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.

Keywords: Defects, Semiconductors, Corrections, Scaling.
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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

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.

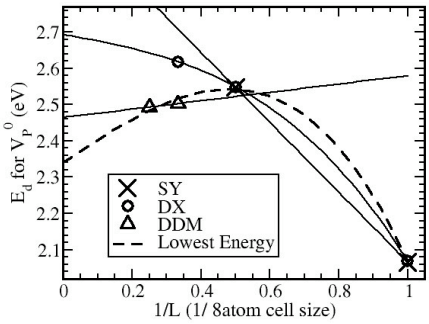

Fig 2. Relaxed E_d for symmetric (SY), DX (DX) & dimerized (DDM) structures of V_P^{+0}. Dashed fit is to the lowest energy alternatives.

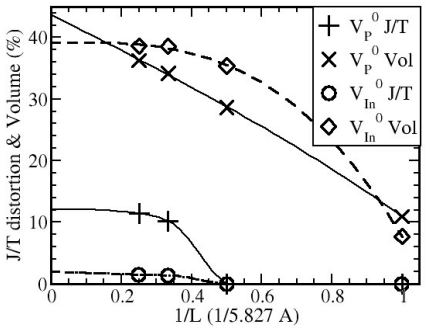

Fig 3. Scaling of vacancy structures versus inverse cell size. J/T is the % distortion in neighbour-neighbour distances, Vol the % volume reduction.

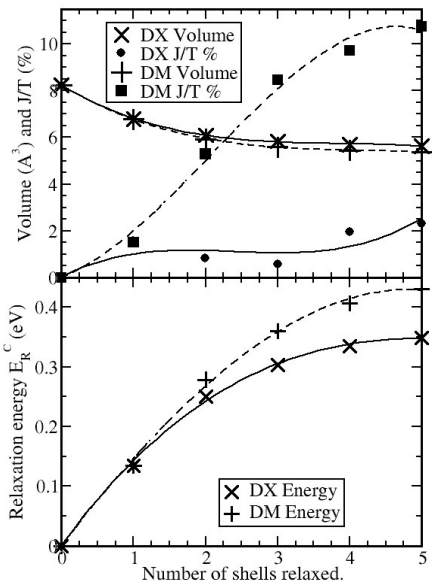

Fig 4. Dependence of relaxation energy and structure for the DX (solid lines) and dimerized (dotted lines) structures of V_P^{+0} on number of shells relaxed in the 216 atom supercell.