First-Principles Calculations of Vacancy Formation Energy

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Through First-Principles Calculations, CALPHAD Modeling, and Experiments

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Why Vacancy?

- Vacancy is the simplest and commonest lattice defect;
- Vacancy migration is the dominant mechanism behind atomic transport;
- Vacancy plays very important role for surface morphology *;
- ……

* K. F. McCarty, et al., Nature, 2001

Experimental Measurement

- Experimental methods regarding the measurement of vacancies are difficult;
- Many technical questions and uncertainties exist for those experiments;
- Different experiments result in a large range of values.

Theoretical Calculation

- Calculate the total energy of a crystal with N atoms, E_0;
- Calculate the total energy of a crystal with N-1 atoms and one defect, E_1;
- Defect formation energy:

$$\Delta E_f = E_1 - \frac{N-1}{N} E_0$$

First-Principles Calculations

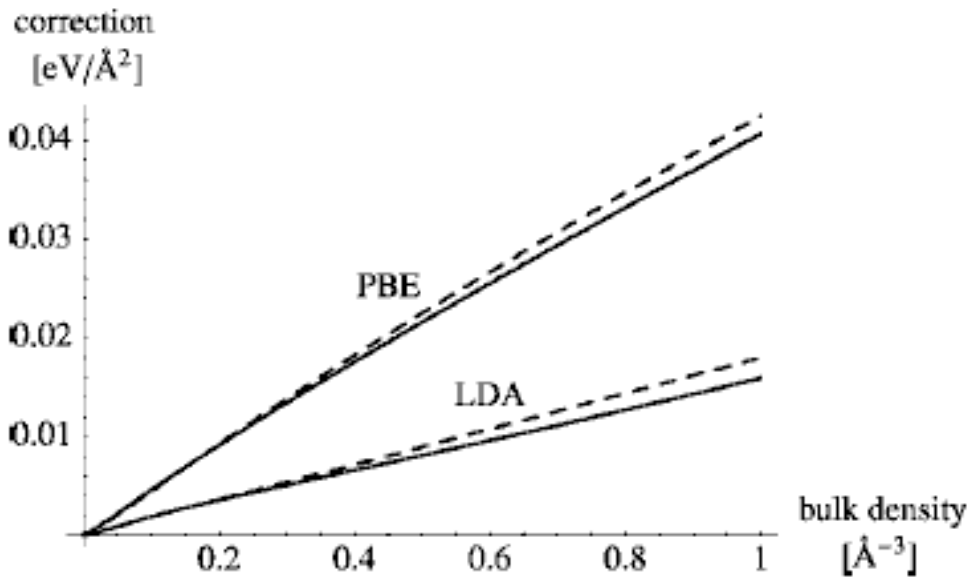
- FP calculations always underestimate vacancy formation energies.
- LDA is better than GGA for the vacancy formation energy calculation?
- Unrelaxed calculation is better than relaxed calculation for the vacancy formation energy calculation?

FP Calculation on Surface Energy

Observation: FP calculations always underestimate surface energies.

Reason: Both the LDA and GGA have intrinsic errors at surface because the many-body interaction is approximated.

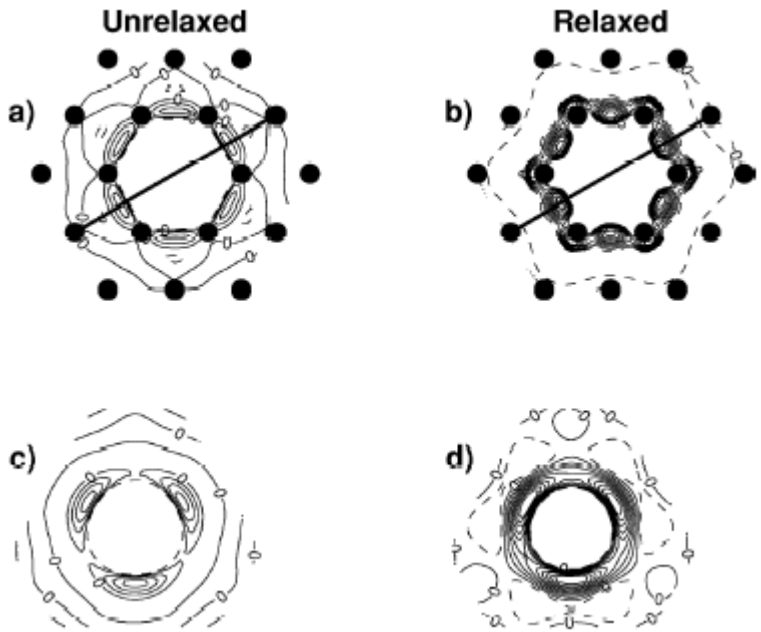
Correction for Calculated Surface Energy

