Ab initio study of neutral vacancies in InP using supercells and finite size scaling.

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Abstract.

The formation energies and relaxed structures of the neutral vacancies in InP are calculated by planewave density functional theory, using supercells of 8, 64 216 and 512 atoms together with finite size scaling. The effects of electrostatic defect-defect interactions and the truncation of elastic relaxations by the finite supercell are examined. The unrelaxed formation energies are 4.95±0.10 eV and 3.00±0.10 eV for V_{In}^{+0} and V_{P}^{+0} respectively, and the relaxed formation energies are 4.20±0.05 eV and 2.35±0.15 eV. When relaxed, V_{In}^{+0} remains very nearly symmetric with a 40% volume reduction. V_{P}^{+0} on the other hand develops a double dimerized structure, with an ≈12% Jahn-Teller distortion and a 45% volume reduction.
It is shown that finite size scaling sometimes reveals that energies are not converged even in the 512 atom supercell, and can thus be important tool in theoretical studies of defects in semiconductors, if sufficient care is taken with strongly Jahn-Teller active defects.

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1. Introduction.

In the last two decades, *ab initio* calculations based upon Density Functional Theory (DFT) have emerged as a very useful tool for studying the properties of defects in semiconductors. The properties of a small group of atoms (10s or 100s) are calculated and the results are applied to physical problems involving many more (1000s or 10000s or more). Two different approaches to this extension are used, involving either a) clusters with open boundary conditions or b) supercells with periodic boundary conditions (PBCs). Both have strengths and weaknesses. With clusters errors enter because the defect interacts with the open boundaries. With supercells the main weakness is that the defect interacts with an infinite array of spurious "images" of itself seen in the periodic boundaries. Whilst elastic interactions can easily be truncated (introducing further errors), electrostatic interactions cannot. They result in errors in the calculated formation, binding and migration energies of defects, errors which can be on the same order as the energies themselves. For practical supercell sizes they need not even be negligible for neutral defects, since dipolar and quadrupolar interactions can remain significant.

In recent years various correction schemes have been suggested (Refs. [1-4]) to compensate for these errors. They are usually based upon fits to quasi-classical models and/or multipole expansions of the electrostatic interactions. They have met with varying levels of success but are generally considered so far insufficiently reliable

for regular use. There are more direct approaches, however. Probert and Payne [5] recently presented a detailed *ab initio* study of the neutral vacancy in Si, considering all aspects of convergence, from basis set and k-point sampling to size and symmetry of supercells. They demonstrated that the use of 'large' supercells (here meaning 200+ atoms) can be essential for obtaining the correct physical results. In this paper we study the formation energies and structures of the neutral vacancies in InP, and demonstrate the advantages of not only using large supercells but also finite size scaling.

InP has the zinc-blende structure, with two vacancies (phosphorus (V_P) and indium (V_{In})) each surrounded by a tetrahedron of nearest neighbouring atoms, giving T_d symmetry when unrelaxed. Pervious *ab initio* studies (Refs. [6-8]) have used relatively small supercells. V_P is a strong Jahn-Teller (J/T) defect, in which the symmetry is reduced by strong distortions which lift degeneracies in the localized defect levels. Symmetry breaking in V_{In}, on the other hand, is much weaker with less effect upon calculated structures and formation energies.

2. Method.

We do planewave *ab initio* DFT within the Local Density Approximation (LDA) together with ultrasoft pseudopotentials, using the VASP code [9]. We recently presented [10] a study of the [Zn_{In}-V_P] complex in InP with the same technique and potentials. The LDA lattice constant was 5.827 Å and the band gap 0.667 eV.

We use simple cubic supercells of 8, 64, 216 and 512 atoms and allow all atoms not located on the surface of the cell to relax. This restriction is truncates the elastic interactions between adjacent supercells, and leaves 1, 5, 7, and 9 shells of atoms free to relax about the vacancy in the four supercells. No restrictions are placed upon the symmetry of relaxations.

The key quantity is the formation energy of the vacancy in the supercell 'C'

$$E_d^C = E_T^C(V_X) - E_T^C(\text{bulk}) + \mu_X \quad (1)$$

where $E_T^C(V_I)$ and $E_T^C(\text{bulk})$ are the total energy of the supercell with and without a vacancy on sublattice 'X'. Both are calculated with the same values of planewave cutoff, k-point grid, etc, to make use of cancellation of errors. μ_X is the chemical potential of the atoms on sublattice X. We use values μ_{In} = 3.4851 eV and μ_P = 6.2429 eV, (Ref. [10]) corresponding to stociometric conditions. A planewave cutoff energy of 200 eV is keeps errors below O(0.01 eV) and a Monkhorst-Pack 4x4x4 k-point grid was found sufficient for converged non-relaxed calculations in the 64 atom supercell. By extension, a 2x2x2 grid should suffice in the larger cells. However, the results presented here have been obtained using k-point grids of 12x12x12, 8x8x8, 4x4x4 and 2x2x2 (4x4x4 for V_{In}) in the 8, 64 216 and 512 atom cells respectively. In Ref. [10] we also showed that the relaxation energy

