Diffusion of Oxygen in Ni and Fe due to Substitutional Vacancy from DFT Calculations

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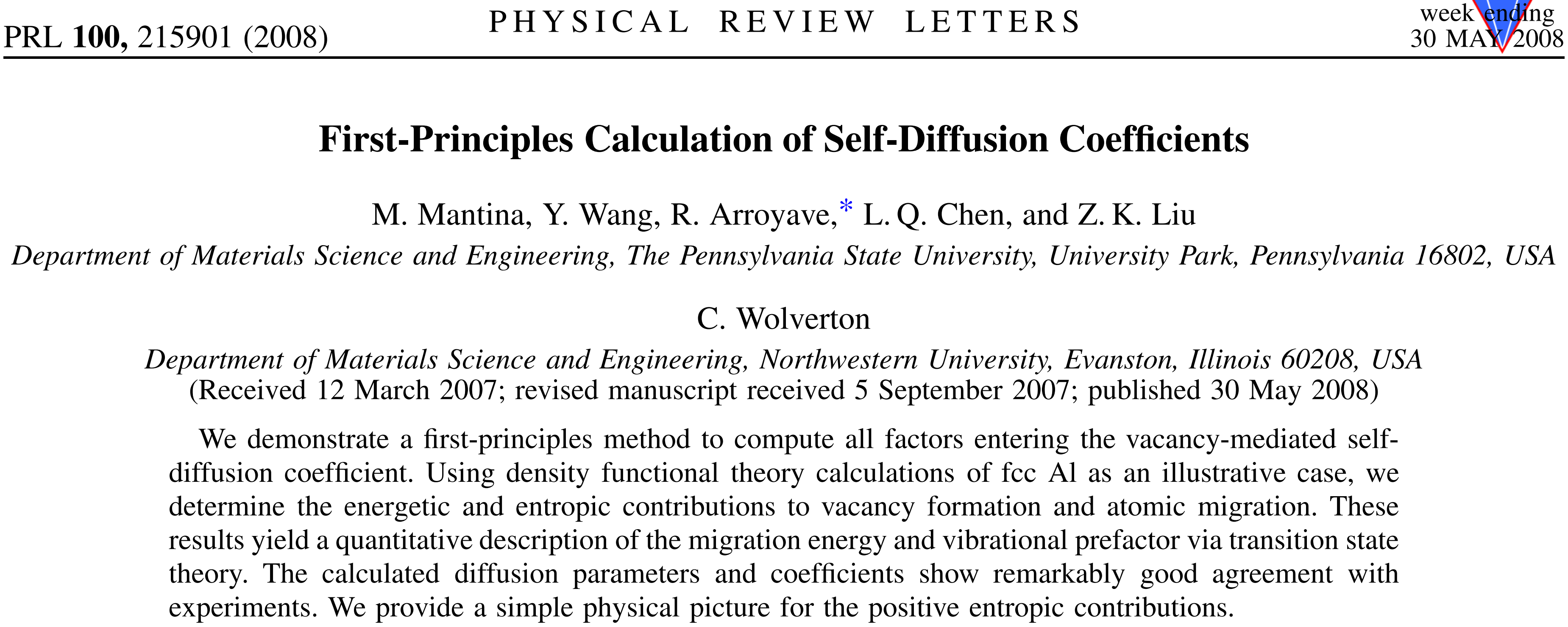

PRL **100,** 215901 (2008) PHYSICAL REVIEW LETTERS week ending 30 MAY 2008

First-Principles Calculation of Self-Diffusion Coefficients

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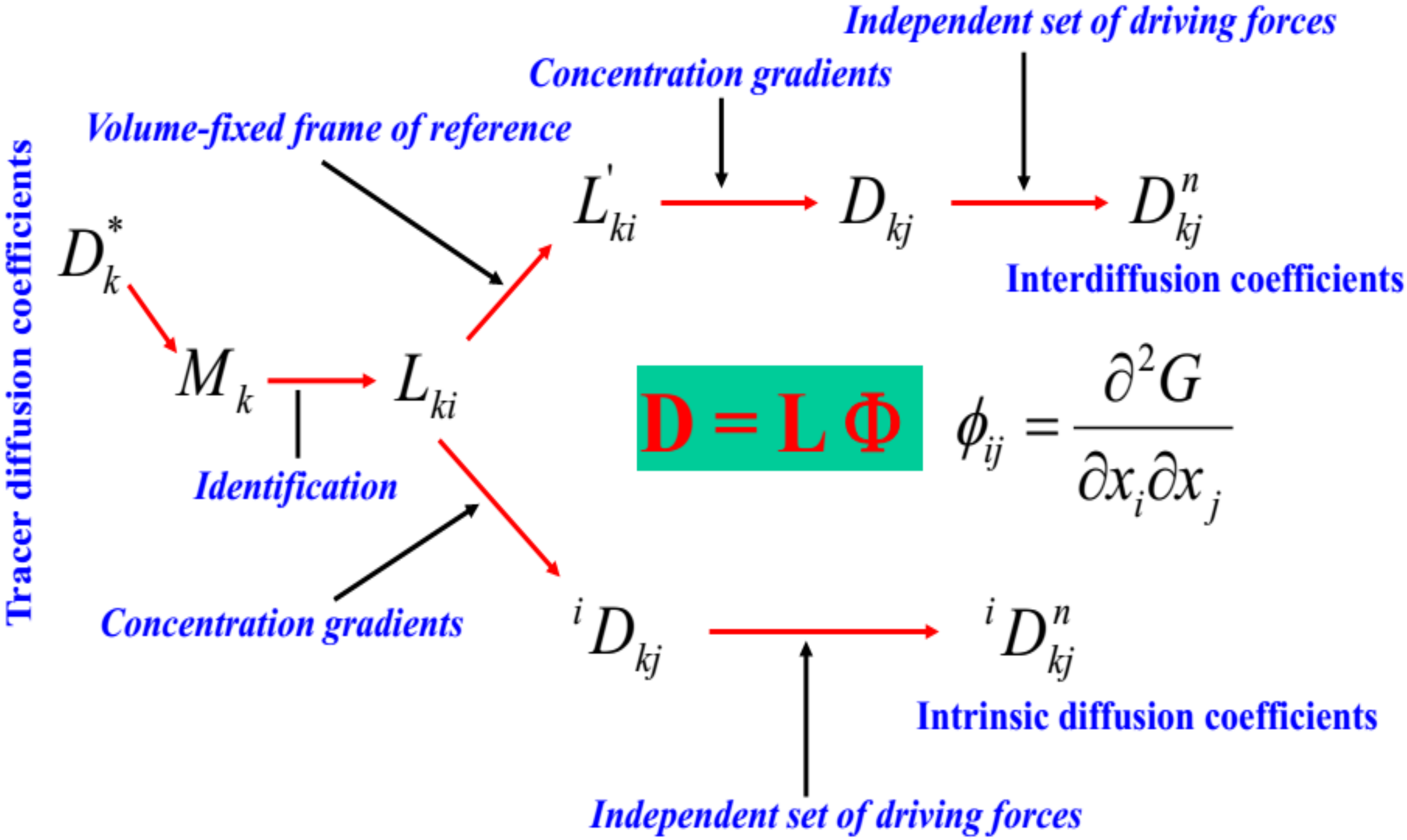
We demonstrate a first-principles method to compute all factors entering the vacancy-mediated self-diffusion coefficient. Using density functional theory calculations of fcc Al as an illustrative case, we determine the energetic and entropic contributions to vacancy formation and atomic migration. These results yield a quantitative description of the migration energy and vibrational prefactor via transition state theory. The calculated diffusion parameters and coefficients show remarkably good agreement with experiments. We provide a simple physical picture for the positive entropic contributions.

- Use density functional theory calculations to determine the energetic and entropic contributions to vacancy formation and atomic migration, i.e. all parameters used to evaluate vacancy-mediated diffusion coefficients
- Compare the calculated values with available experimental data

Outline

- **Interstitial diffusion from first-principles**
  - Theory and finite temperature thermodynamics
- **Oxygen diffusion in fcc nickel**
  - Site preference & diffusion pathway
  - Va-modified site preference & diffusion path
  - Oxygen diffusivity with and without Va
- **Oxygen diffusion in bcc iron**
  - Site preference with and without Va
  - Oxygen diffusivity with and without Va
- **Summary**

Diffusion coefficient **D** is a product of kinetic coefficient **L** and thermodynamic factor **Φ**



Tracer diffusion coefficients

D_k^*

M_k

L_{ki}

Identification

Volume-fixed frame of reference

Concentration gradients

L'_{ki}

Concentration gradients

D_{kj}

Independent set of driving forces

D_{kj}^n

Interdiffusion coefficients

${}^iD_{kj}$

Independent set of driving forces

${}^iD_{kj}^n$

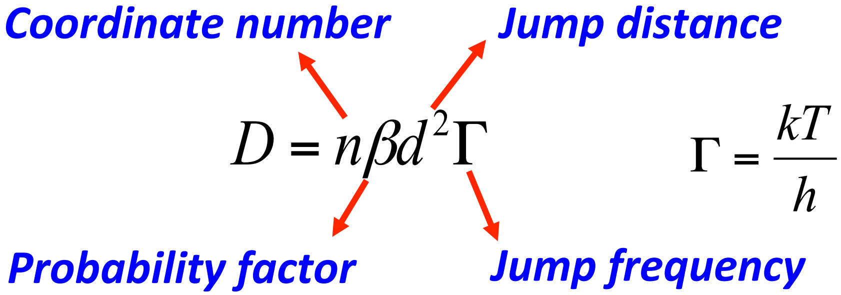
Intrinsic diffusion coefficients

$$\mathbf{D} = \mathbf{L}\,\mathbf{\Phi}$$

$$\phi_{ij} = \frac{\partial^2 G}{\partial x_i \partial x_j}$$

Interstitial diffusion equation

Following Wert & Zener, interstitial diffusivity can be described by:



Coordinate number

Jump distance

$$D = n\beta d^2\Gamma$$

Probability factor

Jump frequency

$$\Gamma = \frac{kT}{h}\frac{Z_{TS}}{Z_{IS}}e^{-\Delta E/kT} = \frac{kT}{h}\frac{\prod_{i=1}^{3N-3}\left[2\sinh\left(\frac{h\nu_i^{IS}}{2kT}\right)\right]}{\prod_{i=1}^{3N-4}\left[2\sinh\left(\frac{h\nu_i^{TS}}{2kT}\right)\right]}e^{-\Delta E/kT}$$

High temperatures ($h\nu/2kT << 1$)
$\Rightarrow$ **Vineyard** equation

$$\Gamma = \frac{\prod_{i=1}^{3N-3}\nu_i^{IS}}{\prod_{i=1}^{3N-4}\nu_i^{TS}}e^{-\Delta E/kT} = \nu^* e^{-\Delta E/kT}$$

Low temperatures ($h\nu/2kT >> 1$)
$\Rightarrow$ **Eyring** equation

$$\Gamma = \frac{kT}{h}\frac{\exp\sum_{i=1}^{3N-3}\frac{h\nu_i^{IS}}{2kT}}{\exp\sum_{i=1}^{3N-4}\frac{h\nu_i^{IS}}{2kT}}e^{-\Delta E/kT} = \frac{kT}{h}e^{-(\Delta E+\Delta G_{vib})/kT}$$

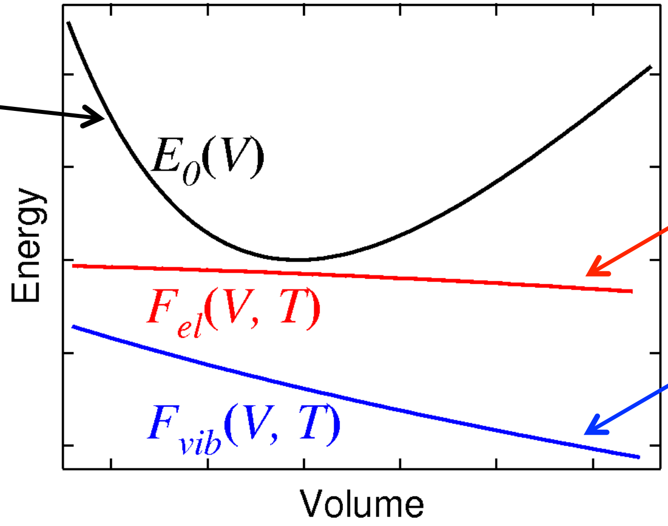
C. Wert & C. Zener, PRB 76 (1949) 1169; E. Wimmer, *et al*, PRB 77 (2008) 134305