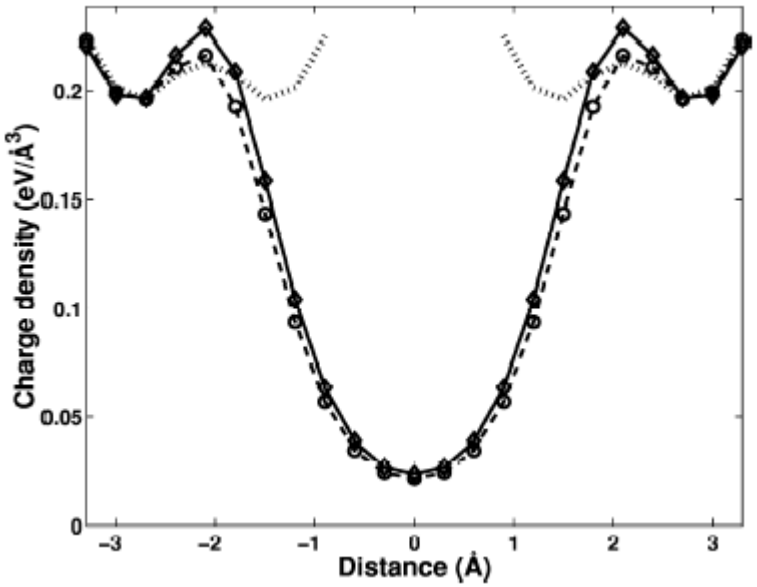


- The intrinsic errors were estimated by jellium model.
- The correction is a function of electron density.
- LDA has smaller intrinsic error than GGA.

T. R. Mattsson and A. E. Mattson, Physical Review B, 2002

Charge Density near Vacancy





K. M. Carling, et al., Physical Review B, 2003

Correction on Vacancy Formation Energy Calculation

- As the first approximation, treat the vacancy as an interior surface:

$$\Delta E_c = 4\pi R^2 \Delta\sigma$$

where R is the radius of the “hole”.

- The corrected vacancy formation energy:

$$\Delta E_f^{corrected} = \Delta E_f + \Delta E_c$$

T. R. Mattsson and A. E. Mattsson, Physical Review B, 2002

Determination of R

- The radius, R, can be estimated by fitting the electron density profile of jellium model to the that of DFT's.
- In fcc Al, R is about 1.2 A.
- Because the above calculation is very complex, the different vacancy formation volumes in different elements are usually ignored.

K. Carling, et al., Physical Review Letters, 2000

Our Treatment on R

1) Vacancy formation volume

$$\Delta V = V_1 - \frac{N-1}{N} V_0$$

2) Case I: consider a sphere of that volume, upper bound

$$R_u = \sqrt[3]{\frac{3}{4\pi}\Delta V}$$

Our Treatment on R (cont'd)

3) Case II: consider a sphere embedded into that volume, low bound

$$R_l = 0.5 * \sqrt[3]{\Delta V}$$

4) Using the ΔV and R of Al and assuming R as a weighted average of R_l and R_u, we obtain a relation between R and R_l and R_u.

Relation between R and R_l and R_u

- ΔV depends on size of supercell.
- For 32 and 54 atom supercells:

$$R = 0.82R_l + 0.18R_u$$

- For 108 and 128 atom supercells:

$$R = 0.71R_l + 0.29R_u$$

- Assume the same relations for different elements.

R of Some Elements

	$\Delta V(A^3)$	$R_l(A)$	$R_u(A)$	$R(A)$
Al (32)	12.23	1.15	1.43	1.20
Al (108)	11.37	1.12	1.40	1.20
Ni (32)	7.12	0.96	1.19	1.00
Ni (108)	6.79	0.94	1.17	1.01
Mo (54)	9.78	1.07	1.33	1.12
Mo (128)	8.99	1.04	1.29	1.11
Ta (54)	10.02	1.08	1.34	1.13
Ta (128)	9.81	1.07	1.33	1.14

Vacancy Formation Energy of Some Fcc Phases

Element	Cell Size, N	E_0	E_1	ΔE_f	ΔE_c	$\Delta E_f^{corrected}$
Al (fcc)	32	-118.0	-113.8	0.568	0.151	0.719
	108	-398.5	-394.3	0.511		0.662
	Exp.	0.64, 0.71, 0.66, 0.62, 0.69, 0.67, 0.66, 0.66, 0.66				
Ni (fcc)	32	-175.4	-168.5	1.40	0.48	1.88
	108	-592.1	-585.2	1.39	0.49	1.88
	Exp.	1.72, 1.73, 1.73, 1.55, 1.54				

Energies in eV.

Vacancy Formation Energy of Some Bcc Phases

Element	Cell Size, N	E_0	E_d	ΔE_f	ΔE_c	$\Delta E_f^{corrected}$
Mo (bcc)	54	-584.7	-571.3	2.58	0.28	2.86
	128	-1386.2	-1372.7	2.69	0.27	2.96
	Exp.	2.24, 3.0, 3.0, 2.9, 3.6				
Ta (bcc)	54	-622.6	-637.3	2.94	0.20	3.14
	128	-1510.8	-1496.1	2.91	0.20	3.11
	Exp.	2.54, 2.8				

Energies in eV.

Summary

- Some corrections should be applied to FP calculation on vacancy formation energy;
- Mattsson's correction can improve the calculated vacancy formation energy in Al, Ni, Mo, but not for Ta.