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Ab initio formation volume of charged defects

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When the formation volume of charged defects is evaluated by a straightforward cell minimization, the obtained *ab initio* formation volume is affected by a bias. Furthermore, the error does not vanish with increasing supercell sizes. The quantity to be minimized with respect to volume is not the defective supercell energy, but rather the formation energy of the charged defect. The formation energy of a charged defects contains additional correction terms, which have a non-vanishing derivative with respect to the volume. Surprisingly, the usually predominant electrostatic correction is shown to have almost no effect on the formation volume, whereas the small potential alignment correction is demonstrated to yield a huge correction that does not vanish for infinitely large systems.

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I. INTRODUCTION

The advances made during the recent years in the *ab initio* description of defects in semiconductors and insulators are impressive.[1] The newest functionals of density functional theory[2] or the progresses in many-body perturbation theory have permitted unprecedented accuracy in the description of the properties of charged or neutral defects in semiconductors.[3,4] However, the convergence with system size (or supercell in the common case of periodic boundary conditions) is still an issue.

While it is an important piece of information,[5] the formation volume of a point defect is one of these properties that is still poorly understood for charged systems. Through its relation with elastic strain field induced by the presence of defects, the formation volume pilots the variation of defect enthalpies with stress,[6] such as defect concentrations and diffusion properties.[7] It contributes to the possible segregation of point defects on extended defects (dislocations, grain boundaries, cavities, etc.)[8] and controls the elastic interaction of defects with these sinks.[9] It is also highly relevant for irradiated materials because it is a major contribution to the swelling effect observed under irradiation.[10]

Despite the importance of the formation volume of defects, it is striking to observe that very few *ab initio* evaluations for charged defects have been published so far. Most of the works on vacancies[11–14] use an indirect evaluation of the volume of defects: the volume enclosed by the tetrahedron formed by the four first nearest neighbors to the vacancy. Whereas this value is relevant for the lifetime of the positron in positron annihilation spectroscopy, it provides a different meaning from the formation volume itself. Furthermore, this somewhat indirect approach cannot easily be generalized to other types of defects beyond vacancies. The studies that actually minimized the energy with respect to the supercell size and shape (see below the formal definitions) obtained a surprising behavior: the formation volume appears almost linear with the charge state. This is exemplified in Fig. 1. Besides the particular case of V_{Si}^{2+} which will be discussed in detail later, all the considered defects show the same linear trend. The same behavior was also observed in a completely different system, ZnO, for a wide variety of defect types.[15]

It is clear that the charge state induces local rearrangement of the neighboring atoms; however, it is more dubious that the charge state should imply a linear change of volume, which would only weakly depend on the defect type. The purpose of the present article is to clarify this puzzling situation.

In the following, we demonstrate that the formation volume is affected by the electrostatic and potential alignment corrections, which should be included to properly define the formation energy of charged defects. In particular, we show that the potential alignment, which is a very small and rapidly converging correction to the formation energy, yields a large correction to the formation volume, which does not vanish but rather converges to a finite value for infinitely large systems. Once the correction is correctly included, the formation volume only weakly varies with the charge state, except for defects exhibiting vastly different arrangements of atoms depending on charge states, as will be exemplified by the silicon vacancy. Finally, we propose a practical way to perform cell relaxation including the required correction.

II. FORMATION ENERGY AND FORMATION VOLUME

Let us recall here the basic definitions of quantities pertaining to charged defects. The formation energy E_f of a charged defect X^q is given by the relation[16,17]

$$E_f(X^q) = E(X^q) - E(\text{perfect}) - \sum_i n_i\mu_i + \Delta E^{\text{e.s.}} + q(\epsilon_{\text{VBM}} + \mu_e + \Delta V), \quad (1)$$

where q is the charge state, $E(X^q)$ is the energy of a supercell containing the defect X^q, $E(\text{perfect})$ is the reference supercell without the defect, and n_i and μ_i are the numbers and chemical potentials of the elements necessary to create the defective supercell starting from the perfect one. When dealing with charged defects, additional terms are added in Eq. (1). First, the additional charge gives rise to an electrostatic interaction with the images induced by the use of periodic boundary conditions, term labeled $\Delta E^{\text{e.s.}}$ Second, the additional charge comes from an electron reservoir with a chemical potential, the Fermi level μ_e. The Fermi level is usually referred to the valence band maximum of the pristine solid ϵ_{VBM}. However, there is a discontinuity in the potential between the defective supercell and the pristine cell, so that a potential alignment correction ΔV has to be added in Eq. (1). The exact form of the two corrections $\Delta E^{\text{e.s.}}$ and ΔV is still the subject of intense