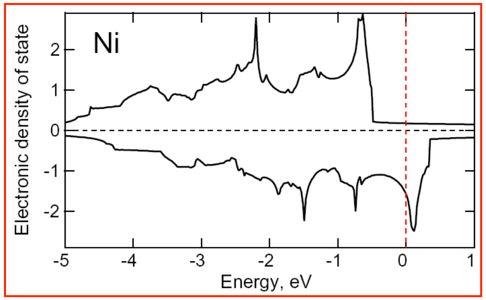
Finite temperature thermodynamics - **The quasiharmonic approach**

$$F(V,T) = E_0(V) + F_{vib}(V,T) + F_{el}(V,T)$$

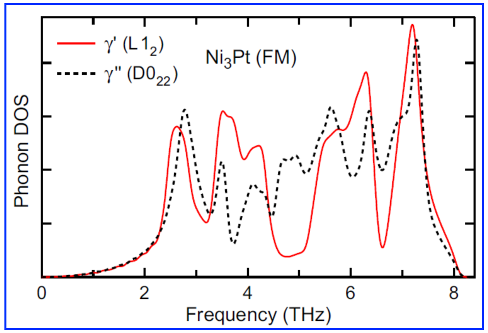
- $E_0(V)$ Static energy at 0 K and volume *V*, i.e., EOS (by VASP)
- $F_{vib}(V,T)$ Vibrational contribution at *V* & *T* (Phonon or Debye model)
- $F_{el}(V,T)$ Thermal electronic contribution at *V* & *T* (by VASP)

DFT directly





E-DOS



P-DOS

Shang *et al,* Comput Mater Sci 47 (2010) 1040, PRB 75 (2007) 147

Calculation methods –

O in fcc Ni & O in bcc Fe

- DFT based first-principles calculations
  - VASP code
  - PAW method for electron-ion interaction
  - Exchange-correctional (X-C) functionals
    - LDA for O in fcc Ni
    - GGA-PBE for O in Fe
    - Also tested others: PW91, PBE+U, PBEsol, AM05
  - CI-NEB for migration barrier calculations
  - Phonon & Debye model for finite T thermodynamics

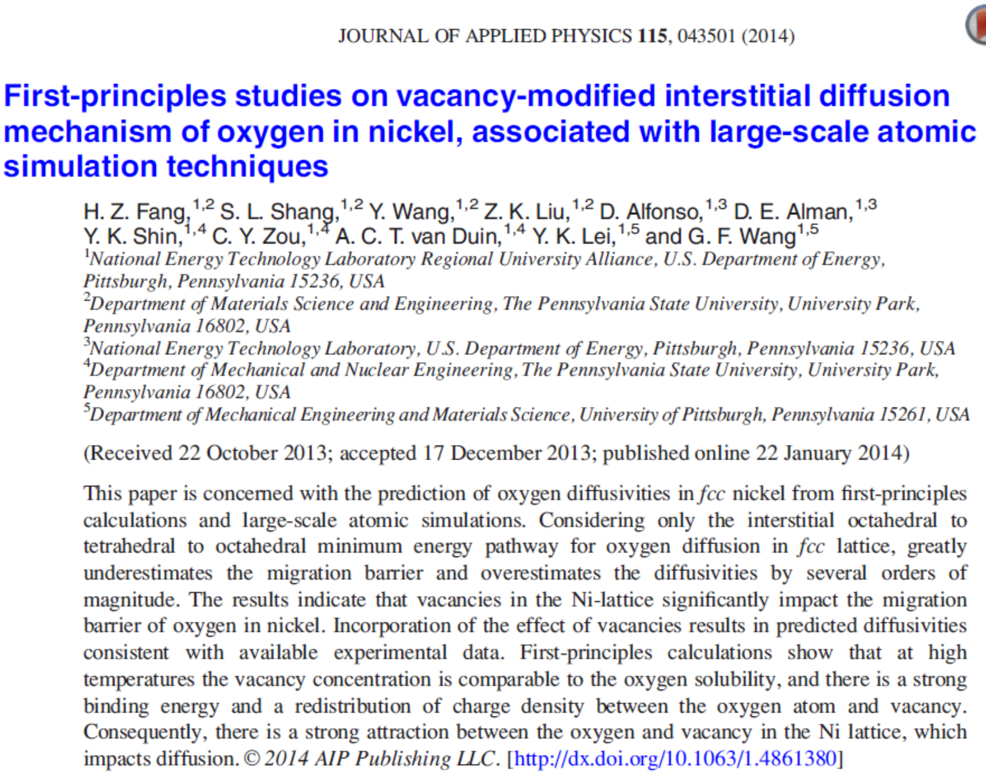
Details: Fang et al. JAP 115 (2014) 043501; Shang, *et al.*, Corros Sci. 83 (2014) 94

Case 1 of 2

- **Oxygen diffusion in fcc Ni with and without vacancy**

Oxygen diffusion in fcc Ni

Featured article and artwork of cover of JAP, 115 (2014): issue 4



JOURNAL OF APPLIED PHYSICS **115**, 043501 (2014)

First-principles studies on vacancy-modified interstitial diffusion mechanism of oxygen in nickel, associated with large-scale atomic simulation techniques

H. Z. Fang,[1,2] S. L. Shang,[1,2] Y. Wang,[1,2] Z. K. Liu,[1,2] D. Alfonso,[1,3] D. E. Alman,[1,3] Y. K. Shin,[1,4] C. Y. Zou,[1,4] A. C. T. van Duin,[1,4] Y. K. Lei,[1,5] and G. F. Wang[1,5]
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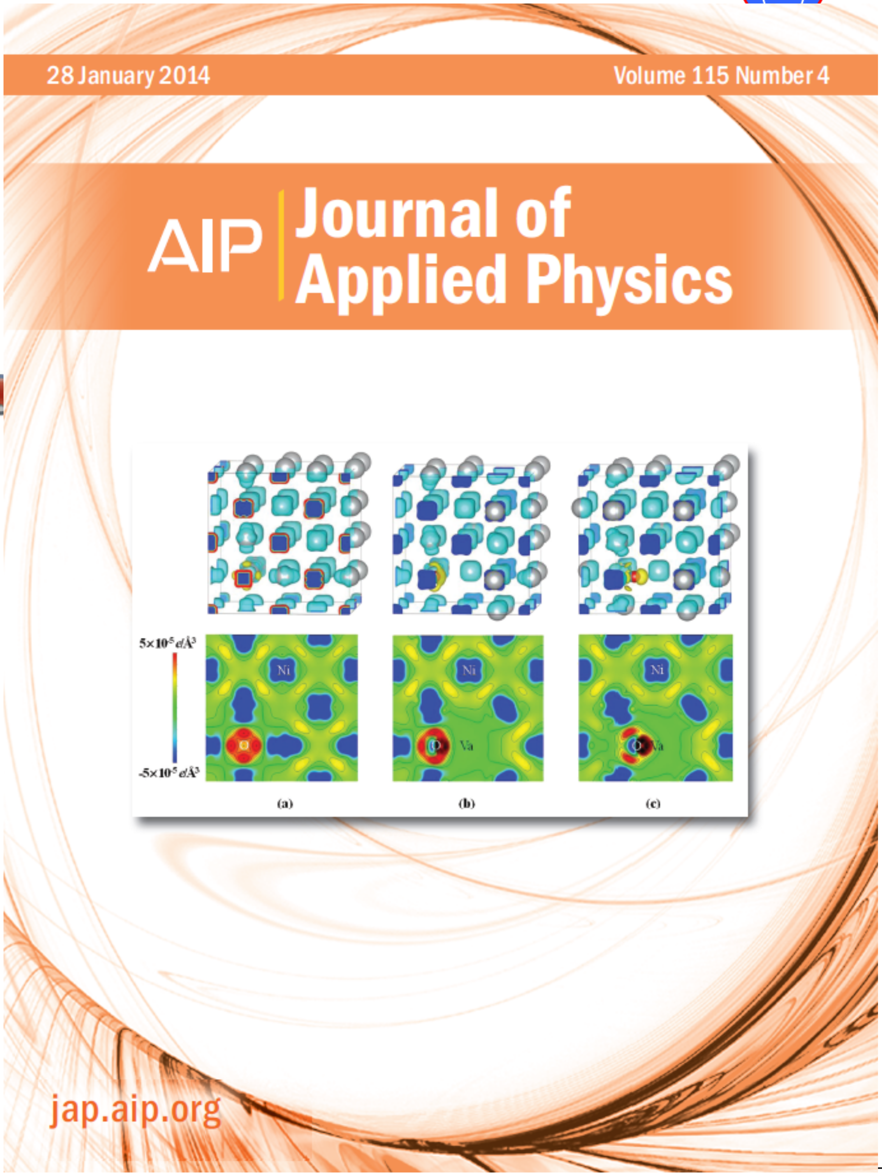
This paper is concerned with the prediction of oxygen diffusivities in *fcc* nickel from first-principles calculations and large-scale atomic simulations. Considering only the interstitial octahedral to tetrahedral to octahedral minimum energy pathway for oxygen diffusion in *fcc* lattice, greatly underestimates the migration barrier and overestimates the diffusivities by several orders of magnitude. The results indicate that vacancies in the Ni-lattice significantly impact the migration barrier of oxygen in nickel. Incorporation of the effect of vacancies results in predicted diffusivities consistent with available experimental data. First-principles calculations show that at high temperatures the vacancy concentration is comparable to the oxygen solubility, and there is a strong binding energy and a redistribution of charge density between the oxygen atom and vacancy. Consequently, there is a strong attraction between the oxygen and vacancy in the Ni lattice, which impacts diffusion. © *2014 AIP Publishing LLC*. [http://dx.doi.org/10.1063/1.4861380]



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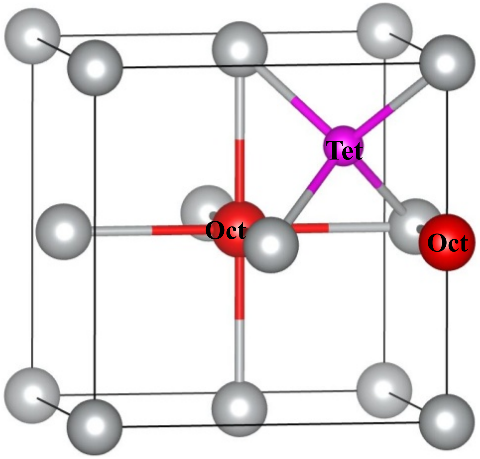
Oxygen diffusion in fcc Ni – **site preference**



Solution energy:

For interstitial solution: $E_{\mathrm{O}}^{\mathrm{sol}} = E_{n\mathrm{Ni+O}} - E_{n\mathrm{Ni}} - E_{\mathrm{O}},$

For substitutional solution: $E_{\mathrm{O}}^{\mathrm{sol}} = E_{(n-1)\mathrm{Ni+O}} - \frac{n-1}{n} E_{n\mathrm{Ni}} - E_{\mathrm{O}}$

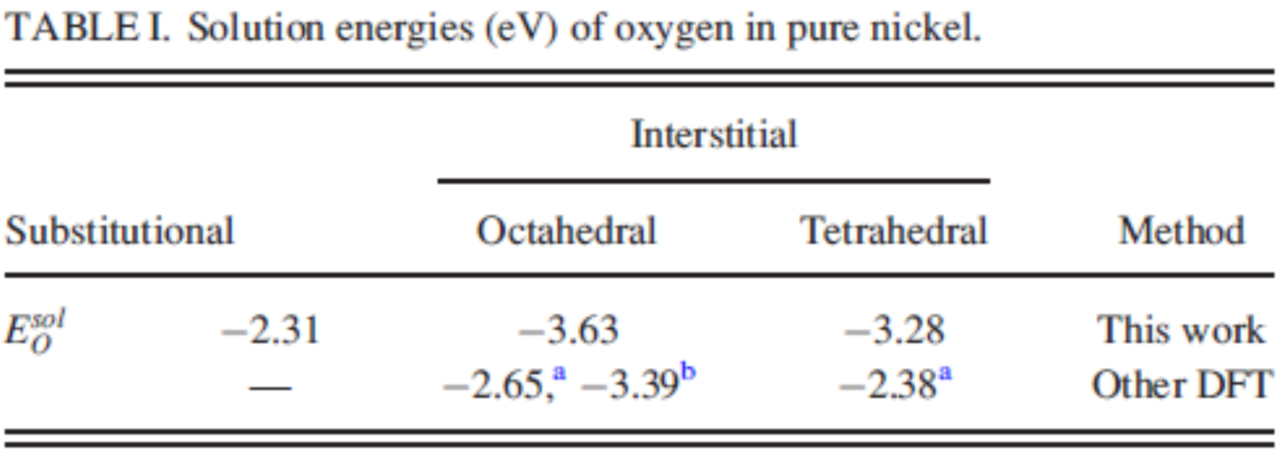
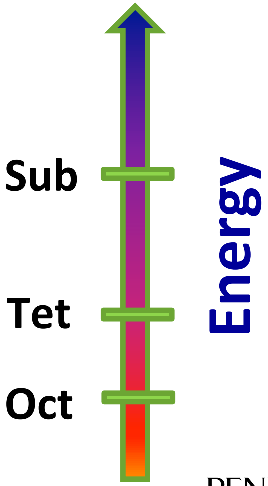


TABLE I. Solution energies (eV) of oxygen in pure nickel.