$$\Delta_R^C = E_{d:R}^C - E_{d:UR}^C \quad (2)$$

($E_{d:R}^C$ and $E_{d:UR}^C$ being relaxed and un-relaxed E_d^C) converges faster with k-point grid than $E_{d:UR}^C$ itself, allowing shorter calculation times for relaxations. We found [10] that a 2x2x2 is usually sufficient in the 64 atom cell, but here use 4x4x4, together with 8x8x8, 2x2x2 and 2x2x2 in 8, 216 and 512 atom supercells. (Incidentally, we find that a 1x1x1 Monkhorst-Pack grid - the Γ point - is *not* sufficient, even for the 512 atom cell.)

3. Results.

In Fig. 1 the formation energies for both V_P and V_{In} are shown, for their unrelaxed and (minimum energy) relaxed structures, plotted against inverse supercell size. Fitting curves (solid lines) have been added. Since it is known [1-4] that the leading electrostatic errors in E_d^C scale as L^{-1} and L^{-3} (where L is supercell size) we fit to

$$E_d^C(L) = E_d + a_1 L^{-1} + a_3 L^{-3} \quad (3)$$

E_d is then the finite size scaled formation energy for an infinitely large supercell. To get an idea of the accuracy of the fitting and of the individual values of E_d^C, four more fits (dotted lines) are added in each case, one of the four data points

being omitted for each line. We find that E_d for the unrelaxed V_{In}^{+0} is 4.95±0.10 eV, which is ~0.2 eV higher even than E_d^C for the 512 atom cell. This demonstrates that finite size scaling can help even when the largest cells we can actually calculate are too small to be fully converged. When relaxed, the formation energy of V_{In}^{+0} is 4.20±0.05 eV. For V_P^{+0} we get 3.00±0.10 eV unrelaxed and 2.35±0.15eV relaxed, also 0.15 eV from the 512 atom cell value.

The error bar on the relaxed V_P^{+0} formation energy is noticeably larger and the data points for the smaller and for the larger supercells do not appear to scale the same way. This is due to the strong J/T effects at this vacancy. For the 8 and 64 atom cells we find the most stable structure to be symmetric, with a metastable DX structure 0.004 and 0.002 eV above it, respectively. (In the DX structure, one atom neighbouring the vacancy moves outwards, reducing the symmetry to C_{3v}.) For the 216 atom cell the symmetric structure is no longer stable, and the DX structure is a metastable excitation 0.046 eV above a double dimerized (DDM) ground state structure. (Here, two opposite sides of the tetrahedron are reduced in length relative to the others, giving D_{2d} symmetry.) This is the most stable structure in the 512 atom cell also. In Fig. 2 we show the formation energies of these alternative structures. The change-over in structure with supercell size is clear. We note also that considering only the DDM structures would suggest E_d lying nearer 2.45 eV than 2.35.

Fig. 3 shows the structural changes as a function of inverse cell size. Both defects relax inwards in all cells, the volume change scaling like Eq. (3), but definitely not with any quadratic. For V_{In}^{+0} this converges to about 40%, whilst J/T distortions remain below ~2%. For V_P^{+0} the inward volume change is about 45%, and there is a J/T distortion of around 12%, though definite scaling is not possible.

The changes in relative stability of the different structures are likely to be due to one or a combination of two things:

a) stabilizing/destabilizing dipolar and/or quadrupolar interactions, which become smaller as the cells grow.

b) The lack of shells of atoms in the smaller cells to absorb the elastic strain, which favours more symmetric structures.

To examine the elastic effects we present in Figs. 4 relaxed formation energies for V_P in the 216 atom cell, in which the number of shells permitted to relax has been restricted to between 1 and 5. Since the cell size is constant, the electrostatic interactions will be (almost) constant. Two starting points are used: DX and DDM. When only one shell relaxes, an anti-DX (ADX) structure is found from both start points (also C_{3v} symmetry, but one neighbour moves inwards rather than outwards) but only with a 1.5% J/T distortion. For 2 to 5 shells relaxed, DX and DDM structures were found, with steadily increasing distortion and relaxation energy. With 3 relaxing shells, (corresponding to the 64 atom cell) the volume change, distortion and relaxation energy are all 80-90% of their values at 5 shells (except for the DX distortion which is very weak anyway.) As far as the elastic errors are concerned, therefore, one might expect the 64 atom cell to behave like the 216 and 512 atom cells. The fact that it does not suggests that electrostatic defect-defect interactions via the PBCs are responsible for the lack of a dimerized structure in the 64 atom cell.