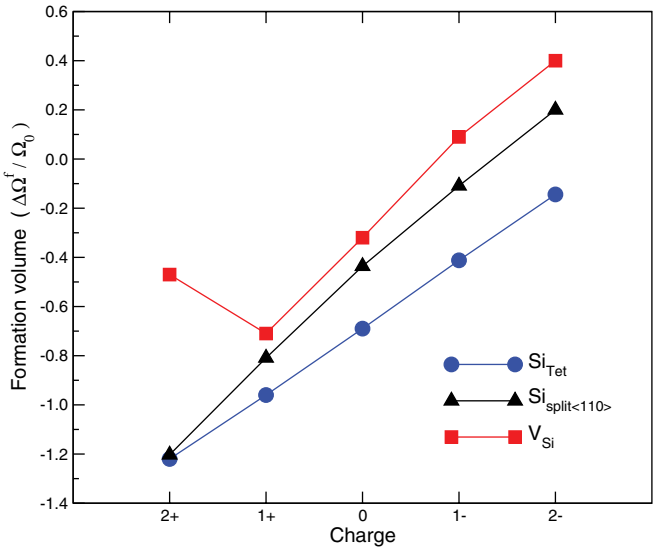

FIG. 1. (Color online) Formation volume of a tetrahedric self-interstitial (Si_{Tet}, circle symbols), a split self-interstitial ($Si_{split\langle 110\rangle}$, triangle symbols), and a vacancy (V_{Si}, square symbols) as a function of charge state, obtained by the straight minimization of the stress in a 216 ± 1 atom silicon supercell.

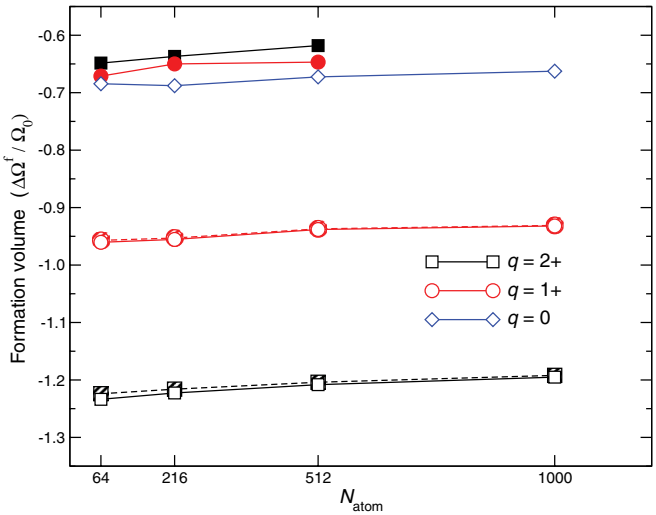

FIG. 2. (Color online) Convergence of the formation volume of a tetrahedric self-interstitial atom Si_{Tet} in silicon as a function of supercell size for charge state 2+ (squares), 1+ (circles), and 0 (diamonds). The open symbols report the uncorrected volumes, the striped symbols the volumes corrected for the electrostatics, and the full symbols the volumes corrected for the potential alignment.

debate in the community.[14,18–27] Our favored expressions for the two corrections will be specified in detail in the following section.

