SAND2007-5441P

Supercell size dependences in density-functional-theory results for defects in silicon

A. F. Wright, N. A. Modine, and R. R. Wixom
Sandia National Laboratories, New Mexico, USA

Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company,
the United States Department of Energy under contract DE-AC04-94AL85000.

Sandia National Laboratories

OUTLINE:

- Technical difficulties in density-functional-theory calculations for point defects in supercells using periodic boundary conditions
- Circumventing the Coulomb divergences that arise when treating charged point defects using the UBC and LMCC methods
- Equivalence of the UBC and LMCC methods when extrapolating supercell formation energies to infinite sized supercells
- Evaluation of analytic corrections for removing supercell dependences in formation energies obtained using the UBC and LMCC methods
- Extrapolated results for the Si vacancy

Technical difficulties in calculations for point defects

- Density-functional-theory (DFT) is widely used to compute formation energies and electronic energy levels of point defects
- DFT calculations typically employ supercells and periodic boundary conditions (PBC's), which yield an efficient computational scheme
- PBC's introduce undesirable strain and electrostatic interactions between the defect and its periodic replicas
- These interactions influence the atomic configuration and formation energy of the defect, yielding a supercell size dependence
- Supercell size dependences are significant for charged defects and non-negligible even for uncharged defects
- Analytic corrections have been proposed to remove supercell size dependences, but results have not been satisfactory

Circumventing the Coulomb divergence

- Two methods are available to remove the Coulomb divergences that arise in supercell calculations for charged defects

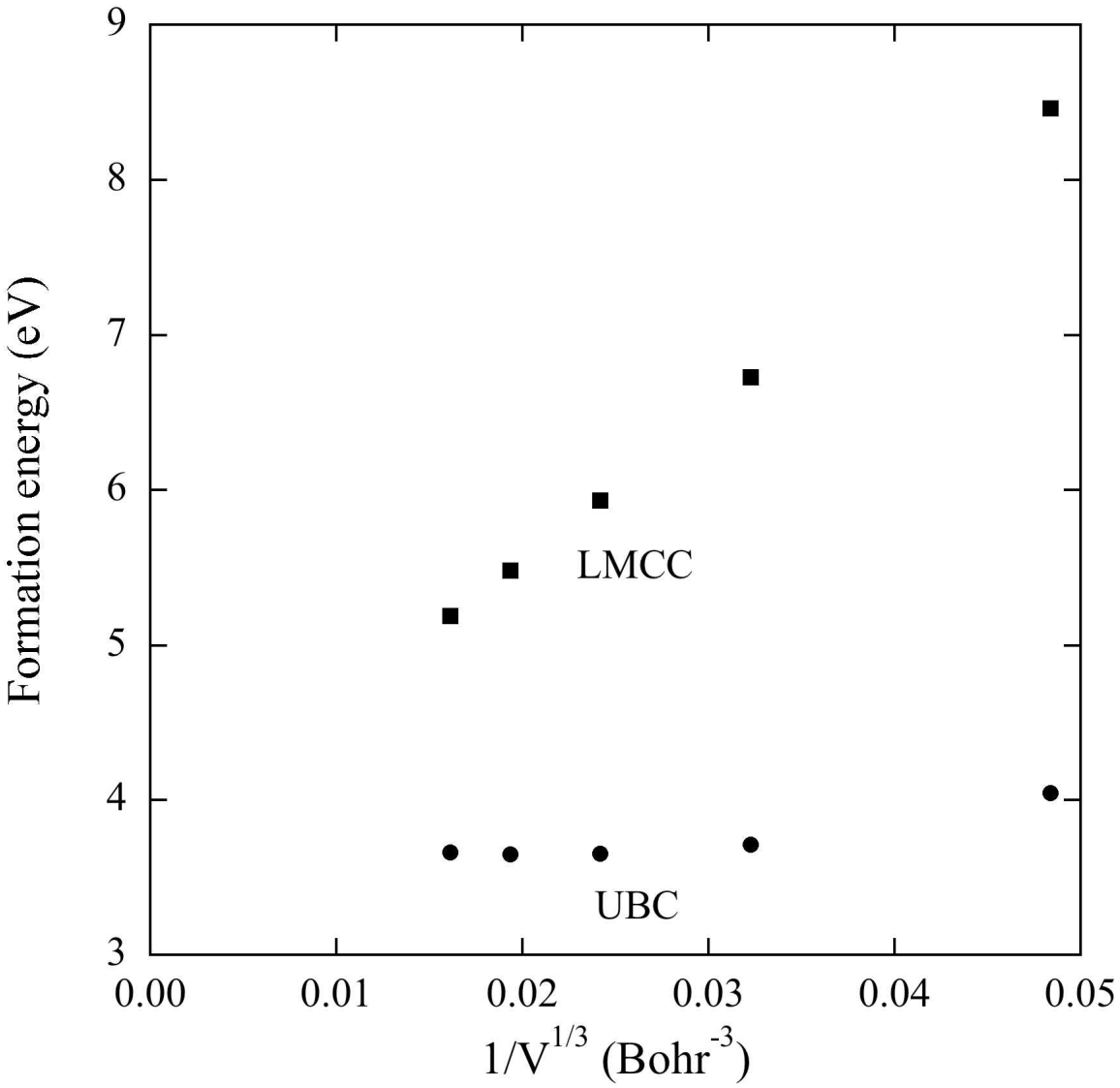
- The uniform-background-charge (UBC) method subtracts a uniform density, $-q/V$, from the supercell electron density where V is the volume of the supercell