4. Conclusions.

We have investigated the formation energies and structural relaxation of the neutral vacancies in InP, and have considered in particular how these scale with supercell size and with the number of shells of atoms around the defect which can relax. We found that for certain cases (V_{In} unrelaxed for example) finite size scaling reveals the true formation energy to be still some way from its value in the 512 atom cell, the largest cell for which we can currently do calculations. Finite size scaling is thus an important tool, although we have also found that care needs to be taken with the symmetry of strongly Jahn-Teller active defects.

5. References.

1. G.Makov & M.C.Payne, Phys Rev B 51, (1995) 4014
2. P.A.Schultz, Phys Rev B 60 (1999) 1551
3. L.N.Kantorovich, Phys Rev B 60 (1999) 15476
4. H.Nozaki & S.Itoh, Phys Rev E 62, (2000) 1390
5. M.I.K.Probert & M.C.Payne Phys Rev B 67 (2003) 75204
6. R.W. Jansen Phys. Rev. B 41 (1990) 7666
7. M.Alatalo, et al. Phys. Rev. B 47 (1993) 6381
8. A.P.Seitsonen et al. Phys. Rev. B 49 (1994) 5253
9. G. Kresse & J. Furthmuller Comp. Mat. Sci. 6 (1996) 15
10. C.W.M.Castleton & S.Mirbt. Accepted for publication in Phys. Rev. B.

Figures.

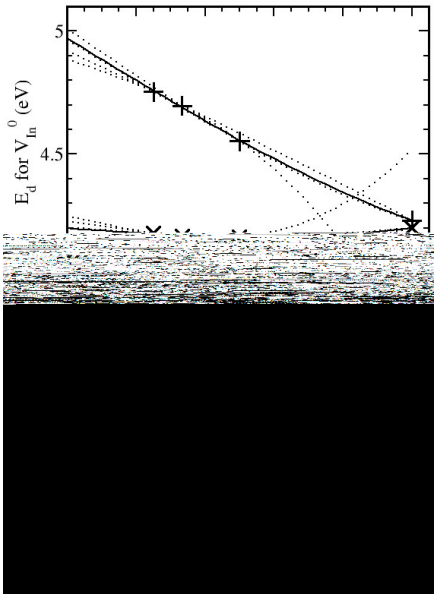

Fig 1. Relaxed (□) and unrelaxed (+) formation energies, E_d, for V_{In}^{+0} (upper) and V_P^{+0} (lower) versus inverse cell size, which is in units of the 8 atom cell size (hence 1.0□ 8 atom cell, 0.5□ 64 cell, 0.333□ 216 cell & 0.25□ 512 cell.) Fits: see text.

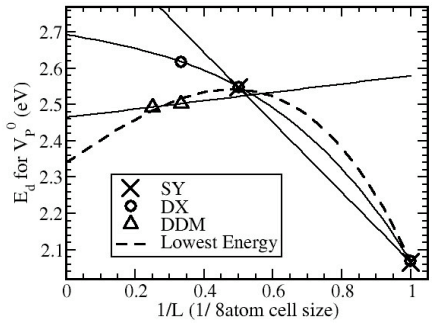

Fig 2. Relaxed E_d for symmetric (SY), DX (DX) & dimerized (DDM) structures of V_P^{+0}. Dashed fit is to the lowest energy alternatives.

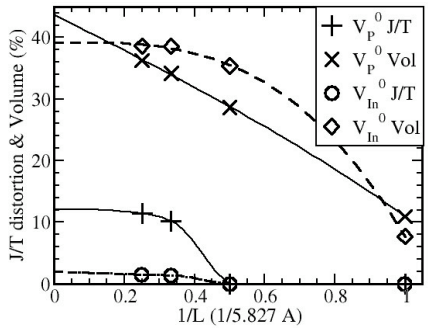

Fig 3. Scaling of vacancy structures versus inverse cell size. J/T is the % distortion in neighbour-neighbour distances, Vol the % volume reduction.

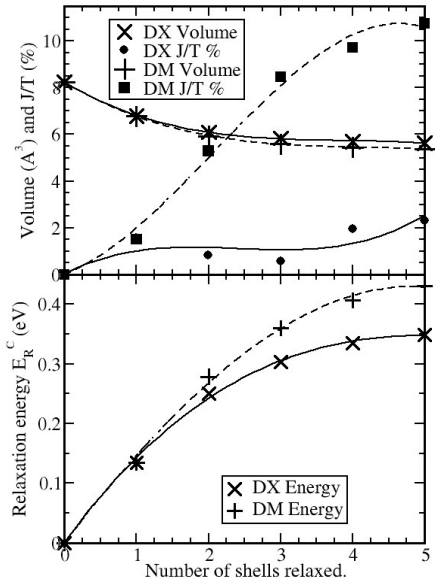

Fig 4. Dependence of relaxation energy and structure for the DX (solid lines) and dimerized (dotted lines) structures of V_P^{+0} on number of shells relaxed in the 216 atom supercell.