PHYSICAL REVIEW B VOLUME 47, NUMBER 11 15 MARCH 1993-I

Phosphorus vacancy in InP: A negative-U center

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(Received 20 October 1992)

Using first-principles simulations, we identify the phosphorous vacancy in InP as a negative-U center. The deep levels associated with this defect are in the upper half of the band gap, and the charge state changes directly from positive to negative as the Fermi level is raised: the vacancy captures two electrons rather than one. We also obtain the relaxed structures and formation energies for the In and P vacancies as a function of both electron and atomic chemical potentials.

I. INTRODUCTION

Point defects in semiconductors show a richness of physical phenomena with important consequences to the material properties.[1] These include deep levels in the energy gap, metastability associated with the atomic relaxations, and atomic diffusion. There is a strong interplay between the electronic states and atomic positions, such as the Jahn-Teller effect in its various variants. Because of the inherent metastability, the determination of ground-state structures is a demanding task. From the computational point of view, it requires sophisticated optimization methods for the minimization of the total-energy functional.

A particularly interesting property of a defect is the so-called negative-U behavior,[2] where the strong coupling between the electronic and the ionic degrees of freedom leads to unexpected ordering of charge configurations when the electron chemical potential is tuned. The best-known example is the vacancy in Si.[3] It cannot bind a single electron on the T_2 deep level, but the occupancy changes directly from zero to two. Energy lowering due to the lattice distortion more than compensates for the interelectron Coulomb repulsion.

In this paper, we report the discovery of the negative-U effect in the compound semiconductor InP, based on detailed total-energy calculations. Recently, negative-U-like behavior for the oxygen impurity in GaAs was reported from infrared absorption measurements of the local vibration modes of the complex.[4] Theoretical calculations for ionization levels at antisites in GaAs also show the negative-U structure.[5] Apart from these and some earlier speculations, there have been few detailed studies, despite the importance of the phenomenon to defect thermodynamics. This may stem from the fact that the negative-U behavior of a given defect is experimentally difficult to distinguish and, on the other hand, its theoretical description by total-energy calculations requires sophisticated methods with essentially no symmetry assumptions imposed. Our results for the single P vacancy in InP strongly suggest that negative-U behavior may be much more prolific in compound semiconductors than hitherto has been realized.

So far there have been few experimental studies of vacancy defects in InP,[6–9] and they do not show clear negative-U effects. The interpretation of these experiments is, however, difficult as the atomistic identification of the defect in question is not straightforward.

II. METHODS

Our calculations are based on density-functional theory and the local-density approximation. The validity of this approach has been amply demonstrated, most recently in a detailed study of the vacancy in Si.[10] To carry out the structural optimization, we use the first-principles molecular-dynamics (Car-Parrinello) technique,[11] where the interatomic forces are iteratively calculated from the electronic wave functions. By using the simulated annealing approach, one can avoid metastable configurations and allow the system to relax to its true ground state. We obtain the total energies, the atomic relaxations, and the one-electron levels, of which particularly interesting are those in the fundamental gap.

We use a 64-atom cubic supercell with periodic boundary conditions, with the point defect at the origin. The atoms are represented by norm-conserving, nonlocal first-principles pseudopotentials.[12] We use nonrelativistic density-functional theory and the local-density approximation in the spin-compensated form, and expand the wave functions in terms of plane waves. The energy cutoff of the plane-wave basis is 15 Ry. This is larger than has usually been used in similar calculations for Si, but is required to assure good convergence in the total energy. The lattice constant is chosen by allowing bulk InP (i.e., containing no defects) to equilibrate with the given cutoff. The resulting lattice constant is 5.61 Å, in good agreement with the experimental value of 5.87 Å. This procedure ensures that there are no residual stresses in the equilibrating system when the vacancy defect is introduced. The calculated band structure of bulk InP agrees well with the results of Chelikowsky and Cohen.[13] For dynamic simulations, we use a time step of 5.2–5.7 a.u. ($\sim 1.3 \times 10^{-16}$ sec), and the electronic mass parameter of 400 a.u. The simulations run up to 7000 time steps,

and the total energies of the order of 7000 eV for the unit cell are converged to the accuracy of 0.001 eV. Moreover, we tested the accuracy of our Car-Parrinello program by verifying the structures of small (2-, 6-, and 8-atom) P clusters. They agree well with the results of Jones and Hohl.[14]