- The local-moment-counter-charge (LMCC) method removes the long-ranged part of the defect potential by subtracting a gaussian density from the supercell electron density and adding the potential due to the gaussian density in a Wigner-Seitz cell to the potential arising from the modified electron density [PRB 60, 1551 (1999)]

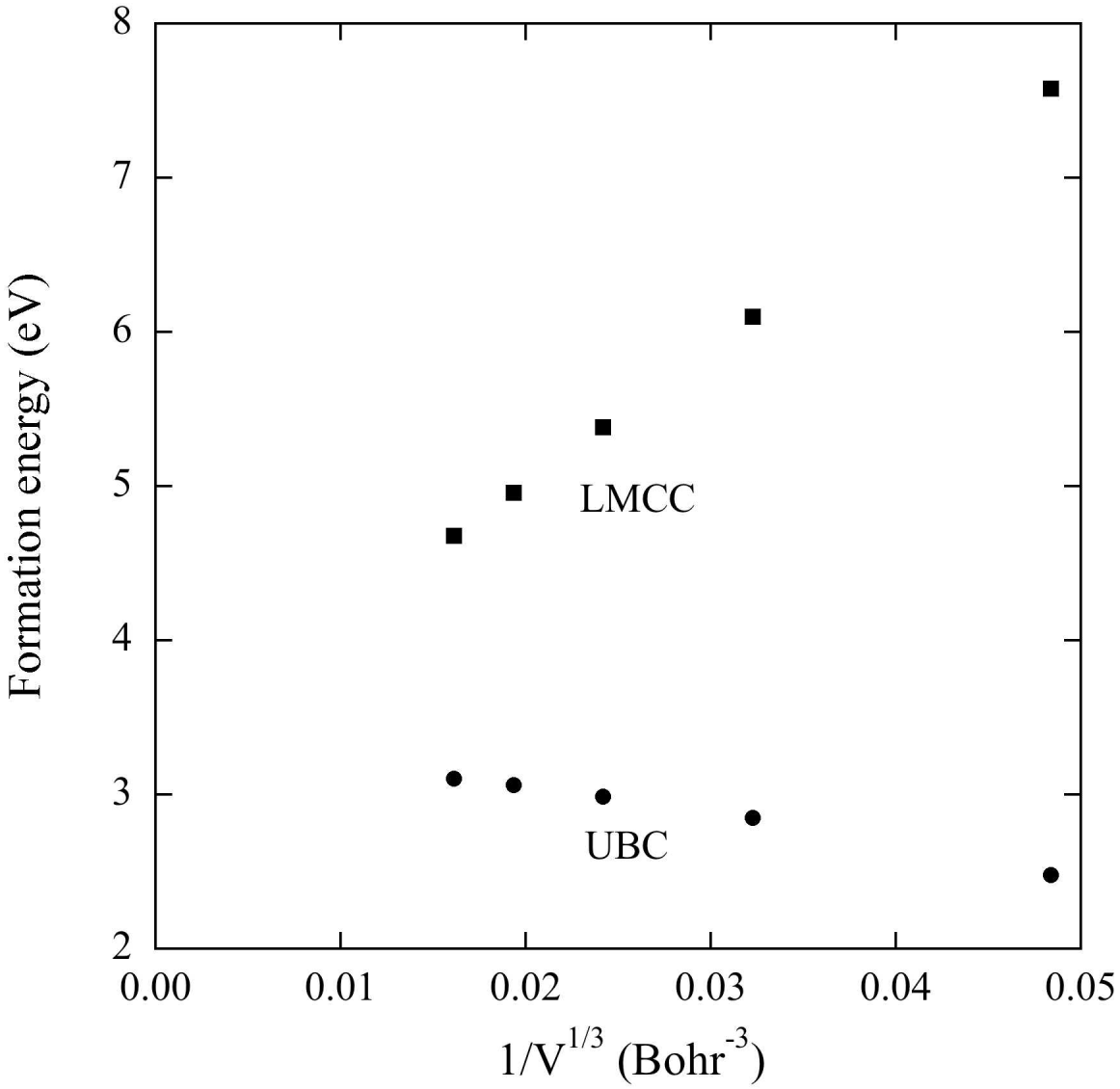
- The LMCC method modifies the expressions for total energy and forces, while the UBC method does not {PRB 74, 235209 (2006)]