The elastic effect of including defects onto the volume of the system is usually measured by two related quantities: the relaxation volume $\Delta\Omega^{\text{rel}}$

$$\Delta\Omega^{\text{rel}} = \Omega(X^q) - \Omega(\text{perfect}), \tag{2}$$

and the formation volume $\Delta\Omega^{\text{f}}$

$$\Delta\Omega^{\text{f}} = \Omega(X^q) - \frac{N_{\text{defective}}}{N_{\text{perfect}}}\Omega(\text{perfect}), \tag{3}$$

where $\Omega(X^q)$ is the equilibrium volume of the supercell containing the defect X^q, and Ω(perfect) is the equilibrium of the perfect supercell. Note that the latter is properly defined for elemental solids only. For simplicity our presentation is restricted to isotropic volume and pressure change, but the generalization to anisotropic deformation and stress is straightforward. These two volumes are easily connected: for a vacancy $\Delta\Omega^{\text{f}} = \Delta\Omega^{\text{rel}} + \Omega_0$ and for an self-interstitial atom $\Delta\Omega^{\text{f}} = \Delta\Omega^{\text{rel}} - \Omega_0$. Ω_0 is the volume of a single atom in the pristine crystal. They measure different properties: the relaxation volume can be related to the lattice parameter change induced by a point defect, whereas the formation volume is related to the macroscopic volume change induced by the defect. For nonelemental solids (binaries, etc.), formation volumes of composite intrinsic defects such as Frenkel pairs, Schottky defects, etc., can be defined by relevant combinations of relaxation volumes.

III. CORRECTIONS TO THE PRESSURE AND FORMATION VOLUME

For charge neutral defects, there is no ambiguity about the practical way to obtain the formation volume: the derivative of the formation energy of Eq. (1) with respect to the cell parameters is simply the derivative of the energy of the defective supercell. The formation volume can hence be deduced by a standard minimization procedure aiming at zero pressure in the defective supercell calculations.

However, the situation is much more intricate for charged defects. It might be tempting to apply the same procedure as for neutral defects. If we do so, we obtain for the tetrahedric self-interstitial in silicon the uncorrected curves of Fig. 2. The values apparently converge very nicely with the system size. However, the converged formation volumes yield the strange linear behavior with charge state reported in Fig. 1.

In fact, the formation energy from Eq. (1) contains several additional terms when q is not zero. Two of them present a nonvanishing derivative with respect to volume that prove to have a non-negligible contribution to the pressure. These terms are the two corrections $\Delta E^{\text{e.s.}}$ and ΔV.

We now have to specify the expression of the mentioned two corrections. In a previous study,[26] we showed the relevance of the simplest correction to the electrostatic issue, namely, the monopole correction of Leslie and Gillan,[18] and the validity of the potential alignment based on the average total potential.[28–30]

In terms of formation energy, the electrostatic term $\Delta E^{\text{e.s.}}$ produces a large correction that slowly vanishes as $\Omega^{-1/3}$. The monopole correction reads

$$\Delta E^{\text{e.s.}} = \frac{\alpha q^2}{2\varepsilon}\Omega^{-1/3}, \tag{4}$$

where α stands for the Madelung constant of the lattice and ε is the dielectric constant of the materials that governs the screening of the Coulomb interaction. From the expression of the monopole correction of Eq. (4), it is clear that there is an induced pressure $P^{\text{e.s.}} = -\partial\Delta E^{\text{e.s.}}/\partial\Omega$:

$$P^{\text{e.s.}} = \frac{\alpha q^2}{6\varepsilon}\Omega^{-4/3}. \tag{5}$$

To evaluate the effect of this additional pressure onto the equilibrium volume, one can expand the pressure as a function of the volume to the first order. Then safely assuming that the bulk modulus of the defective cell is only slightly affected by the presence of a single defect in a large supercell, we obtain an expression for the correction to the formation volume $\Delta\Omega^{\text{e.s.}}$ induced by the electrostatic correction:

$$\Delta\Omega^{\text{e.s.}} \approx \frac{P^{\text{e.s.}}\Omega}{B}, \tag{6}$$

where B is the bulk modulus of the pristine solid.

Now numerically evaluating the effect of this correction, it is proven very small for realistic cases. For example, for a defect with charge 2+ in a cubic 64-atom supercell of silicon, one can evaluate the correction to the pressure to be around 0.01 GPa and the corresponding correction to the formation or relaxation volumes to be around $0.01\Omega_0$. The electrostatic correction has been included in Fig. 2 with the striped symbols. The result is hardly distinguishable from the uncorrected curves. As a conclusion, this correction can be safely disregarded.

