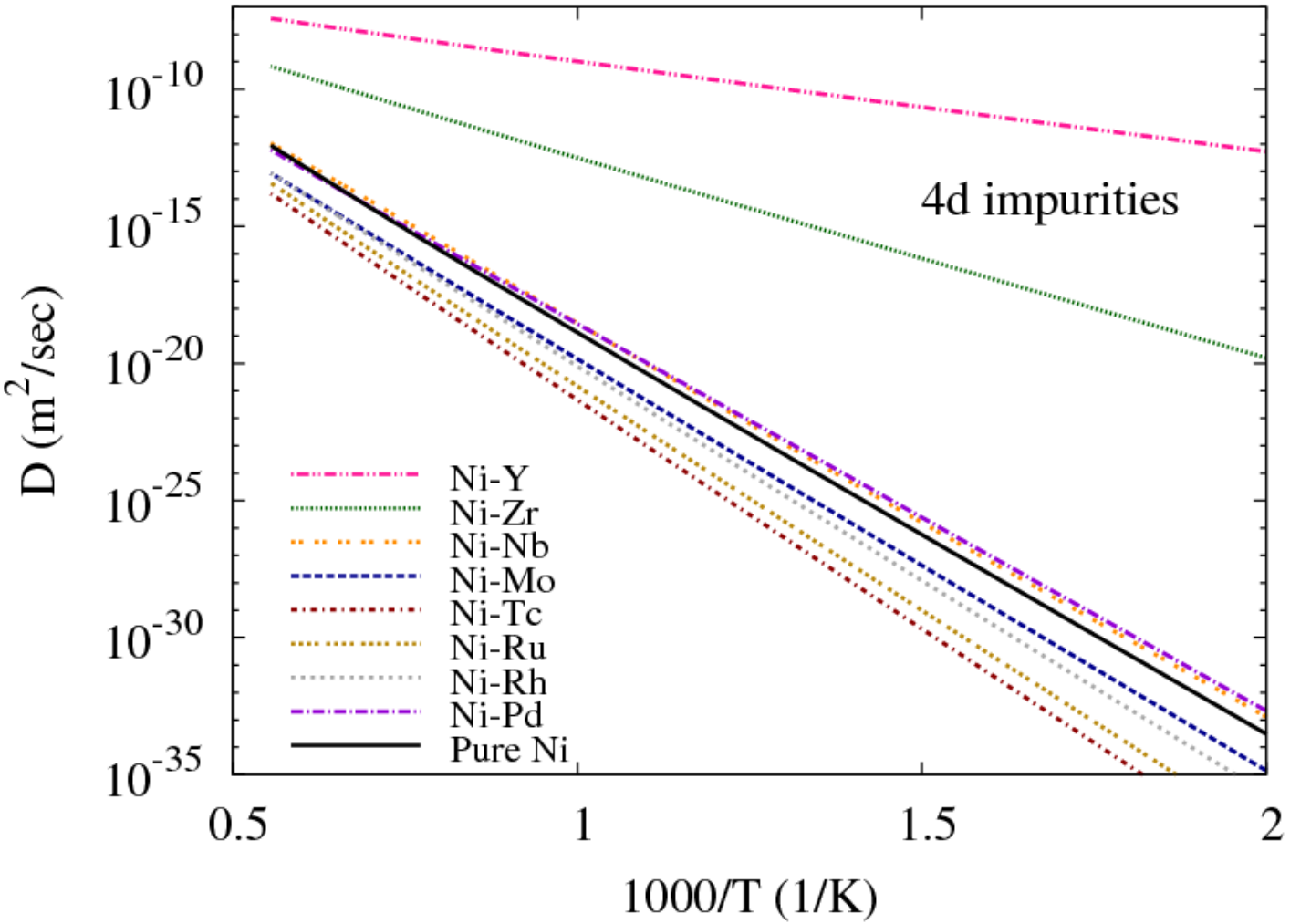
Other impurity elements



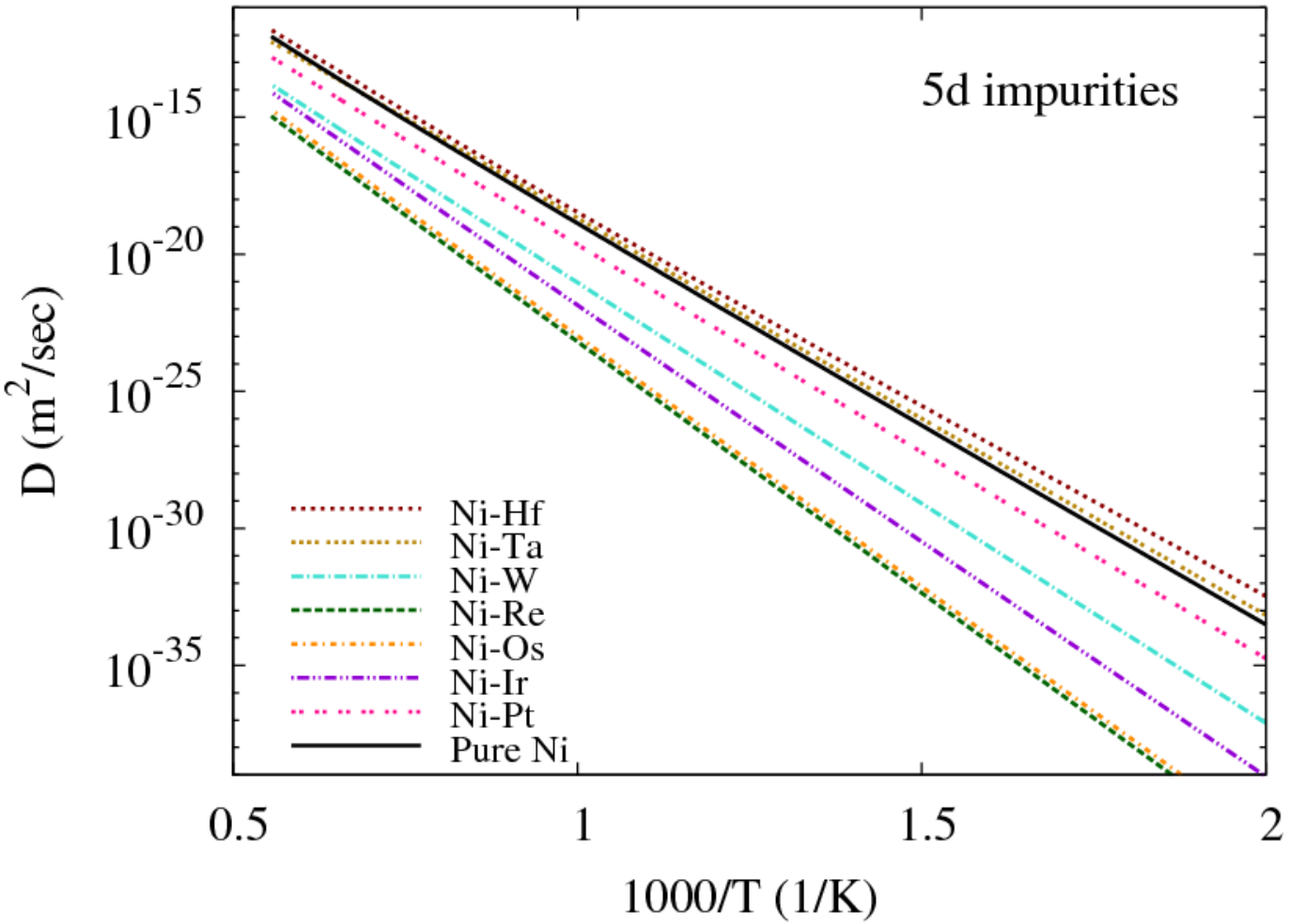
3d transition elements in Ni



4d transition elements in Ni



5d transition elements in Ni



LeClaire's 5 freqnecies

- (1) w_0: solvent–vacancy exchange frequency (far from a solute atom).
- (2) w_1: solvent–vacancy exchange frequency for the rotational jump around one single solute atom
- (3) w_3: solvent–vacancy exchange frequency for the solute–vacancy dissociative jump
- (4) w_4: solvent–vacancy exchange frequency for the solute–vacancy associative jump
- (5) w_2: single solute–vacancy exchange frequency

Bocquet's 14 frequencies

- (6) w_{33}: solvent–vacancy exchange frequency for the jump that takes the vacancy away from the solute pair
- (7) w_{34}: solvent–vacancy exchange frequency for the jump that takes the vacancy away from one solute atom in the single atom configuration but at the same time brings the vacancy into the nearest neighbor position for the other solute atom
- (8) w_{44}: solvent–vacancy exchange frequency for the jump that brings the vacancy to the nearest neighbor position for the solute pair
- (9) w_{14}: solvent–vacancy exchange frequency for the jump that brings the vacancy from the nearest neighbor position to one of the solute atoms in the pair configuration to the nearest neighbor position of both solute atoms in the pair configuration.

Bocquet's 14 frequencies, con't

- (10) w_{13}: solvent–vacancy exchange frequency for the jump that takes the vacancy from the nearest neighbor position to both solute atoms in the pair configuration to the nearest neighbor position to one of the solute atoms in the pair configuration.
- (11) w_{11}: solvent–vacancy exchange frequency for the jump that keeps the vacancy at the nearest neighbor position to both solute atoms in the pair configuration.
- (12) w_{23}: solute–vacancy exchange frequency for the jump that takes a solute atom away from the other solute
- (13) w_{21}: solute–vacancy exchange frequency for a solute rotational jump around the other solute atom
- (14) w_{24}: solute–vacancy exchange frequency for the jump that brings a solute atom to the nearest neighbor position of the other solute atom