- The UBC and LMCC methods produce very different supercell size dependences

Supercell size dependences for the unrelaxed +2 Si vacancy in simple cubic supercells using the UBC and LMCC methods



Supercell size dependences for the unrelaxed +2 Si self-interstitial in simple cubic supercells using the UBC and LMCC methods



Details of the calculations

- Socorro code with a plane wave basis, norm-conserving pseudo-potentials, PBE formulation of the GGA, and Monkhorst-Pack sampling of the Brillouin zone
  - Converged with respect to basis set: 20/80 Ryd energy cutoffs
  - Converged with respect to Brillouin-zone sampling
  - Used nominal 64-, 216-, 512-, 1000-, and 1728-atom supercells

- Formation energies with the Fermi level at the valence-band edge were computed using the equation

$$E^f[D;V] = E_T[D;V] - \left(\frac{N_D}{N_{bulk}}\right) E_T[\text{bulk};V] + q\varepsilon_{VBE}[\text{bulk}]$$

  - D is the defect [vacancy (V_{Si}) or self-interstitial (Si_I)]
  - q is the defect charge state
  - N_D is the number of atoms in the defect supercell and E_T is the energy
  - N_{bulk} is the number of atoms in the bulk supercell and E_T is the energy

Fits to the UBC and LMCC formation energies

- The UBC and LMCC formation energies were fit to the equation

$$E^f[D;L] = E^f[D;L\to\infty] + \frac{A_1}{L} + \frac{A_3}{L^3} + \frac{A_5}{L^5} \;;\; L = V^{\frac{1}{3}}$$

