

Theoretical study of substitutional defects in III-V semiconductors: InP

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The embedded-cluster linear-combination-of-atomic-orbitals-self-consistent-field method, within the local-density framework, is used to study the substitutional impurities Li, Be, B, C, N, and O in InP. The pure semiconductor gap is found to be 0.8 eV, in fair agreement with experiments. Impurities (Im) are substituted at either In or P sites in succession forming $(\text{Im})\text{P}_4\text{In}_{12}$ and $(\text{Im})\text{In}_4\text{P}_{12}$ variational clusters. Li, Be, and O are found to be acceptors whereas B and C are donors. N is ambivalent: a donor at the In site, and an acceptor at the P site. Binding-energy calculations indicate that Li, Be, and B prefer to occupy the In site while C, N, and O settle at P sites. Our calculated results are compared with experiments and other calculations wherever available.

I. INTRODUCTION

III-V semiconductors have drawn considerable attention in recent years. They are technologically important as their electronic properties can be varied easily with different dopants. Their higher mobilities are suited for high-speed switching circuits. The band structure of III-V semiconductors provides some important advantages over the column-IV semiconductors due to their direct band gap. A wide range of optoelectronic devices are possible using the direct gap (light-emitting diodes, field-effect transistors) and the indirect gap (Gunn effect). Thus III-V semiconductors are a most promising group of materials for semiconductor optoelectronics.

Among III-V semiconductors, InP stands out. The thermal conductivity is 60% higher than that of GaAs.¹ It also has a higher mobility, with a high peak-to-valley ratio in the velocity electric-field characteristics. These qualities are essential for high-speed microwave field-effect transistors, transferred electron oscillators, and high-speed logic. The energy gap of InP is close to the optimum value for efficient conversion of solar radiation into electric power by single-junction photovoltaic cells.²

With the increased importance of InP, detailed theoretical and experimental studies of its electronic structure are necessary. The major problem with interpreting the experimental data on InP is the absence of ultrahigh-purity material; the sample is usually never defect free. Apart from impurity contamination, single defects and defect complexes may also form through defect-impurity interaction. Since both electrical and optical properties depend on the defect structure, a good knowledge of the chemical nature of impurities, charge states, defect concentrations, and energy levels is essential. However, despite considerable effort the defect structure of InP is not clearly understood, especially in the distinction between effects due to impurities, and those due to native defects. Some of the deep levels have been studied theoretically,³⁻⁶ but a major part remains unexplored.

Impurities are known to introduce levels in the gap region of the semiconductor,⁷ and thereby to control the

electrical transport properties which are relevant to device operation. These levels in the band gap can either be shallow or deep. Shallow impurities introduce energy levels close to the band edges with activation energies of a few meV, and supply electrons or holes for conduction. In other words, a shallow level can be defined with a small binding energy of the trapped electron relative to the appropriate band-edge state, so that its wave function may be expanded via effective-mass theory in terms of Bloch functions of the host lattice. The shallow levels can function as donors or acceptors depending on the position of the impurity in the Periodic Table with respect to the substituted host atom. The difference in formal valence of the impurity and host, if positive, indicates a donor, and if negative an acceptor level. Certain impurities can have either donor or acceptor states, and are known as isovalent or amphoteric. A deep level, on the other hand, is one lying farther than approximately 100 meV from any of the band edges. Theoretically, the impurity potential alone is sufficiently strong enough to pin the state in the gap, even when the conduction- or valence-band edge is perturbed by alloying or pressure. These deep states act as a trapping or recombination center, and can alter the electronic conductivity markedly.

The effective-mass theory has been successfully used in handling shallow-impurity levels.⁸ No such theory exists for the deep levels, and existing analyses are based largely on molecular-cluster models. It is of much interest both from theoretical and applied points of view to understand the variation of defect levels with different dopants. In this paper, we calculate the volume charges, Mulliken populations, and one-electron energy-level spectra of some of the impurities that usually contaminate or are useful dopants in the InP semiconductor. We consider the cases of Li, Be, B, C, N, and O as substitutional impurities both at In and at P sites. A further calculation of binding energy is initiated on defect clusters by substituting the impurity at an In site and comparing its relative stability with the impurity at the P site. In the absence of impurity-defect complex formation, this will determine the site at which the impurity prefers to settle.

II. COMPUTATIONAL METHOD

The molecular-cluster model is a useful method for studying the localized electronic properties associated with vacancies, substitutional, and interstitial defects, and local moments. Systems with little or no symmetry which are outside the scope of conventional energy-band-structure calculations, can be described in a straightforward manner.

We choose a variational cluster of atoms scooped out of the solid. The rest of the crystal is accounted for by generating a surrounding microcrystal which enables the surface atom to sense a potential similar to the bulk, thus suppressing most surface or cluster-size effects. The system Hamiltonian includes intracluster and host-cluster Coulomb and exchange-correlation interactions in a self-consistent manner. In this scheme, one can reproduce bulk properties such as the charge and spin densities, crystal-field splitting, and binding energy for comparison with the perturbed system.