		Interstitial		
Substitutional		Octahedral	Tetrahedral	Method
E_O^{sol}	−2.31	−3.63	−3.28	This work
	—	−2.65,[a] −3.39[b]	−2.38[a]	Other DFT

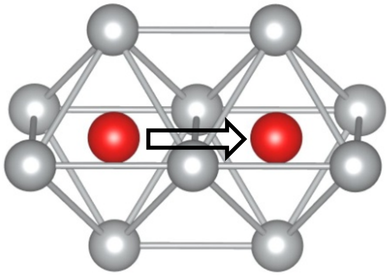


[a] E. H. Megchiche, et al, JPCM 19 (2007) 296201

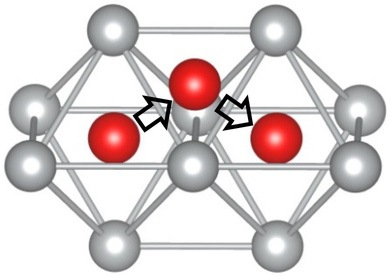
[b] J. J. Kim, et al, APL 100 (2012) 131904

Oxygen diffusion in fcc Ni – **diffusion pathway**

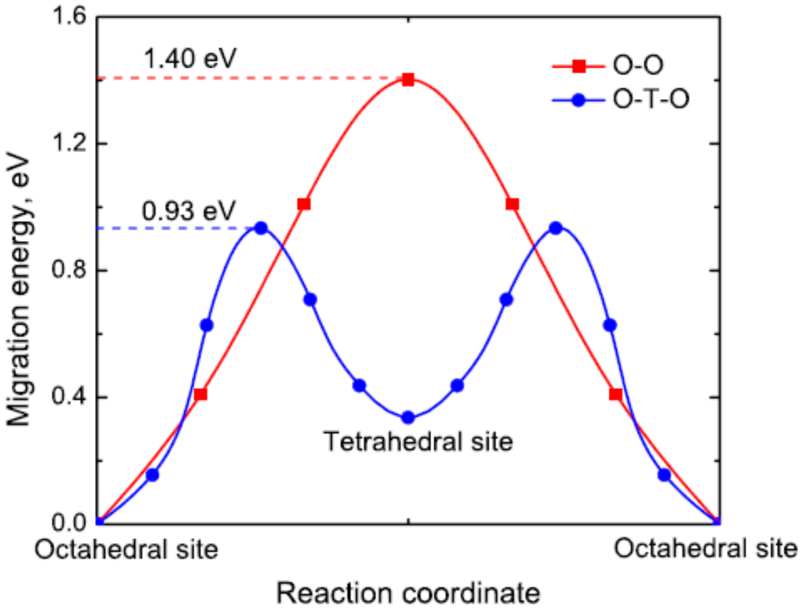
- Two migration pathways are considered



O-O



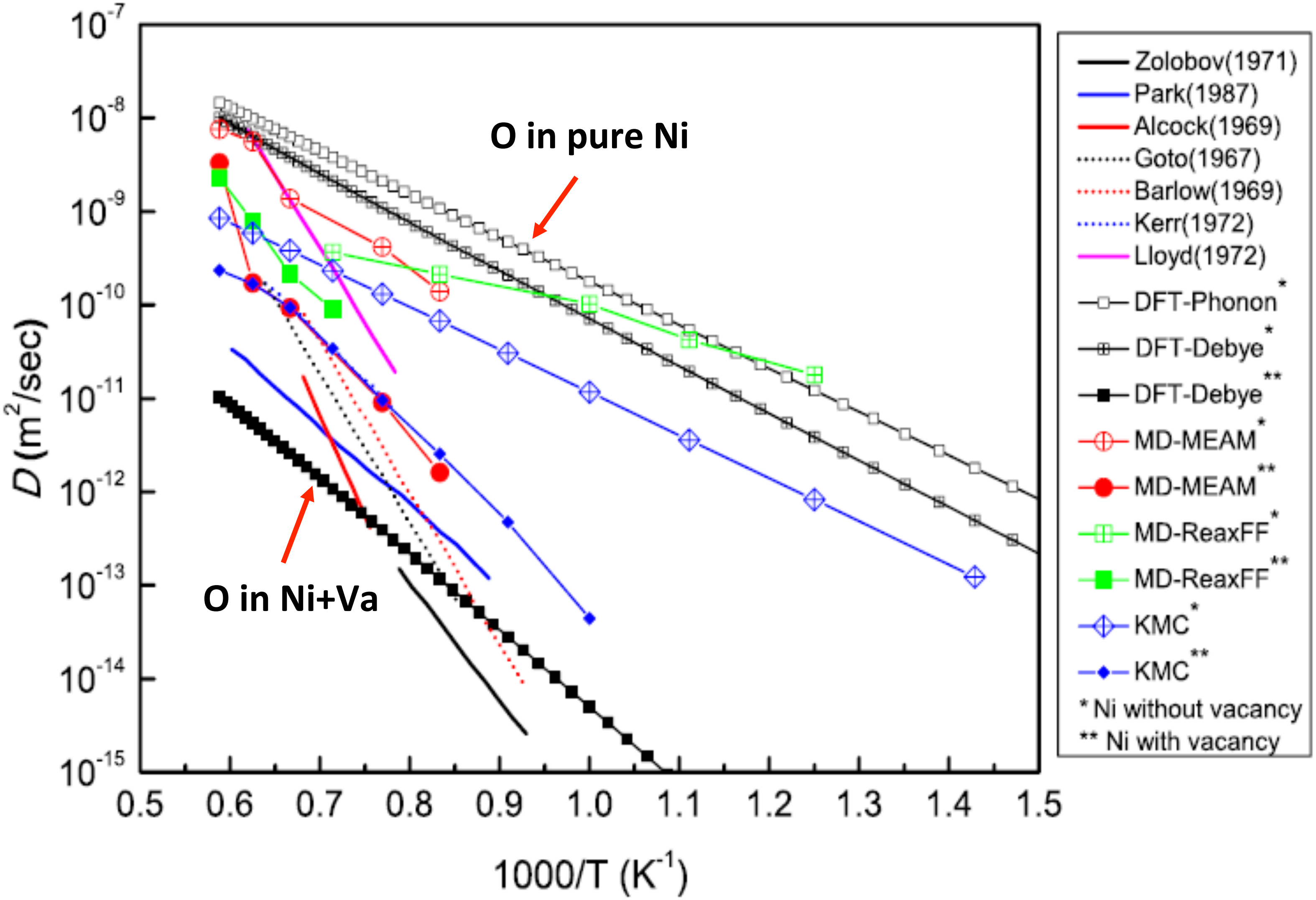
O-T-O



	O-O	O-T-O
This work	1.40	0.93
Other DFT	1.57 1.44	1.23 1.12
Experiment	1.70, 3.20, 3.12, 3.08, 4.28, 2.49, 1.89	

Predicted barriers much lower than measurements

Oxygen diffusion in fcc Ni – **finite T diffusivity**



O in pure Ni

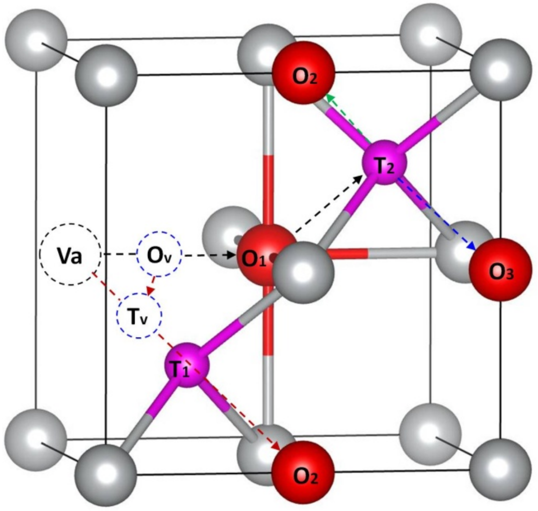
O in Ni+Va

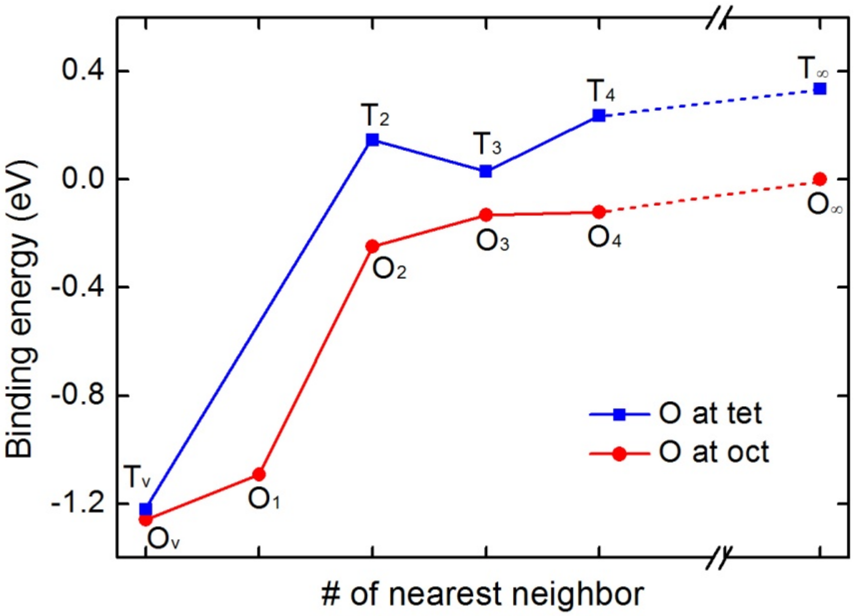
H. Z. Fang, *et al*, JAP 115 (2014) 043501

Oxygen diffusion in fcc Ni – **vacancy modified site preference**

- With Va, the neighboring Oct & Tet sites shift, *i.e.*:

$O_1 \rightarrow O_v$; $T_1 \rightarrow T_v$

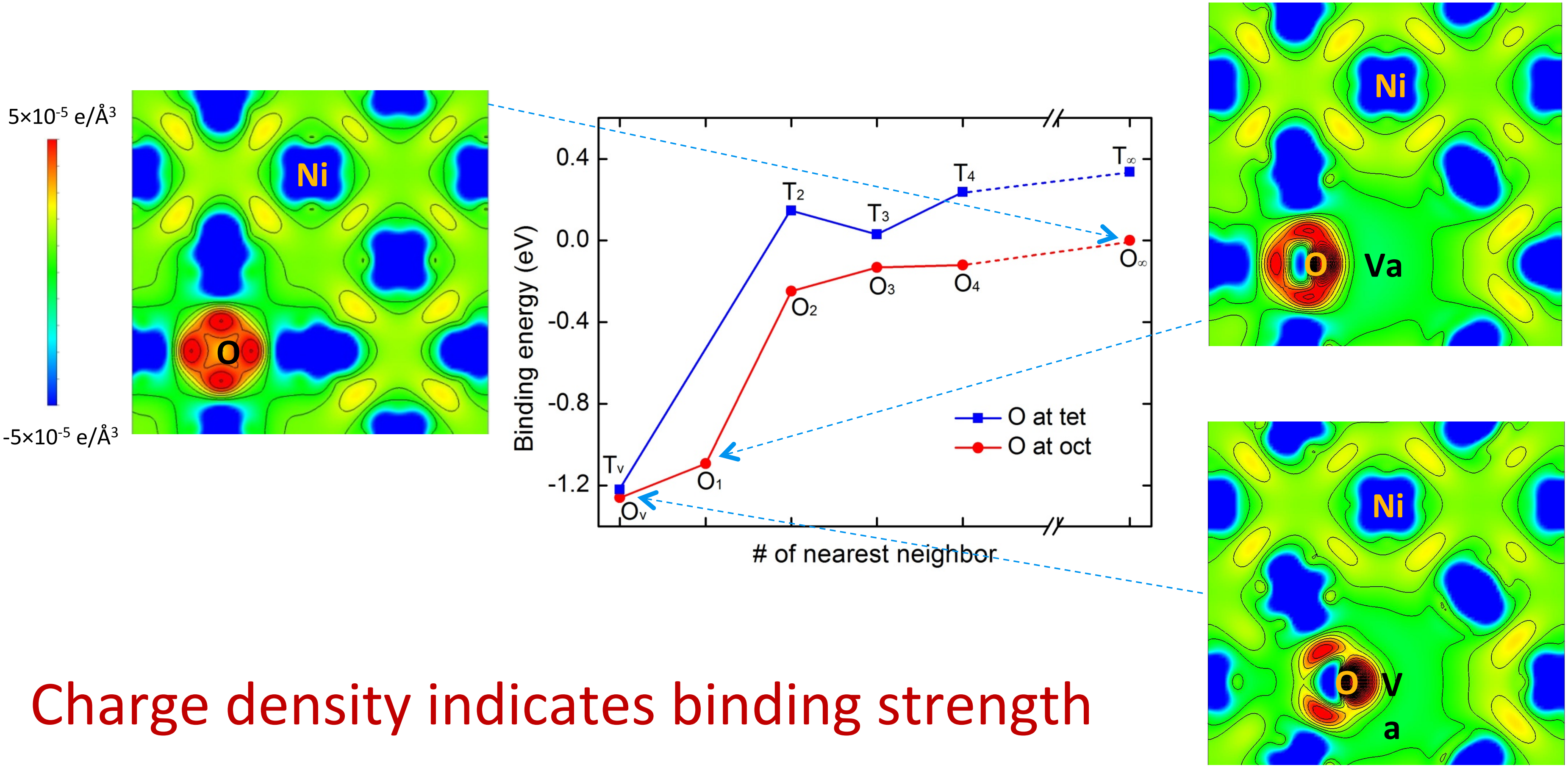




- O-Va binding energy ~1.2 eV.
- Effect up to the 3rd NN (O_3).