  and the results are plotted on the next two pages

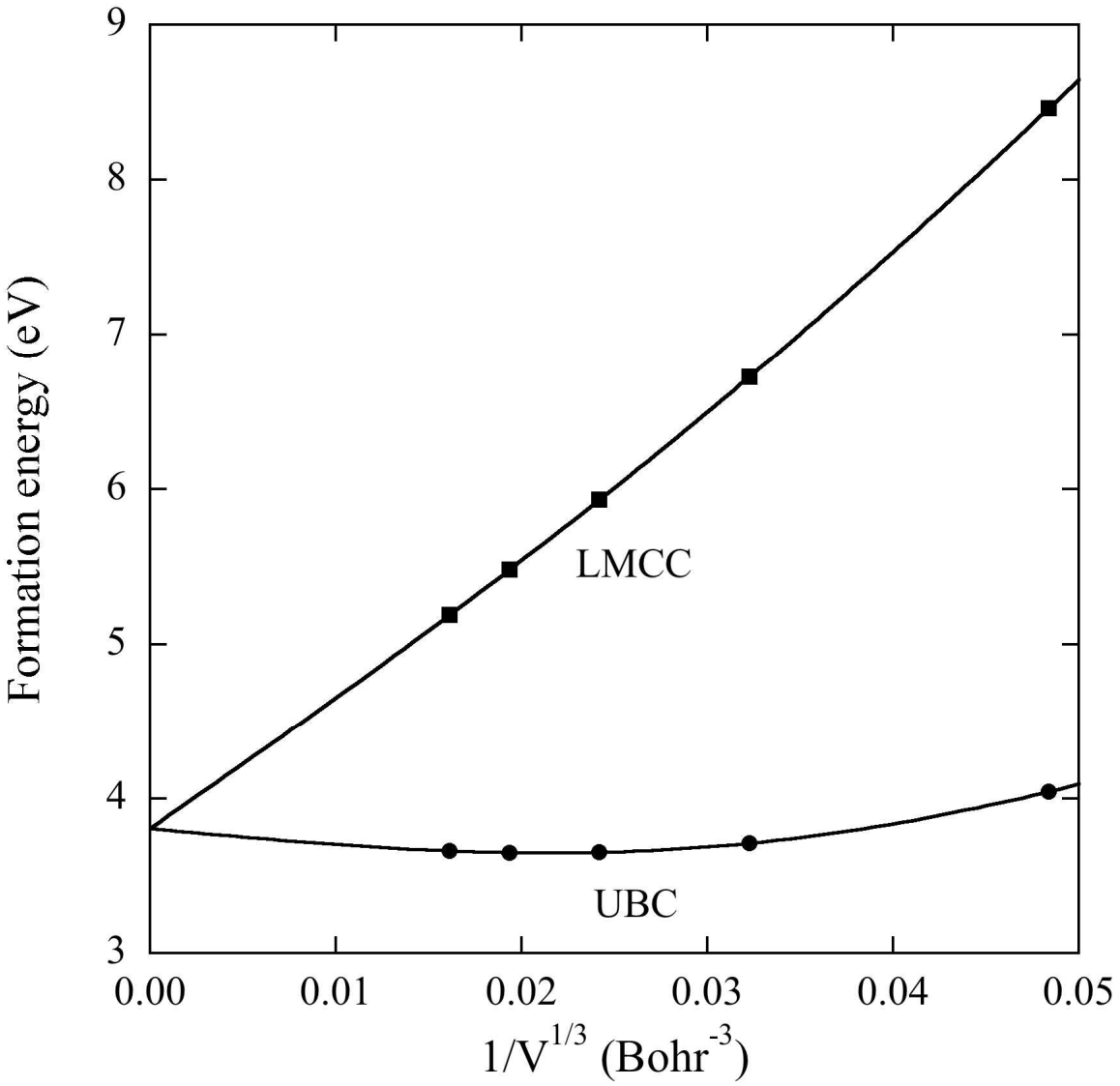
- The extrapolated UBC and LMCC formation energies (at $L\to\infty$) differ by only 2 meV for V_{Si} and 13 meV for Si_I as expected from their total energy expressions [PRB 74, 235209 (2006)]

- The fits are good judging from the sum of the squared differences between the computed and fitted results (X^2):