The second correction, namely, the potential alignment ΔV, is known to have a smaller effect on formation energies, which probably explains why many contradicting expressions for it can be found in the literature.[17,22,26–34] In Ref. 26, a potential alignment ΔV based on the average total potential was selected:

$$\Delta V = \langle v_{\text{KS}}(\text{perfect})\rangle - \langle v_{\text{KS}}(X^q)\rangle. \tag{7}$$

v_{KS} labels the total Kohn-Sham potential and the brakets $\langle\cdots\rangle$ imply an average over the whole supercell. Let us summarize the advantages of such an expression for ΔV: it avoids the double counting of the electrostatic correction, it induces the correct limit when an electron is brought infinitely far from the defect, and it has been successfully tested down to very small supercells.[26]

The potential alignment of Eq. (7) has a nonvanishing derivative with respect to the volume as we show in the following. When considering the variation with respect to the volume, only the second term of Eq. (7) varies. This derivative cannot be evaluated from ground-state quantities: it would indeed involve derivatives of the density. However, we can proceed by now with magnitude arguments.

For large systems, the relative variations of the volume induced by the defect are small. One observes that down to relatively small supercells, the average potential nicely behaves as

$$\langle v_{\text{KS}}(X^q)\rangle \propto \langle\rho\rangle^{1/3}, \tag{8}$$

with $\langle\rho\rangle = N/\Omega$ the average density in the supercell. This behavior can be traced back to the exchange potential. Since the average local pseudopotential and average electrostatic potentials have been set conventionally to zero in codes employing periodic boundary conditions, the average potential reduces to the average exchange-correlation potential. Within local density approximation (LDA),[2] for instance, the exchange potential is one order of magnitude larger than the correlation counterpart and the LDA exchange potential behaves as $\langle\rho\rangle^{1/3}$. Anyway, the precise exponent in Eq. (8) is not an issue, since any other exponent would yield the same final result.

When considering the limit to infinitely large supercells, both the number of electrons N and the volume Ω go to infinity while retaining the ratio $\langle\rho\rangle$ constant. As a consequence, the correcting pressure $P^{\text{p.a.}}$ is found inversely proportional to the volume and proportional to the charge:

$$P^{\text{p.a.}} = q\frac{\partial\langle v_{\text{KS}}(X^q)\rangle}{\partial\Omega} \tag{9}$$

$$\propto q\,\langle\rho\rangle^{1/3}\,\Omega^{-1}. \tag{10}$$

Hence, provided that the bulk modulus is not affected by the presence of a single defect, one finally obtains the correction to the formation volume:

$$\Delta\Omega^{\text{p.a.}} \approx \frac{P^{\text{p.a.}}\Omega}{B} \propto q\,\langle\rho\rangle^{1/3}. \tag{11}$$

Strikingly the correction to the volume converges very quickly but not to zero: it has a finite limit when both N and Ω tend to infinity while keeping $\langle\rho\rangle$ constant. This explains the seemingly good converging behavior of the uncorrected curves of Fig. 2.

Then, the corrected curves in Fig. 2 with the closed symbols have been obtained by a minimization of the formation energy, including the two corrections, as a function of the volume for each supercell size and each charge state. Eventually we observe that the formation volume only weakly depends on the charge state. The corrected formation volume converges quickly with supercell size, however, to a completely different value compared to the uncorrected formation volume.

IV. PRACTICAL MINIMIZATION SCHEME FOR THE FORMATION VOLUME

In the previous section, we employed a manual optimization procedure of the formation energy E_f as a function of the volume in order to obtain the data for Fig. 2. Unfortunately, it is much less handy than the usual minimization of the supercell based on the calculated stress tensor that all *ab initio* codes use. It becomes even more critical when the defect induces nonisotropic deformation: one should optimize with respect to supercell size and shape. Hereafter we propose a practical way to perform the minimization of the formation energy with respect to the supercell size and shape with only a small overhead work with respect to the standard procedure.