H. Z. Fang, *et al*, JAP 115 (2014) 043501

Oxygen diffusion in fcc Ni – **binding energy of O and Va**

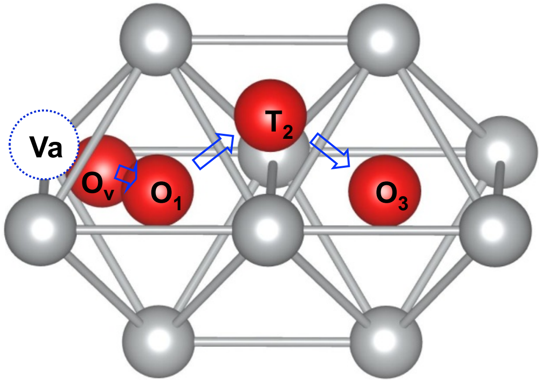


Charge density indicates binding strength

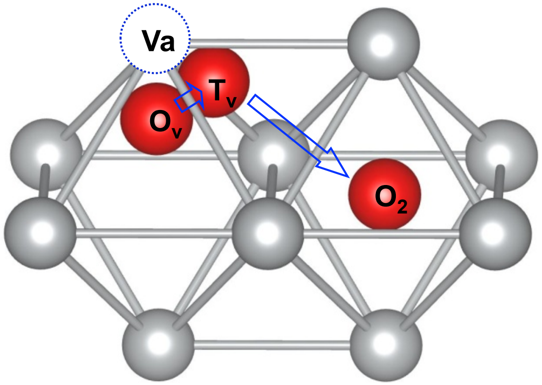
H. Z. Fang, *et al*, JAP 115 (2014) 043501

Oxygen diffusion in fcc Ni – **Va modified diffusion pathway**

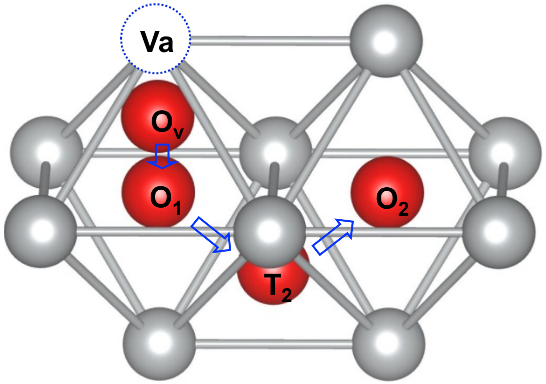
- Three possible paths for O diffusion from Va



(a) O_v-O_1-T_2-O_3

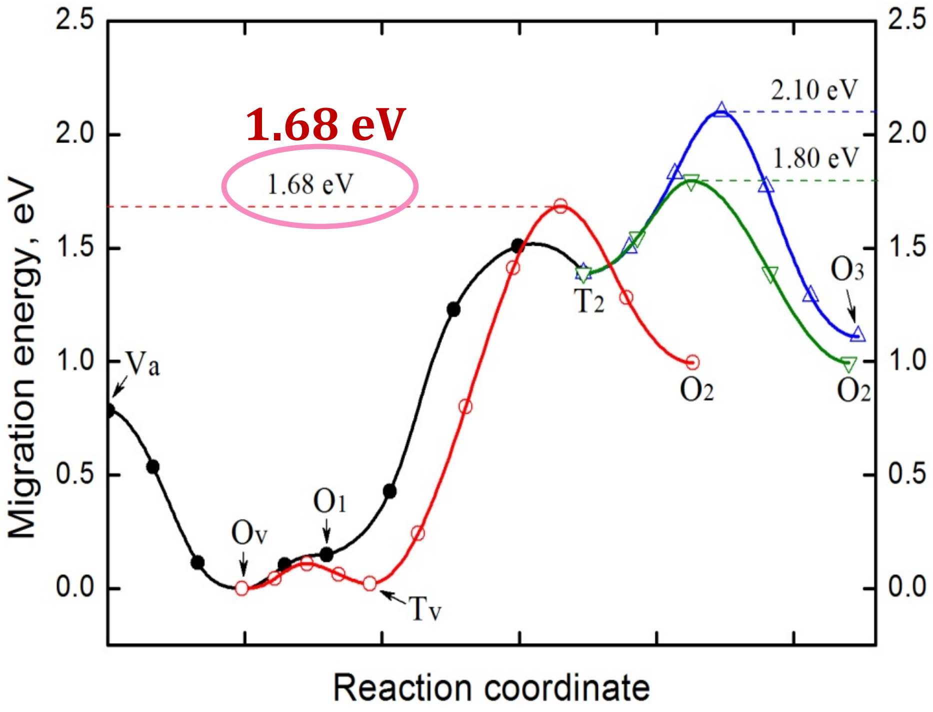


(b) O_v-T_v-O_2



(c) O_v-O_1-T_2-O_2

Oxygen diffusion in fcc Ni –
Va modified diffusion barrier



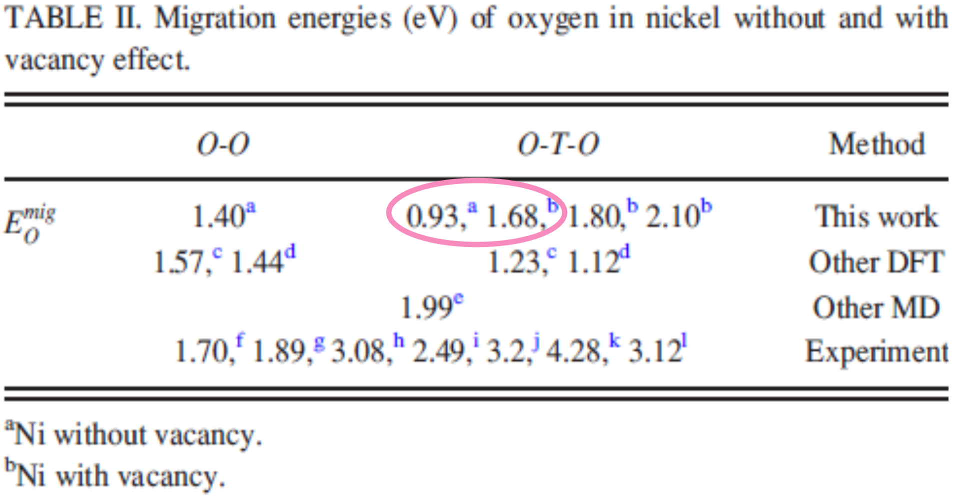


TABLE II. Migration energies (eV) of oxygen in nickel without and with vacancy effect.

	O-O	O-T-O	Method
E_O^{mig}	1.40[a]	0.93,[a] 1.68,[b] 1.80,[b] 2.10[b]	This work
	1.57,[c] 1.44[d]	1.23,[c] 1.12[d]	Other DFT
	1.99[e]		Other MD
	1.70,[f] 1.89,[g] 3.08,[h] 2.49,[i] 3.2,[j] 4.28,[k] 3.12[l]		Experiment

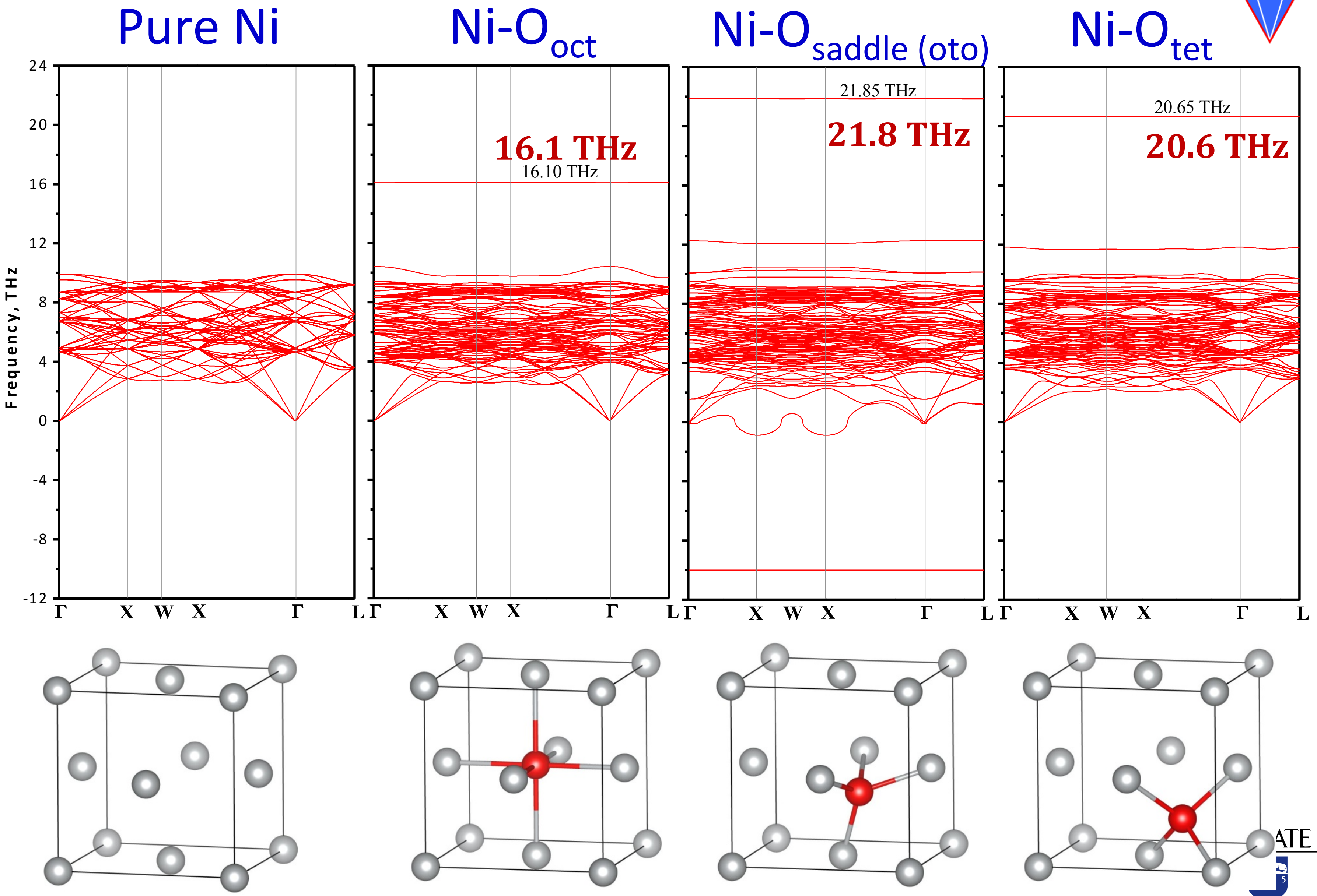
[a] Ni without vacancy.

[b] Ni with vacancy.