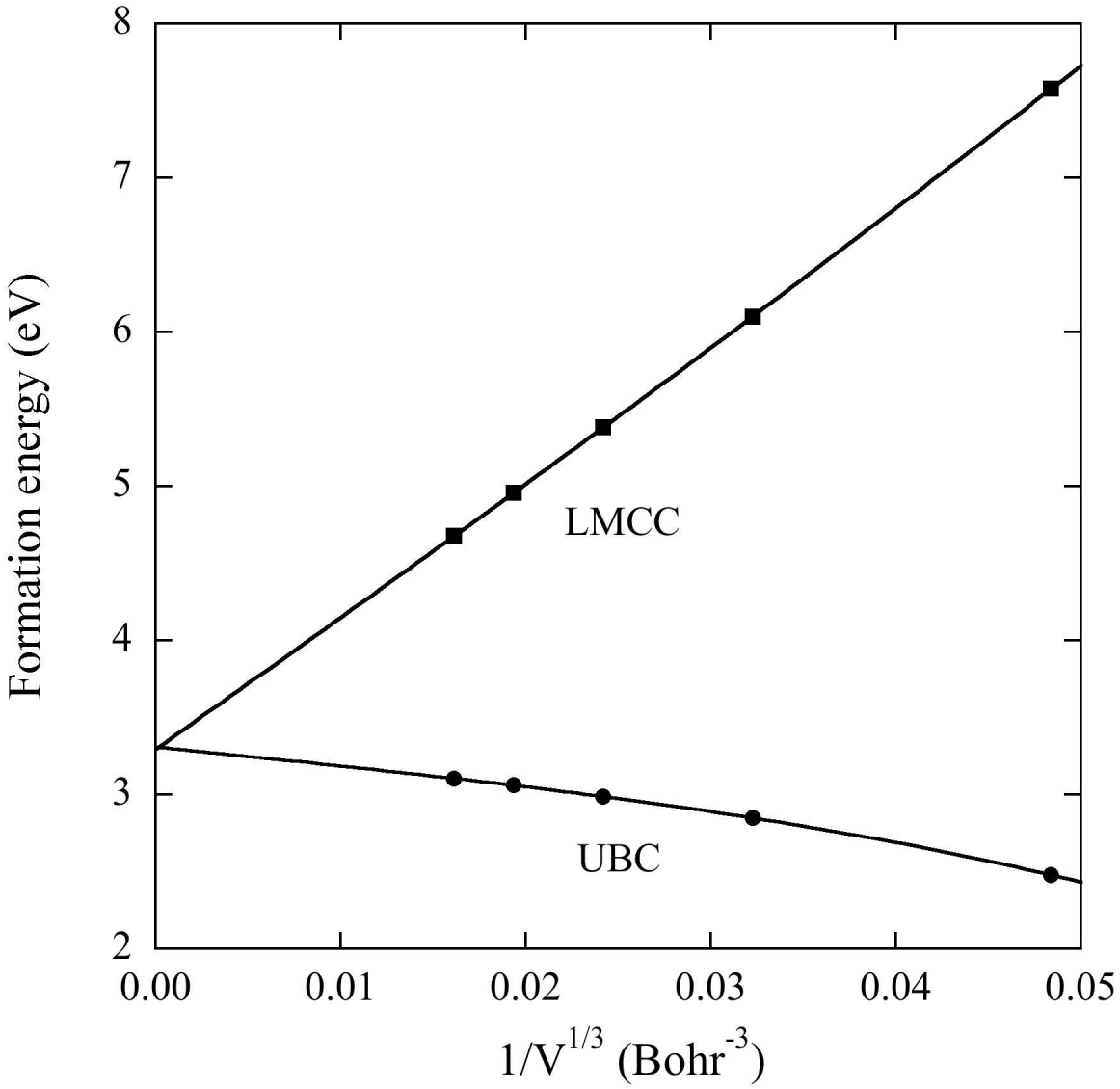
  - V_{Si}: X^2 = 4.579×10^{-8} (UBC) and 9.322×10^{-9} eV^2 (LMCC)
  - Si_I: X^2 = 4.357×10^{-8} (UBC) and 2.073×10^{-7} eV^2 (LMCC)

- Fitted values of A_1, A_2, and A_3 indicate that both the UBC and LMCC formation energies have consequential supercell dependences that differ for V_{Si} and Si_I

Fits to the supercell formation energies of the unrelaxed +2 Si vacancy obtained in simple cubic supercells using the UBC and LMCC methods



Fits to the supercell formation energies of the unrelaxed +2 Si self-interstitial obtained in simple cubic supercells using the UBC and LMCC methods



Analytic corrections:

- For the UBC method, a simple expression is available for A_1:

$$A_1 = -\frac{2.8373q^2}{\varepsilon}$$

- Our tests indicate that this correction does not fully remove supercell dependences [PRB 74, 235209 (2006)]

- For the LMCC method, Schultz suggested that supercell dependences can be removed by subtracting a polarization energy of the form

$$E_p = \left(1-\frac{1}{\varepsilon}\right)\frac{q^2}{\left(R_{Jost}-0.8\right)} \; ; \; R_{Jost} = L\Big/\left[\frac{4\pi}{3}\right]^{\frac{1}{3}}$$

- Our tests indicate that this correction does not fully remove supercell dependences and yields results that disagree with the extrapolated values [PRB 74, 235209 (2006)]

Extrapolated results for the Si vacancy:

- Formation energies were computed for relaxed Si vacancies in the +2, +1, 0, -1, and -2 charge states in 216-, 512-, and 1000-atom supercells using LDA and PBE exchange and correlation