Monovacancies and antisites are the simplest point defects in compound semiconductors, and they can appear in different charge states, as the level occupancy of the localized gap states varies with varying electron chemical potential. We calculate a defect with a net charge Q by removing (adding) Q electrons from (to) the supercell and introducing a rigid neutralizing background charge uniformly distributed over the supercell. This is equivalent to the statement that Q electrons are removed to the noninteracting vacuum level, where they do not contribute to the exchange-correlation or Hartree potential except through the zero-Fourier component of the charge density. The total energy E_Q of the defect system in charge state Q is a function of the electron chemical potential μ_e

$$E_Q(\mu_e) = E_Q^0 + Q(E_v + \mu_e), \tag{1}$$

where E_Q^0 is the total energy of the supercell containing the defect and E_v denotes the top of the valence band in the perfect lattice. The chemical potential μ_e is measured relative to E_v. The charge state of the defect for a given electron chemical potential is determined by minimizing the total energy. The values of the chemical potential at which the charge state changes are the ionization (thermodynamic transition) levels.

III. RESULTS

The atomic relaxations are substantial around vacancies in InP, and the associated relaxation energies can be large. Table I summarizes the thermodynamic transition levels for the various vacancy defects, and Table II lists the atomic relaxations for the different cases. The relaxations have a breathing component towards the vacancy center, and pairing components perpendicular to this direction. These components are schematically shown in Fig. 1. The relaxations beyond the nearest-neighbor shell are small and will not be discussed here.

The transition levels associated with In vacancies are close to the valence-band maximum, and the energy rises nearly parabolically with the occupation number. The atomic relaxations are mainly inwards, typically 15% of the bond length, and show little dependence on the charge state. There is a small pairing component. These features reflect the relatively delocalized character of the electron wave functions on the deep levels of the In vacancy.

The relevant charge states for the P monovacancies are V_P^+, V_P^0, V_P^-, V_P^{2-}, and V_P^{3-}. The ionization levels are shown in Table I, and Table II summarizes the relaxations. The ionization levels are now at and above midgap. The important observation is that there is neither an ionization level from the singly positive to the neutral vacancy nor a level from the neutral to the singly negative vacancy. Instead it is preferable to switch from the positively charged V_P^+ directly to the negatively charged V_P^- when the Fermi level rises in the gap, and the neutral P vacancy is not thermodynamically stable. This is the famous negative-U effect, where a large lattice distortion compensates for the Coulomb repulsion between two electrons in the localized state. The relaxations for the different cases (Table II) are consistent with this picture.

The ionization levels for vacancies in InP have been previously calculated by omitting the lattice relaxation.[15–17] In order to compare with these results we made also calculations for these ideal vacancies. The results are included in Table I. According to all calculations the levels for In vacancy are close to the valence-band maximum, but their number depends on the method in question. The inclusion of the relaxation does not alter the picture for the In vacancy. This is because the deep level wave functions are relatively delocalized. Except for the Green's-function calculations,[15] which give a (0/+) ionization level just below the conduction band, the P vacancy has only the singly positive charge state. In contrast to the results for the In vacancy, the relaxation is essential for the proper description of the ionization levels of the P vacancy. The relaxation results in a very localized deep level wave function which binds the four nearest-neighbor atoms of the vacancy pairwise together. The effect is so strong that the negative-U behavior becomes possible. Moreover, according to our calculations the P vacancy can bind a third electron in a doubly negative charge state which has the same symmetry as the lowest deep level state. If a fourth electron (in the triply

TABLE I. The ionization levels of InP. All values are in eV relative to the maximum of the valence band.