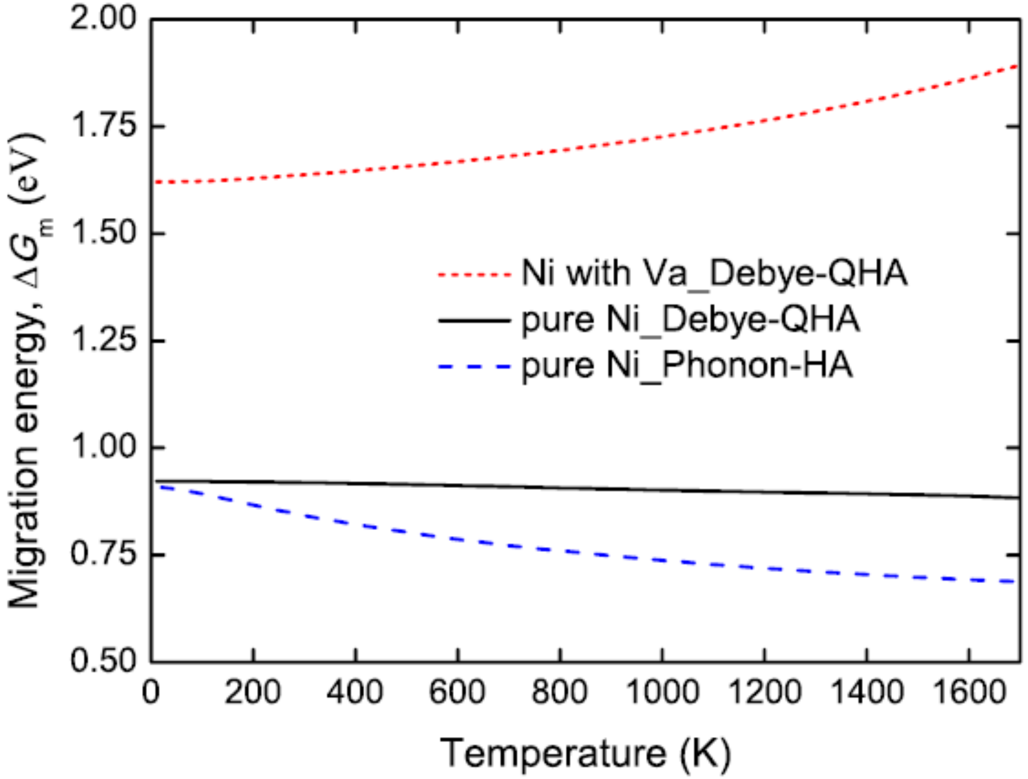
Significant increase of diffusion barrier from 0.93 to 1.68 eV

H. Z. Fang, *et al*, JAP 115 (2014) 043501

Oxygen diffusion in fcc Ni - **phonon**



Oxygen diffusion in fcc Ni – **migration barrier at finite T**



Migration free energies for O_v-T_v-O_2 pathway

Jump frequency:

$$\Gamma = \frac{kT}{h} e^{-\Delta G_m / kT}$$

- **Phonon:** accurate but expensive
- **Debye:** efficient but less expensive

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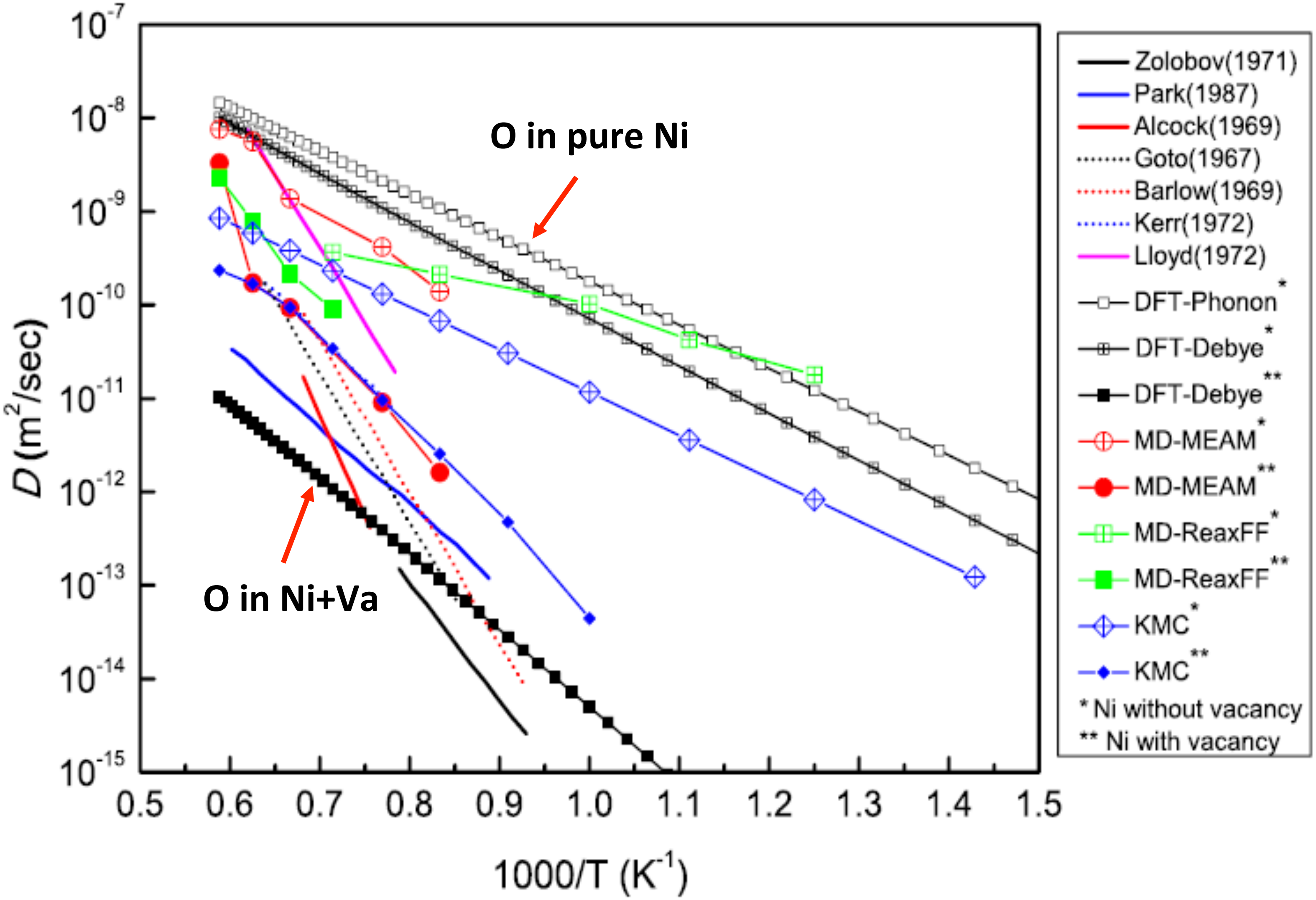
Oxygen diffusion in fcc Ni – **finite T diffusivity**



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Oxygen diffusion in fcc Ni – **Arrhenius parameters**

$$D = D_0 \exp(-Q/kT)$$

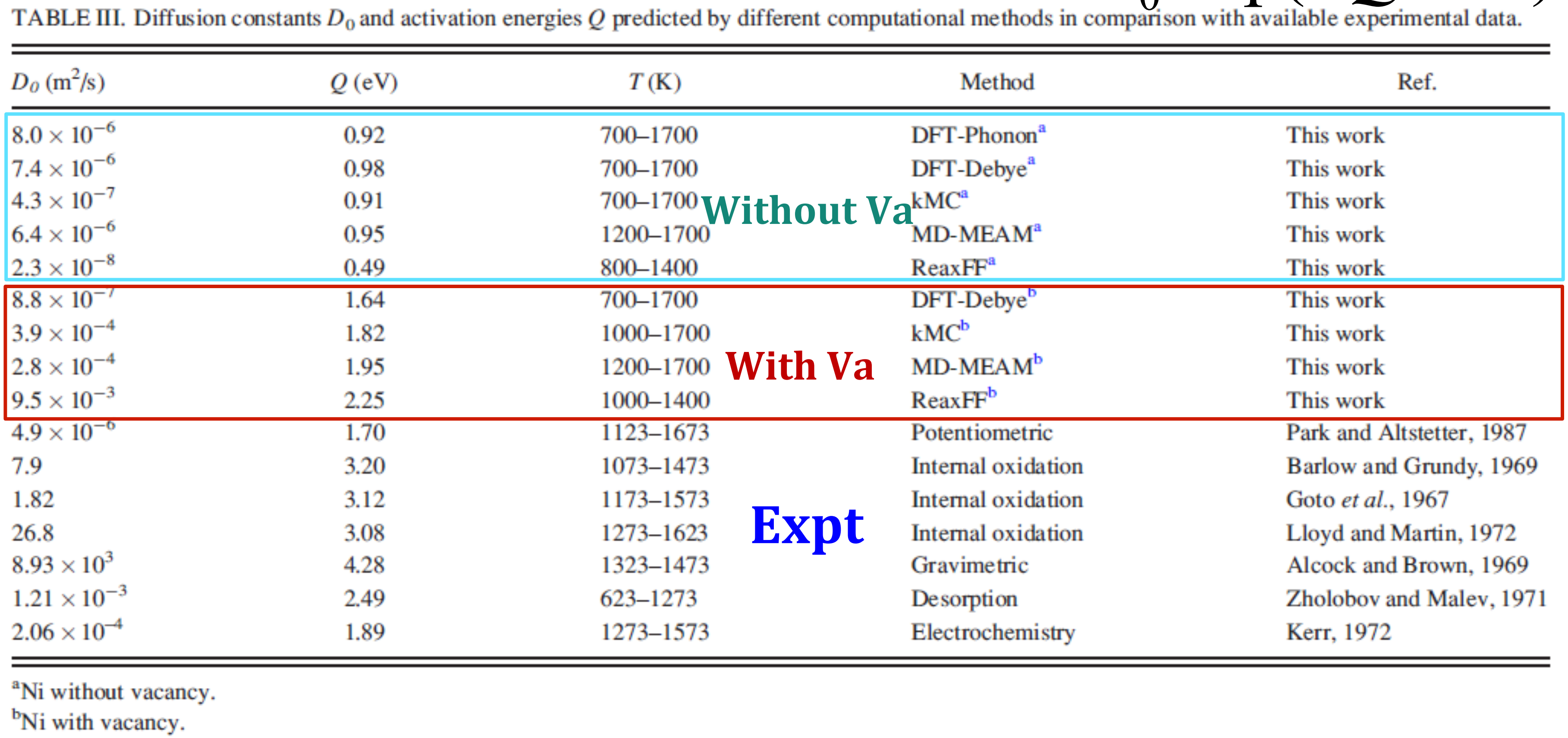

TABLE III. Diffusion constants D_0 and activation energies Q predicted by different computational methods in comparison with available experimental data.

D_0 (m^2/s)	Q (eV)	T (K)	Method	Ref.
8.0×10^{-6}	0.92	700–1700	DFT-Phonon[a]	This work
7.4×10^{-6}	0.98	700–1700	DFT-Debye[a]	This work
4.3×10^{-7}	0.91	700–1700	kMC[a]	This work
6.4×10^{-6}	0.95	1200–1700	MD-MEAM[a]	This work
2.3×10^{-8}	0.49	800–1400	ReaxFF[a]	This work
8.8×10^{-7}	1.64	700–1700	DFT-Debye[b]	This work
3.9×10^{-4}	1.82	1000–1700	kMC[b]	This work
2.8×10^{-4}	1.95	1200–1700	MD-MEAM[b]	This work
9.5×10^{-3}	2.25	1000–1400	ReaxFF[b]	This work
4.9×10^{-6}	1.70	1123–1673	Potentiometric	Park and Altstetter, 1987
7.9	3.20	1073–1473	Internal oxidation	Barlow and Grundy, 1969
1.82	3.12	1173–1573	Internal oxidation	Goto *et al.*, 1967
26.8	3.08	1273–1623	Internal oxidation	Lloyd and Martin, 1972
8.93×10^{3}	4.28	1323–1473	Gravimetric	Alcock and Brown, 1969
1.21×10^{-3}	2.49	623–1273	Desorption	Zholobov and Malev, 1971
2.06×10^{-4}	1.89	1273–1573	Electrochemistry	Kerr, 1972

Without Va

With Va

Expt

[a] Ni without vacancy.
[b] Ni with vacancy.