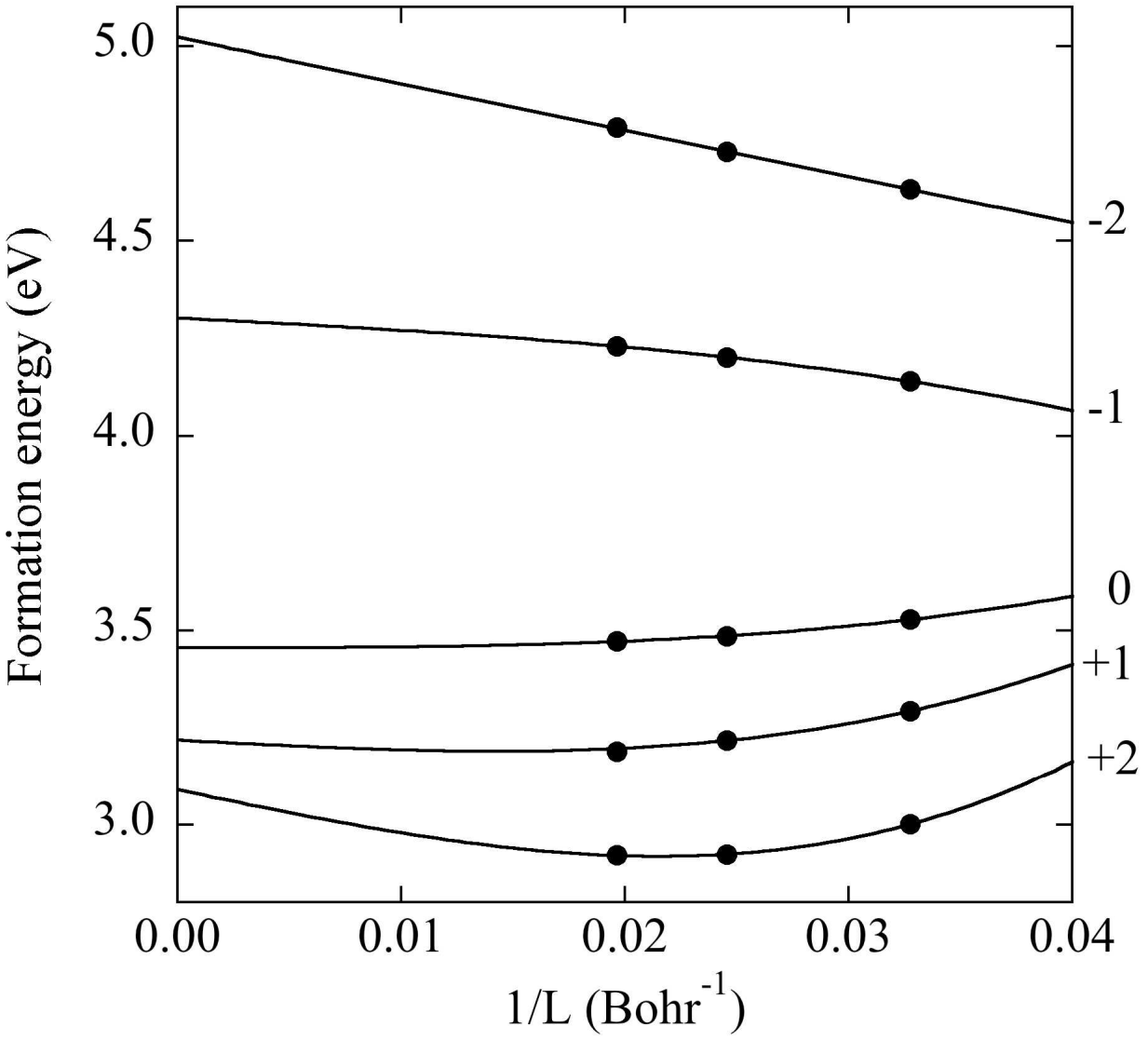
- The supercell formation energies with the Fermi level at the valence band edge were fit to the equation

$$E^f\left[\mathrm{V}_{\mathrm{Si}}^q;L\right]=E^f\left[\mathrm{V}_{\mathrm{Si}}^q;L\to\infty\right]-\frac{\alpha q^2}{\varepsilon L}+\frac{A_3}{L^3}\ ;\ L=V^{\frac{1}{3}}$$