Vacancy	Ionization level	Relaxed	Unrelaxed	Unrelaxed vacancy Ref. 15	Unrelaxed vacancy Ref. 16
V_{In}	(+/2+)	−0.04	0.07		
	(0/+)	0.10	0.13		
	(−/0)	0.13	0.19	0.14	
	(2 − /−)	0.18	0.36	0.20	0.12
	(3 − /2−)	0.23	0.56	0.38	0.31
V_P	(0/+)		Always	1.37	Always
	(−/+)	0.68	positive		positive
	(3 − /−)	1.31			

TABLE II. Nearest-neighbor relaxations for different vacancies in InP. The relaxation components (corresponding to V_P^-) are schematically shown in Fig. 1. The breathing and pairing mode relaxations are given in percent of the bulk bond distance in InP. The negative (positive) breathing mode sign denotes inward (outward) relaxation. A positive value of the pairing 1 component indicates pairing of the nearest-neighbor atoms. For V_{In}^{2+} and V_P^{3-} the relaxation pattern is more complicated.

Vacancy	Breathing (%)	Pairing 1 (%)	Pairing 2 (%)
V_{In}^+	−16.0	3.6	0.0
V_{In}^0	−16.1	2.0	0.7
V_{In}^-	−14.9	2.7	0.0
V_{In}^{2-}	−15.0	1.7	0
V_{In}^{3-}	−15.5	0.0	0.0
V_P^+	−7.5	0.0	0.0
V_P^0	−11.4	11.3	−0.1
V_P^-	−15.8	17.3	−0.1
V_P^{2-}	−17.1	16.4	−0.1

negative charge state) is brought to the band-gap levels, the relaxation symmetry of the vacancy changes and the energy is lowered so that it is again more preferable to have four electrons than just three. This second negative-U effect, however, is much weaker than that in the transition from the positive to singly negative charge state.

Following the method suggested by Zhang and Northrup,[5] we have calculated the formation energies of the vacancies in InP as a function of both the electron chemical potential and the atomic chemical potentials μ_{In} and μ_P. The defect formation energy is calculated in the supercell method as

$$\Omega(\mu_e,\mu_{In},\mu_P) = E_Q^0 + Q(E_v+\mu_e) - n_{In}\mu_{In} - n_P\mu_P, \tag{2}$$

where n_{In} and n_P are the numbers of the In and P atoms in the unit cell, respectively. Defining the chemical potential difference

$$\Delta\mu = (\mu_{In}-\mu_P) - (\mu_{In(bulk)} - \mu_{P(bulk)}), \tag{3}$$

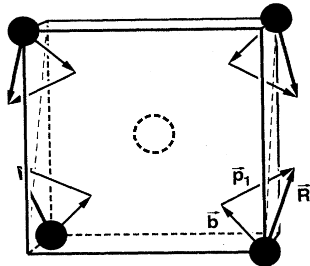

FIG. 1. The nearest-neighbor relaxations associated with a tetragonally relaxed vacancy in a zinc-blende structure semiconductor. The components of one relaxation vector are labeled; **b** denotes the breathing mode and $\mathbf{p}_1$ the pairing mode 1. They both lie on the (110) plane shown. The third component, pairing 2, is defined as the cross product $\mathbf{p}_2 = \mathbf{b}\times\mathbf{p}_1$. The directions of the vectors shown correspond to the singly negative P vacancy but the lengths are scaled by a factor of 2.5. The pairing-2 component is negligible and is therefore neglected.

where $\mu_{In(bulk)}$ and $\mu_{P(bulk)}$ are the atomic chemical potentials of the bulk In and bulk P, one obtains

$$\Omega(\mu_e,\mu_{In},\mu_P) = E_Q^* + Q(E_v+\mu_e) - \tfrac{1}{2}(n_{In}-n_P)\Delta\mu. \tag{4}$$

This form is useful because E_Q^* is independent of μ_e and $\Delta\mu$. Moreover, the magnitude of $\Delta\mu$ cannot exceed the heat formation ΔH of InP, defined as $\Delta H = -(\mu_{InP} - \mu_{In(bulk)} - \mu_{P(bulk)})$. Here μ_{InP} is the chemical potential of bulk InP per In-P atom pair.