D_0: $8.8\times10^{-7} \sim 9.5\times10^{-3}$ (Expt: $4.9\times10^{-6} \sim 8.93\times10^{3}$)

Q: 1.64 ~ 2.25 (Expt: 1.7 ~ 4.28)

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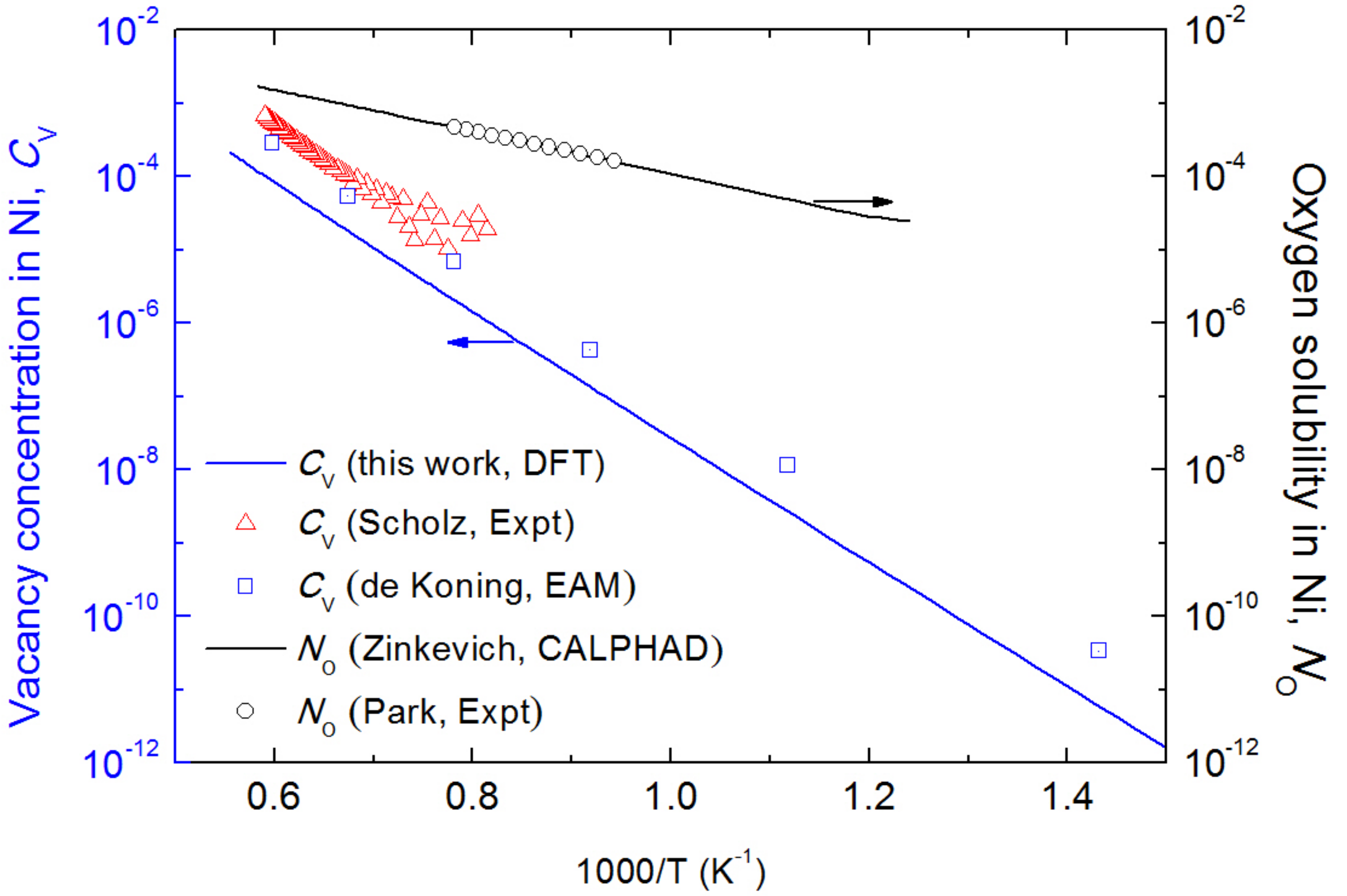
Discussion – **equilibrium O & Va contents in Ni**



Vacancy concentration vs. oxygen solubility in Ni

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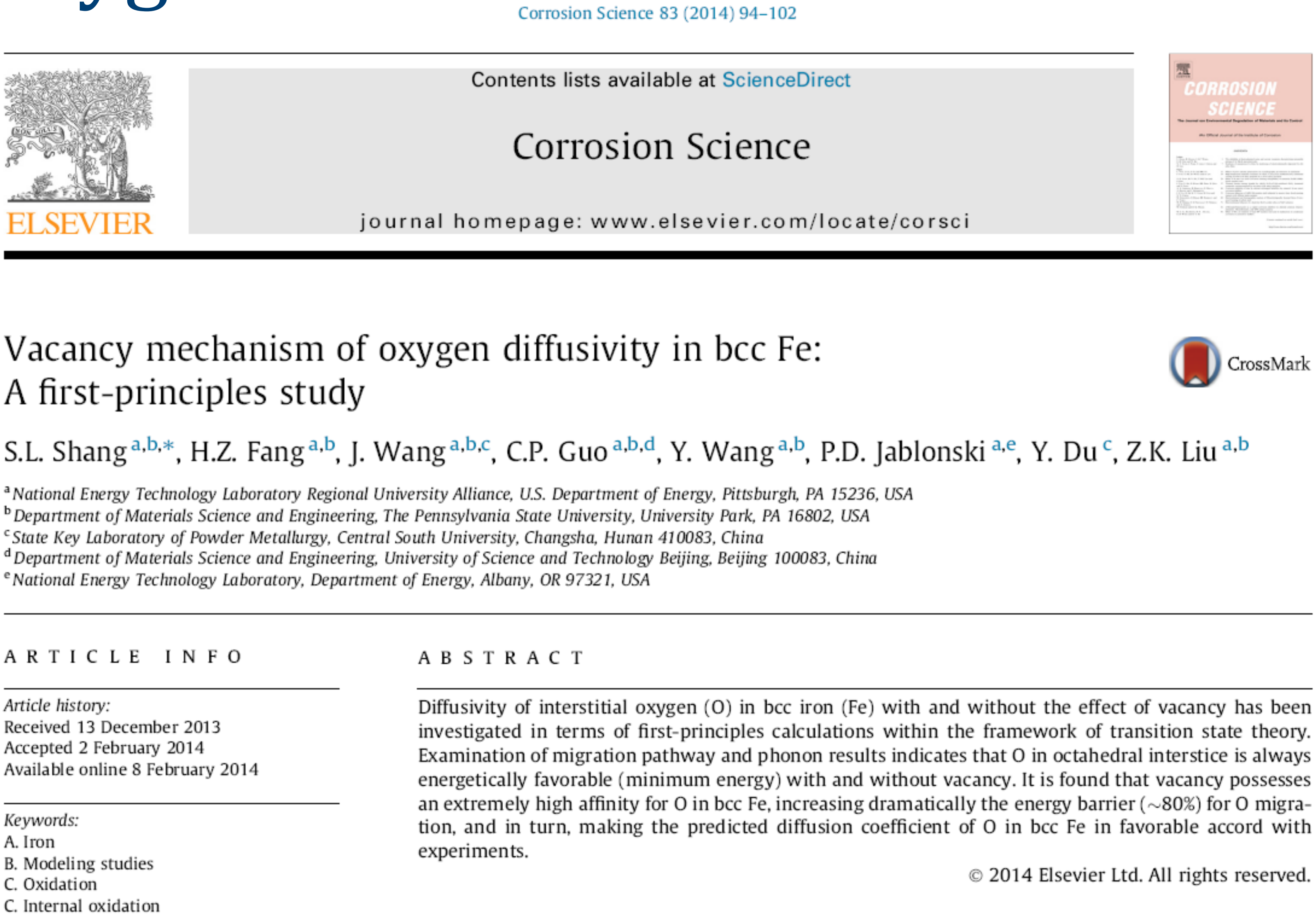
Case 2 of 2

- **Oxygen diffusion in bcc Fe with and without vacancy**

Oxygen diffusion in bcc Fe



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Vacancy mechanism of oxygen diffusivity in bcc Fe: A first-principles study

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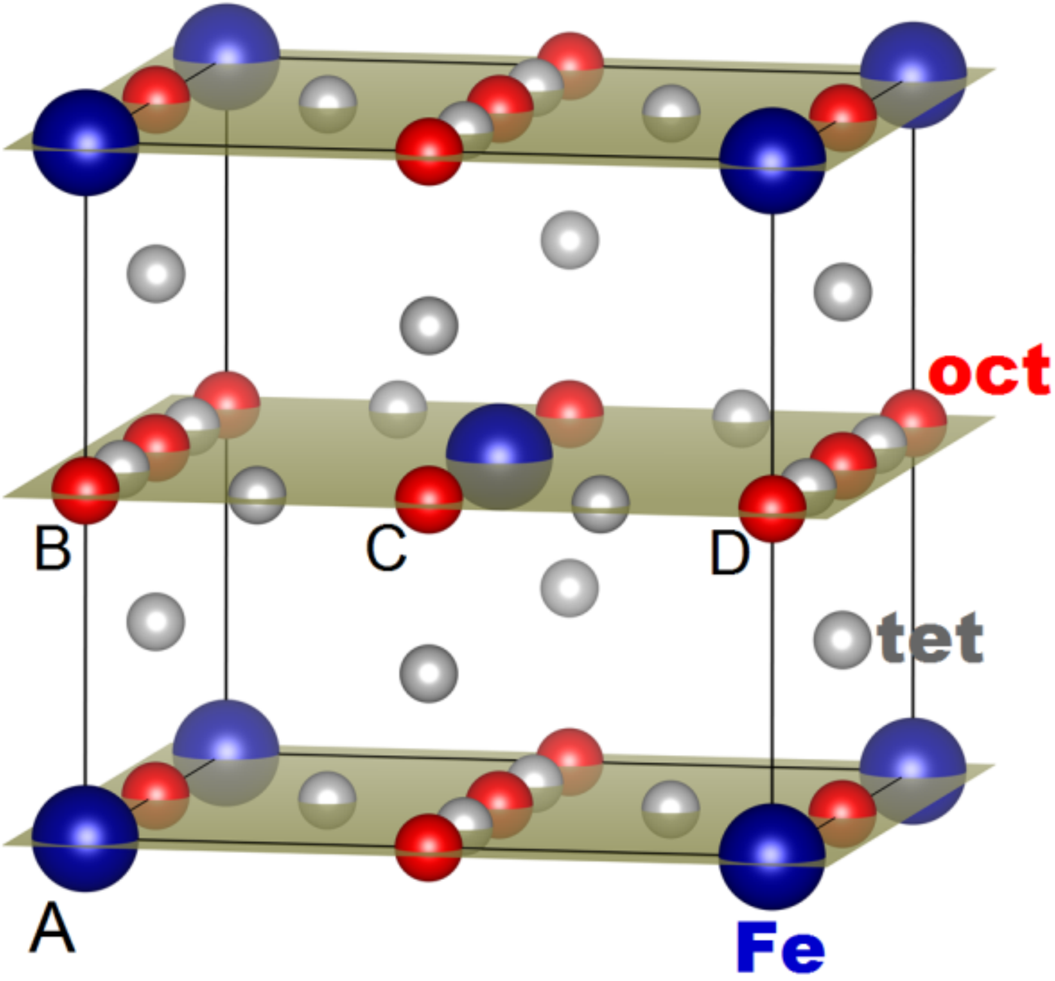
ABSTRACT