We observe in practical calculations that the correcting pressure $P^{\text{p.a.}}$, as evaluated from a finite difference, is almost insensitive to the supercell size or shape. We propose here to evaluate it numerically out of two single point calculations. In practice, we perform two separated total energy calculations for different volumes of the same supercell and then evaluate

$$P^{\text{p.a.}} \approx q\frac{\langle v_{\text{KS}}(X^q)\rangle_{\Omega_2} - \langle v_{\text{KS}}(X^q)\rangle_{\Omega_1}}{\Omega_2 - \Omega_1}. \tag{12}$$

As the potential alignment correction is a function of the volume, it induces simply a diagonal correction stress tensor. Finally, one can relax the supercell size and shape with a target stress tensor with the diagonal values $-P^{\text{p.a.}}$.

The prescribed procedure has been checked against the previous results of Fig. 2 for Si_{Tet}. The obtained volumes are virtually superimposed onto the one we got by minimizing the formation energy directly (not shown). In Fig. 3 we present

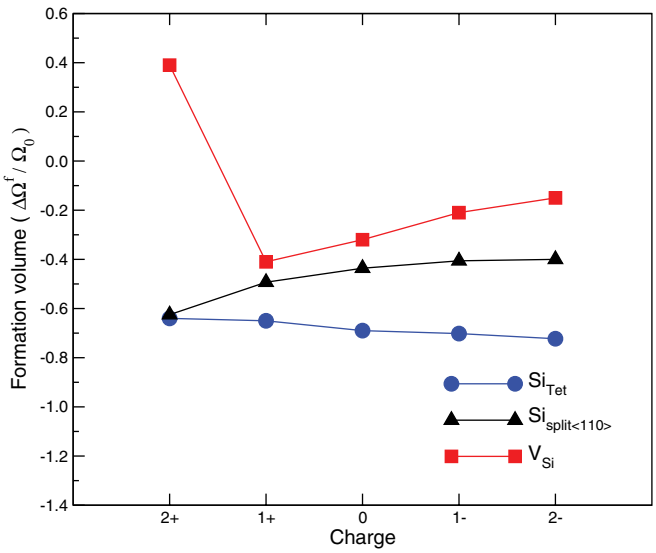

FIG. 3. (Color online) Formation volume of a tetrahedric self-interstitial (Si_{Tet}, circle symbols), a split self-interstitial ($Si_{split\langle 110\rangle}$, triangle symbols), and a vacancy (V_{Si}, square symbols) as a function of charge state, obtained by the minimization of the stress correcting for the potential alignment pressure in a 216 ± 1 atom silicon supercell.

the corrected formation volumes of the vacancy and self-interstitials in silicon. One finds that the formation volumes are now approximately independent of the charge state for a given defect. However, formation volumes prove to depend on the defect types. Just the vacancy presents a special behavior, since the vacancy point group changes along with the charge state. Whereas V_{Si}^{2+} has a tetrahedric environment, all the other charge states experience a Jahn-Teller distortion. In the uncorrected data, the effect of the Jahn-Teller distortion was partially hidden by the spurious charge effect. With the corrected data, V_{Si}^{2+} appears as clearly different from the other charge states. Note that the finally relaxed supercells are not isotropic, due to the Jahn-Teller effect. This was obtained almost effortlessly from the described procedure.

V. CONCLUSIONS

In the present article, we presented a consistent method to evaluate the formation volume of point defects for charged defects. We demonstrated that the two corrections to the formation energy, namely, the electrostatic correction and the potential alignment correction, do induce a correction to the formation volume. Surprisingly, the electrostatic correction that is sizable for the energy affects only slightly the formation volume and can be safely disregarded in all practical cases. It is also astonishing that the potential alignment term, which is usually regarded as a tiny correction (if not simply disregarded), yields indeed a massive correction to the formation volume. Furthermore, this correction converges extremely quickly with supercell size. If it is not included, the formation volume quickly converges to a biased value. If included, the formation volume rapidly tends to a more sensible value, as we have demonstrated here with silicon.

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