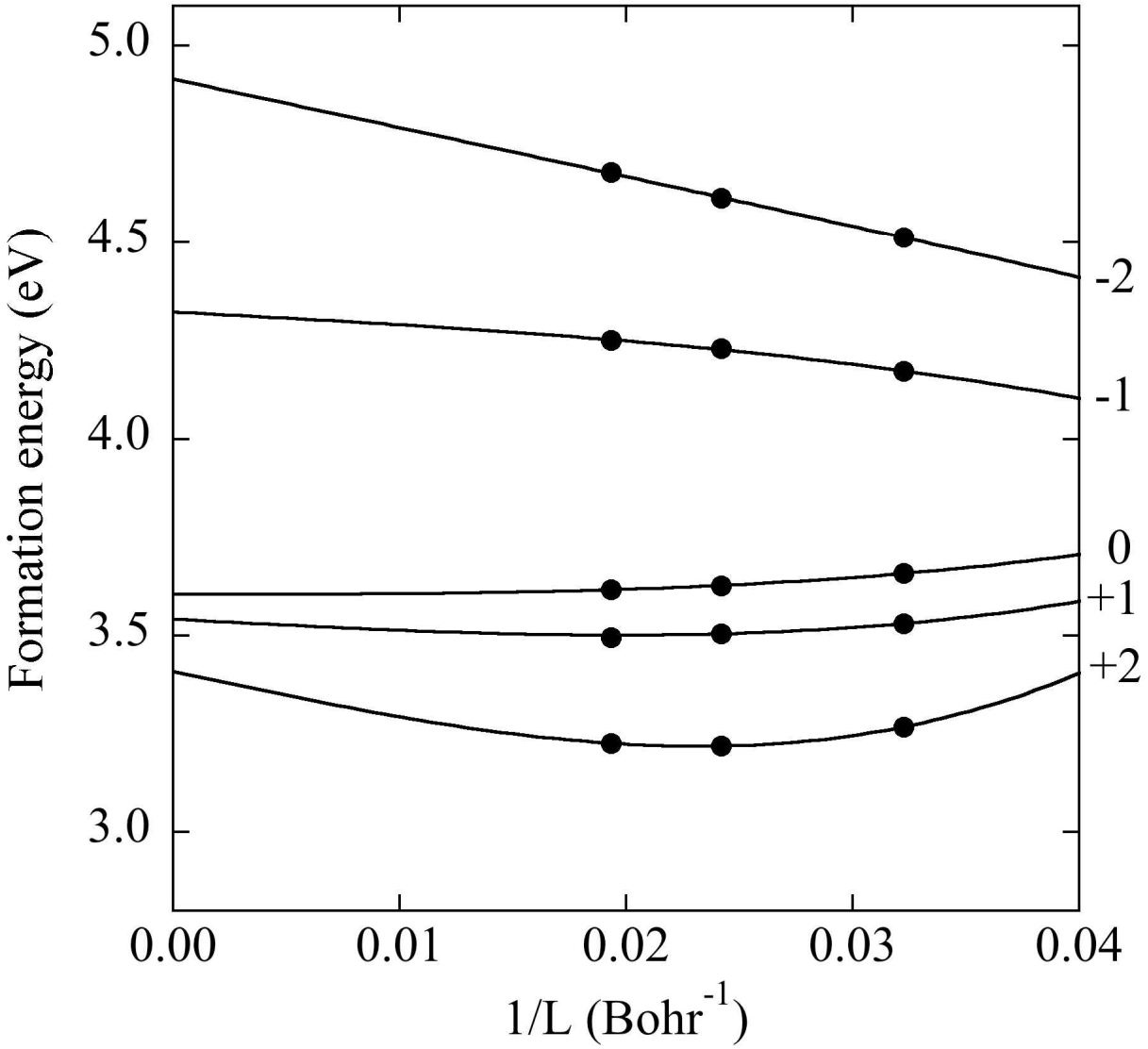
  - α = 2.8373 is the Madelung constant for a simple cubic lattice of point charges
  - ε is the computed DFT dielectric constant (LDA: 12.9, PBE: 12.6)

- The fits were good as shown on the following three pages

Fits to the supercell formation energies of relaxed Si vacancies obtained in simple cubic supercells using the UBC method and the LDA



Fits to the supercell formation energies of relaxed Si vacancies obtained in simple cubic supercells using the UBC method and the PBE



Fits to the supercell formation energies of Si vacancy saddle points obtained in simple cubic supercells using the UBC method and the PBE