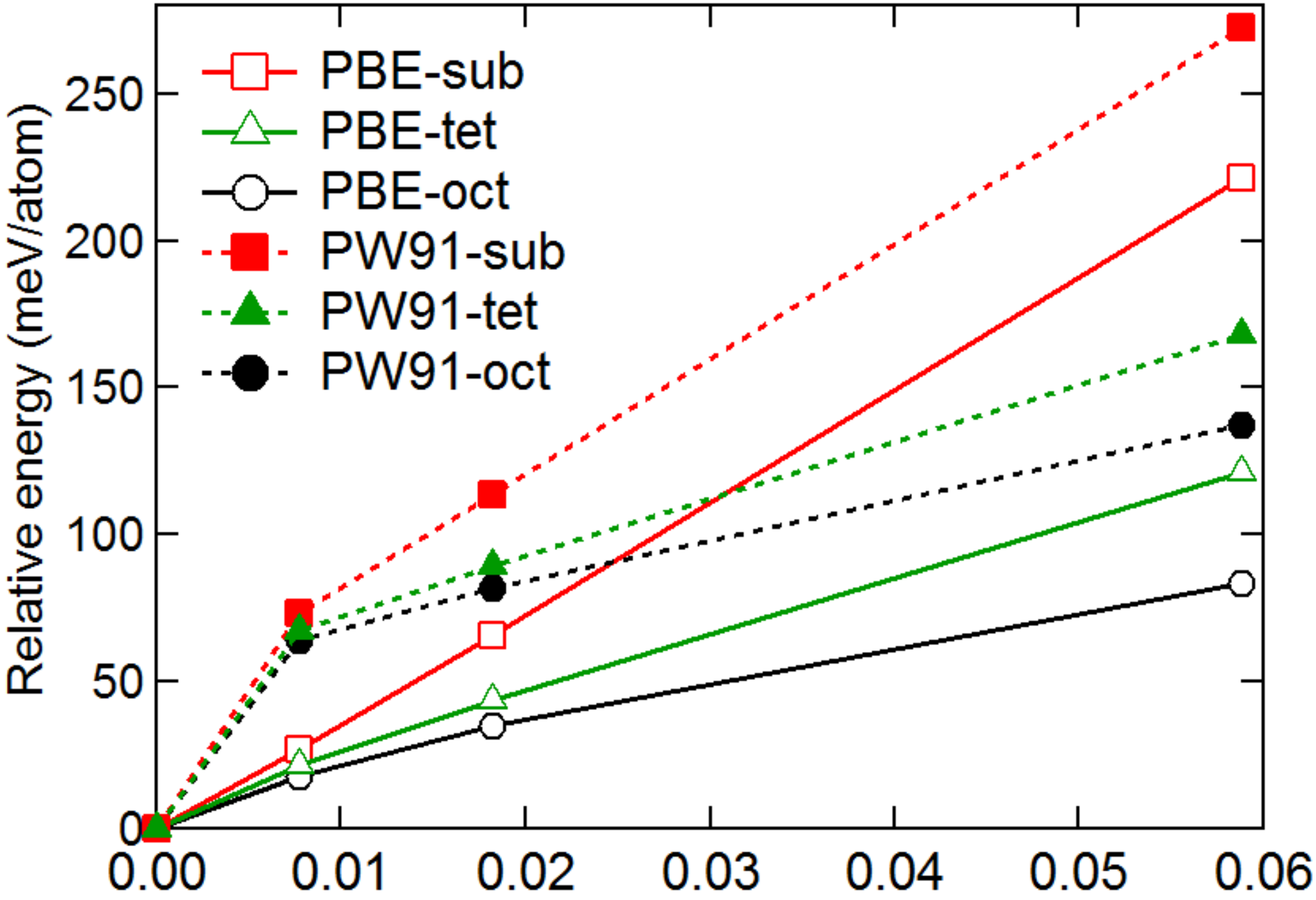
Diffusivity of interstitial oxygen (O) in bcc iron (Fe) with and without the effect of vacancy has been investigated in terms of first-principles calculations within the framework of transition state theory. Examination of migration pathway and phonon results indicates that O in octahedral interstice is always energetically favorable (minimum energy) with and without vacancy. It is found that vacancy possesses an extremely high affinity for O in bcc Fe, increasing dramatically the energy barrier (~80%) for O migration, and in turn, making the predicted diffusion coefficient of O in bcc Fe in favorable accord with experiments.

bcc Fe & its oct & tet interstitial sites – **structure**

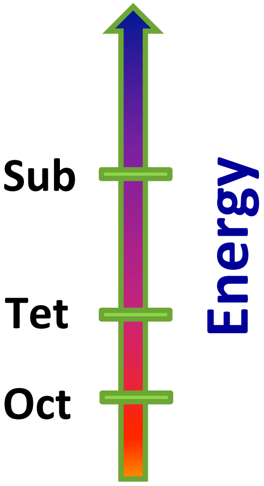


Fe:	**2a**	**(0, 0, 0)**
O-oct:	**6b**	**(0 ½ ½)**
O-tet:	**12d**	**(0 ½ ¼)**

Site preference of O in bcc Fe – w.r.t. bcc Fe and AFM α-Fe_2O_3



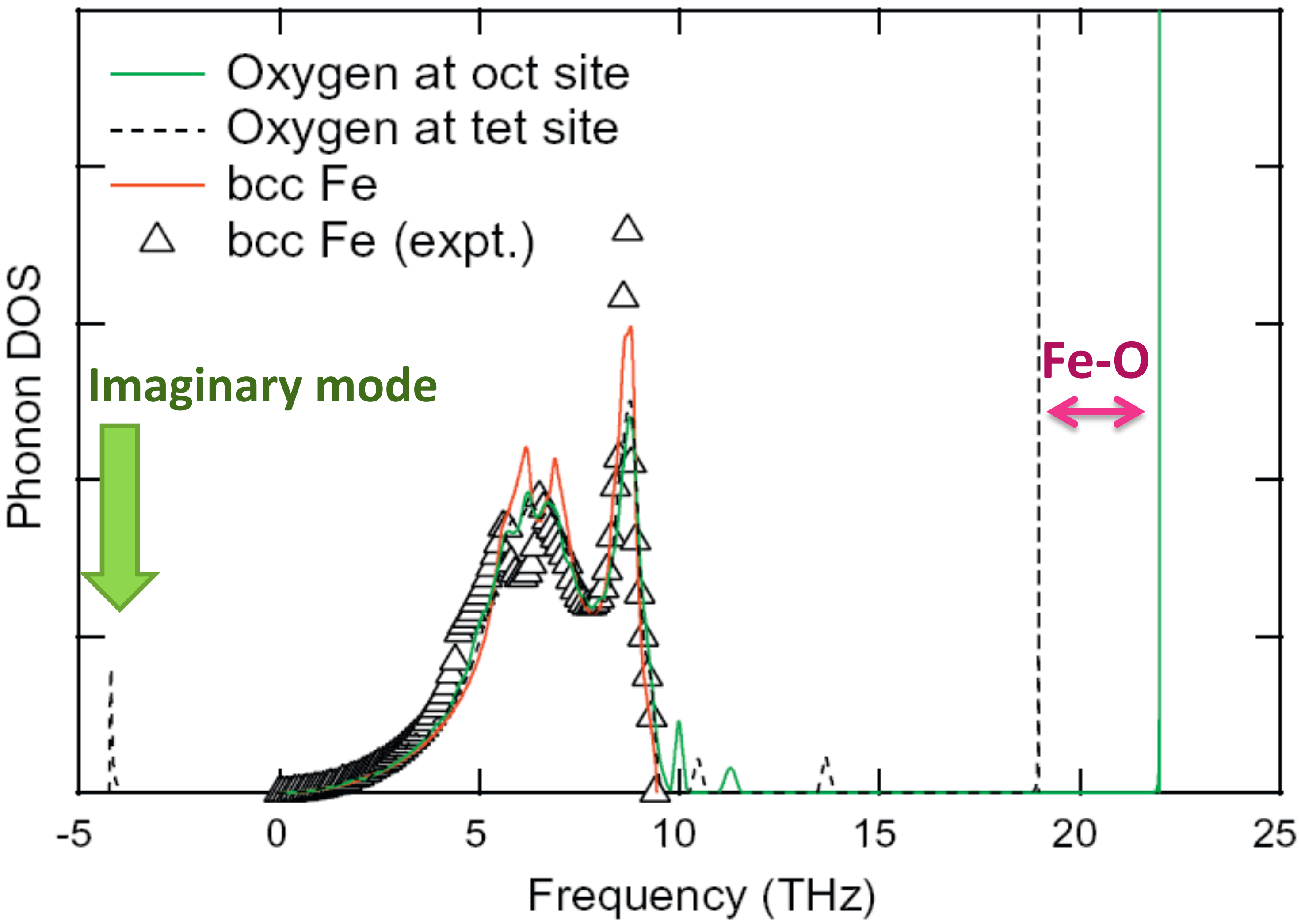
bcc Fe … **AFM Fe_2O_3**



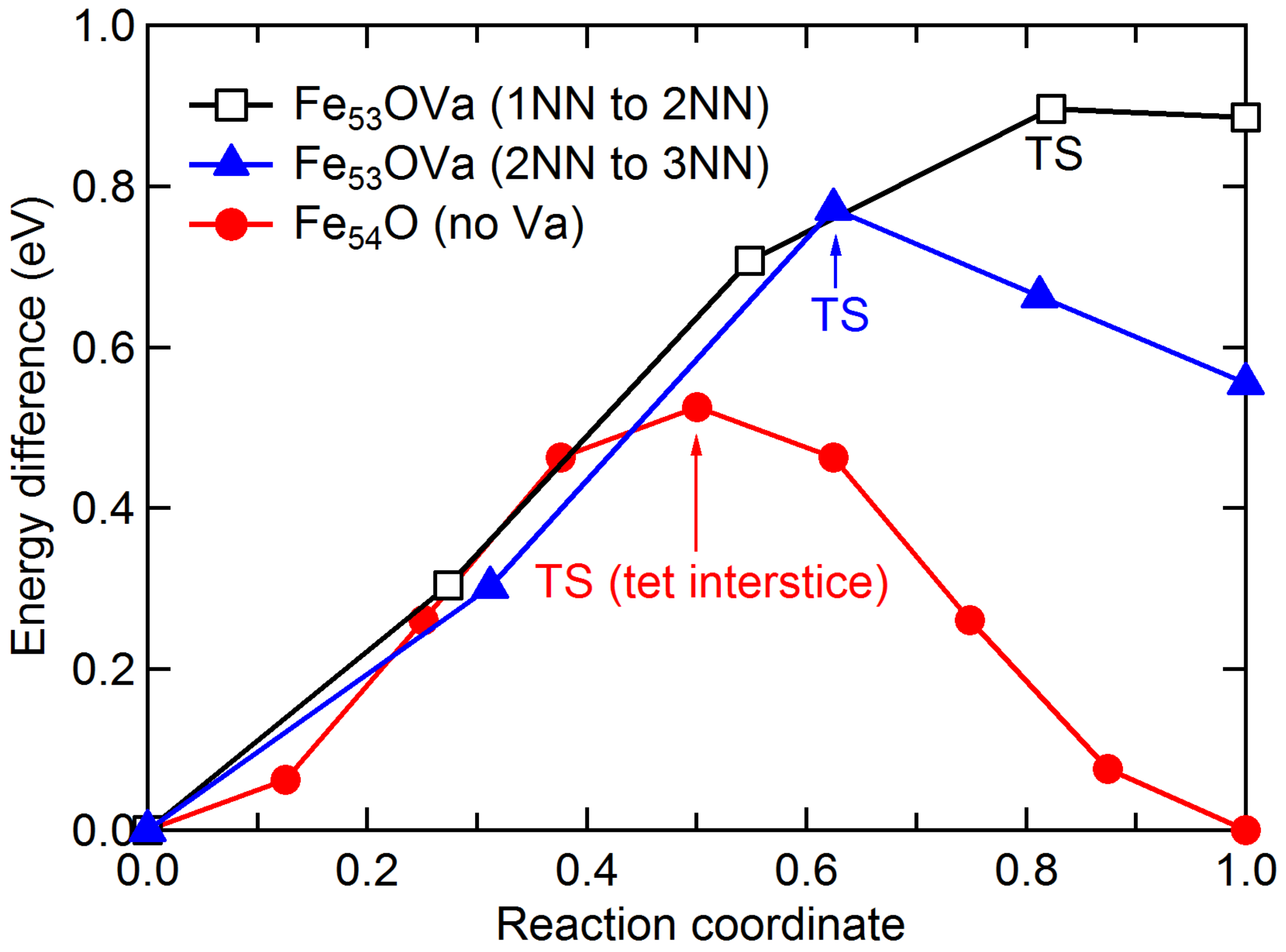
Each composition

Phonon DOS of bcc Fe (without Va)