Figure 2 shows the formation energies of In and P vacancies in different charge states as a function of the electron chemical potential. This plot corresponds to the case $\Delta\mu = 0$. For P vacancies it confirms the negative-U effect: the formation energy of the neutral vacancy lies considerably above the crossing point of the singly positive and negative cases.

Figure 3 displays the formation energies as a function of the chemical potential difference $\Delta\mu$ for three values of the electron chemical potential μ_e. For ΔH we have used the calculated value of 0.94 eV, which is in a good agreement with the measured value of 0.92 eV (for the electron energy band gap we use the experimental value

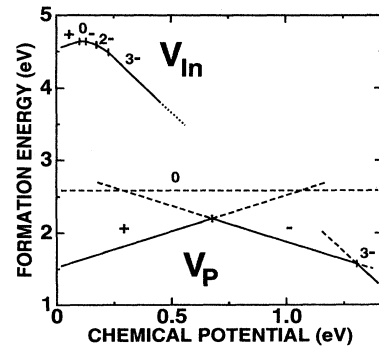

FIG. 2. The formation energies of In and P vacancies in different charge states as a function of the electron chemical potential. The figure corresponds to the representative case $\Delta\mu = 0$. The symbols denote the charge state, and the full line corresponds to the thermodynamically stablest situation.

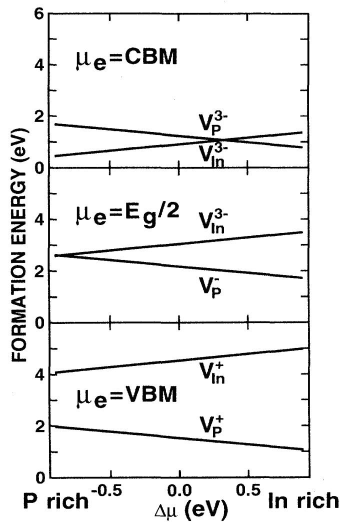

FIG. 3. The vacancy formation energy as a function of the atomic chemical potential $\Delta\mu$. The electron chemical potential is at the top of the valence band (VBM), at the midgap ($E_g/2$), and at the bottom of the conduction band (CBM).

of 1.42 eV).[18] In comparison with GaAs,[5] the anion (P) vacancy formation energies are lowered relative to those for cation (In) vacancies. This indicates that, especially in strongly p-doped InP, the role of P vacancies should be important for many processes, such as self-diffusion.

Little is known experimentally about the ionization levels at the P vacancy in InP. von Bardeleben[6] has measured the EPR spectrum from electron-irradiated p-type (Zn-doped) InP. In his analysis von Bardeleben assigns the observed absorption spectrum to the neutral P vacancy. This is in contrast to our assertion of the negative-U behavior. However, it should be noted that in heavily doped samples (such as the InP:Zn used by von Bardeleben) there are other native point defects and complexes which should be taken into account in the EPR analysis. In particular, it has been argued[7–9] that the Zn-P vacancy pair is important.

IV. DISCUSSION

The negative-U character of the anion vacancies is most probably not restricted to InP among the different III-V compound semiconductors. Recent Car-Parrinello calculations[19] for GaAs, similar to those presented here, showed a strong strengthening of pairing-type relaxation when the charge state of As vacancy changes from neutral to negative. This was associated with a remarkable lowering of the one-electron energy level in the band gap. This kind of behavior is suggestive for a negative-U center, and calls for more accurate total-energy calculations in GaAs as well as in other compound semiconductors.

In conclusion, our first-principles calculations predict the existence of P vacancies as negative-U defects in n-type InP. Native and thermally generated P vacancies are expected to be important for many material properties, as they probably anneal out only at high temperatures.

ACKNOWLEDGMENTS

This research has been supported in part by the Academy of Finland. We acknowledge the generous supercomputer resources obtained through the Centre for Scientific Computing in Espoo, Finland.

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