– O at oct & tet sites

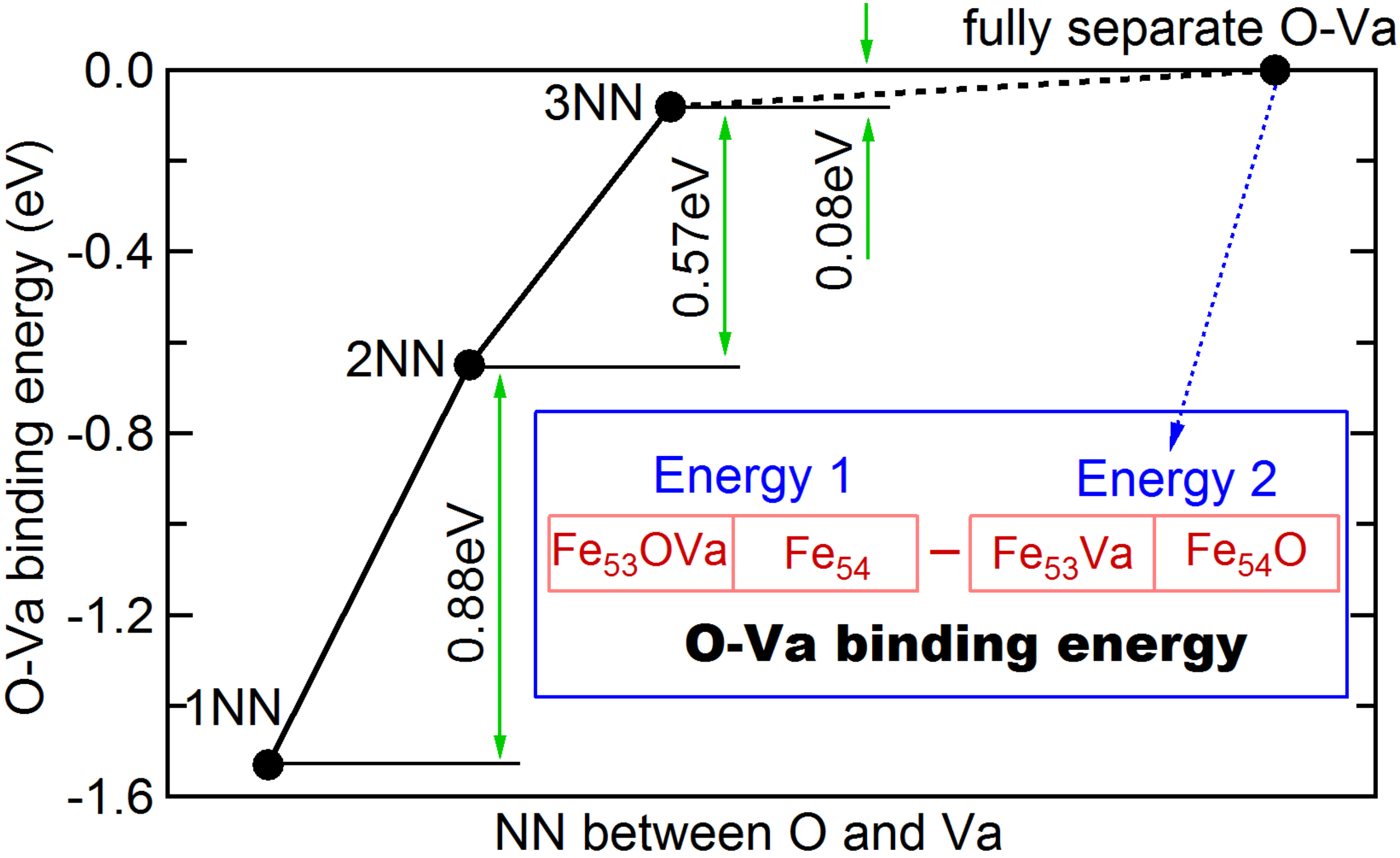


Minimum energy pathways of O diffusion in bcc Fe **with/without Va**



O-Va binding energy in bcc Fe

- **using the 3×3×3 supercell**



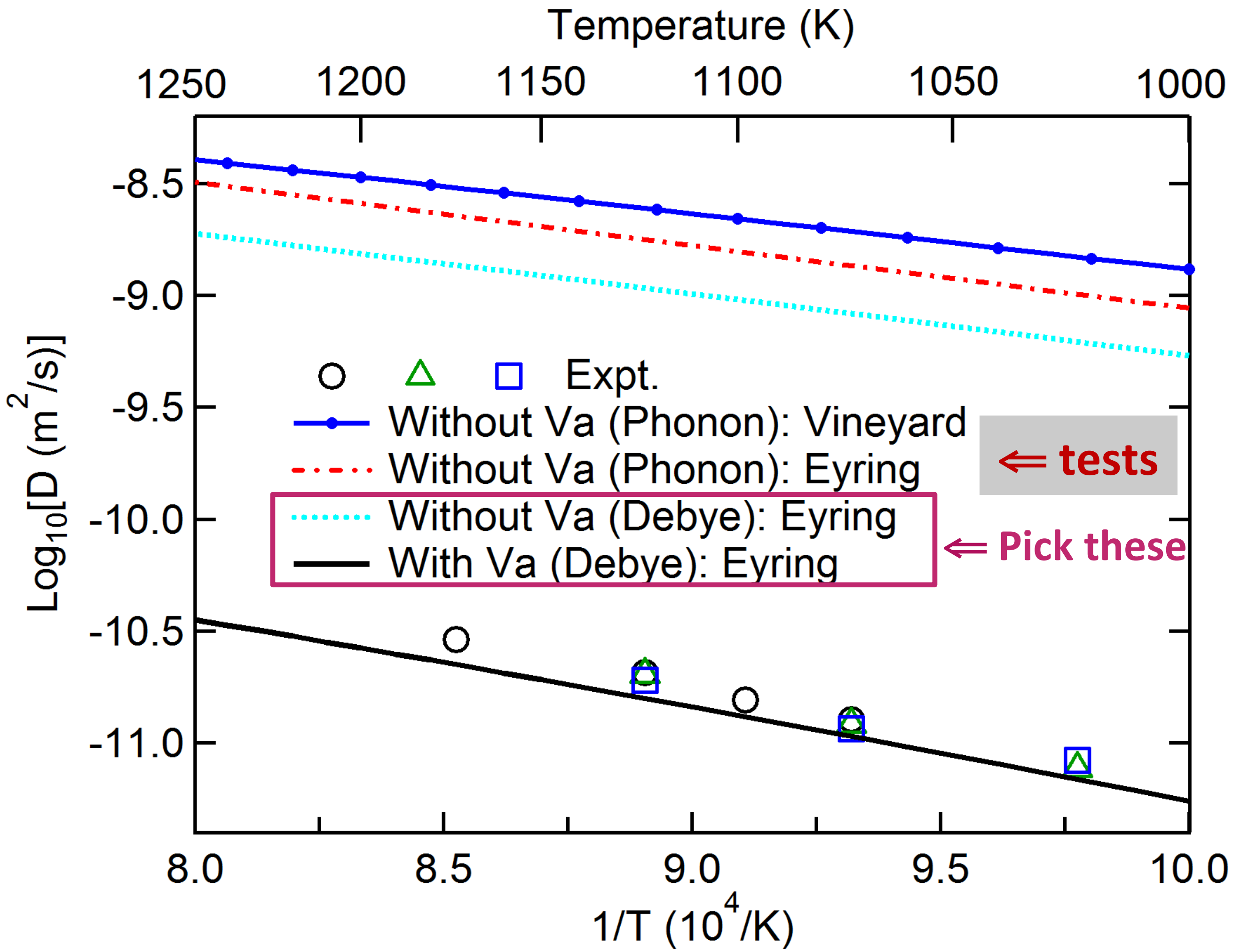
Activation energy of O diffusion in bcc Fe

- energy (kJ) between oct & tet sites

PW91: 2×2×2 cell	49.8	PBEsol: 3×3×3 cell	39.1
PW91: 3×3×3 cell	38.8	PBE-CINEB-bulk-relax (O-T)	51.4
PW91: 4×4×4 cell	38.9	PBE-CINEB-bulk-relax (O-T-O)	49.6
PBE: 2×2×2 cell	61.5	PBE-CINEB-bulk-fix (O-T-O)	52.1
PBE: 3×3×3 cell	47.0	PBE-CINEB-relax-**Va** (O-T-O)	**98.8**
PBE: 4×4×4 cell	47.8	Expt.: Swisher 1967	177
PBE: 3×3×3 (charged)	51.9	Expt.: Barlow 1969	167
LDA: 3×3×3 cell	16.1	Expt.: Takada 1986	**86±6** **90±7**

Arrhenius plots of O diffusion in bcc Fe **with/without Va**

$$D = D_0 \exp(-Q/kT)$$

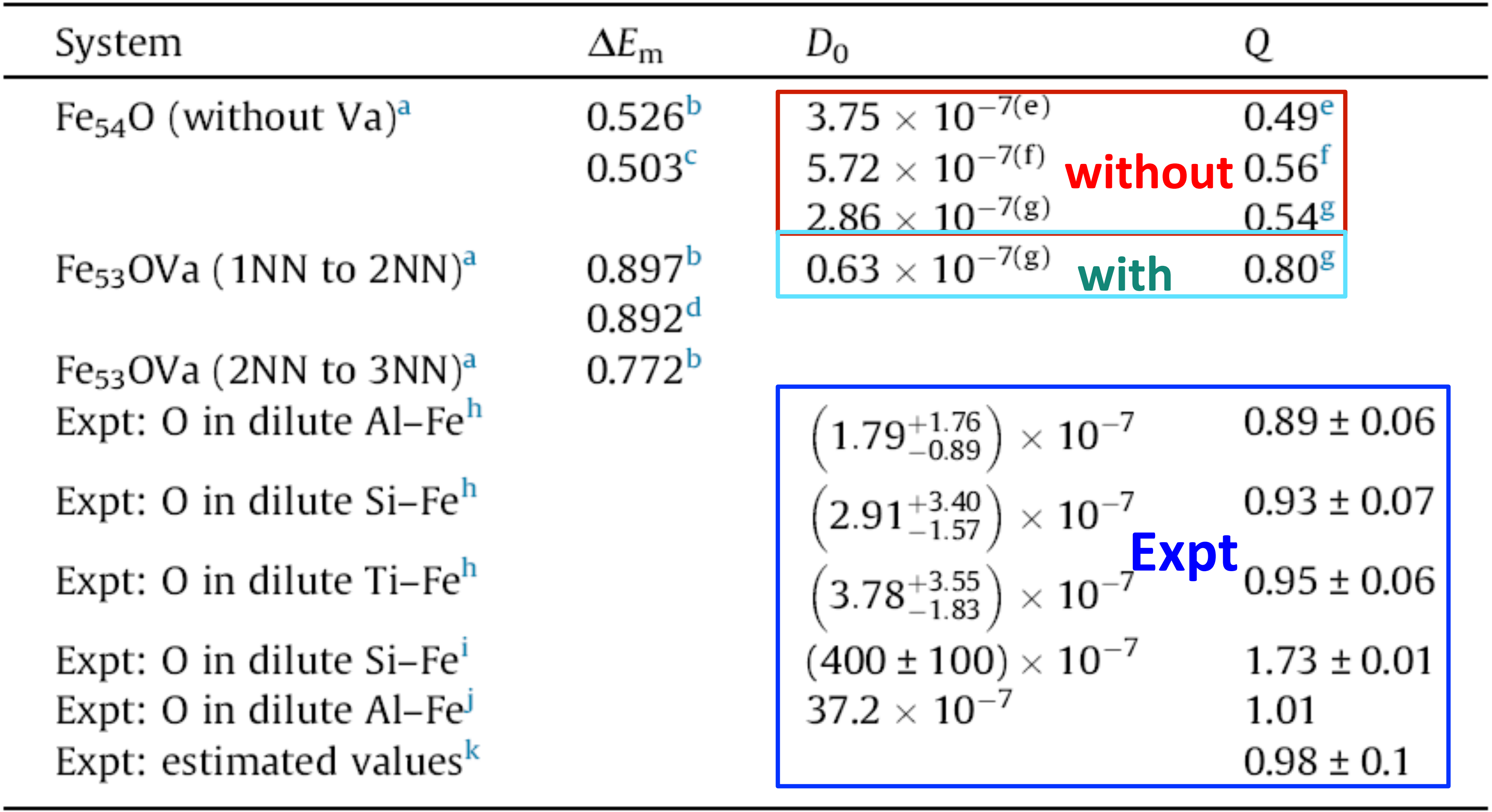


⇐ **tests**

⇐ **Pick these**

Arrhenius plots of O diffusion in bcc Fe **with/without Va (details)**

$$D = D_0 \exp(-Q/kT)$$



System	ΔE_m	D_0	Q
$Fe_{54}O$ (without Va)[a]	0.526[b]	$3.75 \times 10^{-7(e)}$	0.49[e]
	0.503[c]	$5.72 \times 10^{-7(f)}$	0.56[f]
		$2.86 \times 10^{-7(g)}$	0.54[g]
$Fe_{53}OVa$ (1NN to 2NN)[a]	0.897[b]	$0.63 \times 10^{-7(g)}$	0.80[g]
	0.892[d]		
$Fe_{53}OVa$ (2NN to 3NN)[a]	0.772[b]		
Expt: O in dilute Al–Fe[h]		$\left(1.79^{+1.76}_{-0.89}\right) \times 10^{-7}$	0.89 ± 0.06
Expt: O in dilute Si–Fe[h]		$\left(2.91^{+3.40}_{-1.57}\right) \times 10^{-7}$	0.93 ± 0.07
Expt: O in dilute Ti–Fe[h]		$\left(3.78^{+3.55}_{-1.83}\right) \times 10^{-7}$	0.95 ± 0.06
Expt: O in dilute Si–Fe[i]		$(400 \pm 100) \times 10^{-7}$	1.73 ± 0.01
Expt: O in dilute Al–Fe[j]		37.2×10^{-7}	1.01
Expt: estimated values[k]			0.98 ± 0.1

Summary

- Exploration of site preference, diffusion pathways & barriers, and diffusivities of oxygen
- Existence of strong O-Va binding energy in metals
- Va-modified interstitial diffusion mechanism proposed to quantitatively predict diffusivity of oxygen in metals
- Case studied in fcc Ni and bcc Fe