Our aim is to approximately solve the Schrödinger equation

$$H\phi_{i\sigma}^\beta = \epsilon_{i\sigma}^\beta \phi_{i\sigma}^\beta \quad (1)$$

in a local representation. The nonrelativistic one-electron Hamiltonian in the Hartree-Fock-Slater model is given (in Hartree a.u.) by⁹⁻¹³

$$H = -\frac{1}{2}\nabla^2 + V_c(r) + V_{\text{ex},\sigma}(r), \quad (2)$$

where V_c is the Coulomb potential and $V_{\text{ex},\sigma}(r)$ is the simple Kohn-Sham-Slater exchange potential.

The discrete variational (DV) method^{10,11,14} is a numerical scheme in which the matrix elements of the effective Hamiltonian and overlap are computed directly as discrete sums rather than integrals, thus avoiding calculation and assembly of separate multicenter integrals. The Hamiltonian matrix and the overlap matrix are evaluated as weighted sums over a set of sampling points r_k :

$$H_{ij} = \sum W(r_k) \phi_i^*(r_k) H \phi_j^*(r_k), \quad (3)$$

$$S_{ij} = \sum W(r_k) \phi_i^*(r_k) \phi_j^*(r_k), \quad (4)$$

to obtain energy eigenvalues and eigenfunctions. The eigenvalues and eigenfunctions obtained from point-by-point balance of the kinetic, Coulomb, and exchange-correlation energies can be determined with precision sufficient for the present study with a sampling grid of a few hundred points per atom.

The cluster charge density on the DV grid is given by

$$\rho_{\text{cluster}}(r) = \sum_{\beta i \sigma} f_{i\sigma}^\beta |\phi_{i\sigma}^\beta(r)|^2, \quad (5)$$

where $f_{i\sigma}^\beta$ are the occupancy of the molecular orbitals (MOs) determined self-consistently using the Pauli exclusion principle and Fermi-Dirac statistics. The host microcrystal extends out to about 20 a.u. from the center of the cluster and includes about 250–300 of the surrounding atoms. In the simple self-consistent-charge (SCC) approximation, each atom in the host generates a spherically symmetric charge density and a Coulomb po-

tential. The total charge density is now written as

$$\rho_{\text{total}}(r) = \rho_{\text{cluster}}(r) + \rho_{\text{host}}(r). \quad (6)$$

The resultant nonspherical crystal potential is a lattice sum of spherically symmetric contributions from all the atoms in the microcrystal. Without further constraints, the electrons in the cluster sampling the potential well of the atoms exterior to the cluster will try to occupy these wells. In practice, the cluster wave functions must remain orthogonal to the occupied exterior atom states. The repulsive pseudopotential effect due to the Pauli exclusion principle is simulated by truncating the attractive potential wells around the external nuclei at a radius R_W to some depth V_W typically chosen about equal to the Fermi energy.

Finally the statistical exchange expression for total energy is given by

$$E_t = \sum_{\sigma} \left[\sum_{i\beta} f_{i\sigma}^\beta \epsilon_{i\sigma}^\beta - \frac{1}{2} \int \rho_{\sigma}(r') \rho(r) / r - r' dr dr' \right. \\ \left. + \int \rho_{\sigma}(r) [E_{\text{xc},\sigma}(r) - V_{\text{xc},\sigma}(r)] dr \right] \\ + \frac{1}{2} \sum_{\mu} \sum_{\nu} Z_{\mu} Z_{\nu} / r_{\mu\nu}, \quad (7)$$

where the exchange-correlation contributions to the chemical potential are related by

$$E_{\text{xc},\sigma}(r) = \frac{3}{4} V_{\text{xc},\sigma}(r) \quad (8)$$

for the simplest Kohn-Sham potential. The calculated total energies for a cluster like $\text{InP}_4\text{In}_{12}$ are not accurate enough for direct use in the chosen sampling scheme. An accurate binding energy may be obtained, however, by taking the difference:

$$E_b = E_t - E_{\text{ref}}, \quad (9)$$

where E_{ref} is a reference-state energy calculated by placing the atoms at their lattice positions. Now, however, the atoms are assumed to be noninteracting over the same integration mesh.¹⁵

III. RESULTS AND DISCUSSION

A. Ideal InP host

As a starting point, we consider a “perfect cluster” where In is placed at the center of the cluster with four nearest-neighbor P atoms and 12 next-nearest-neighbor In atoms ($\text{InP}_4\text{In}_{12}$) in a tetrahedral configuration. The impurities are then substituted at the central In site to study the defect structure. Another basic configuration for the “perfect cluster” is to place the phosphorus at the center with four neighboring In atoms and 12 distant phosphorus atoms ($\text{PIn}_4\text{P}_{12}$). This choice leads to the study of defect structure, without distorting the symmetry, when the impurity occupies the central P site.

Table I shows the volume charges and Mulliken population analysis for pure InP for the two different types of clusters discussed above. The volume charges are ob-

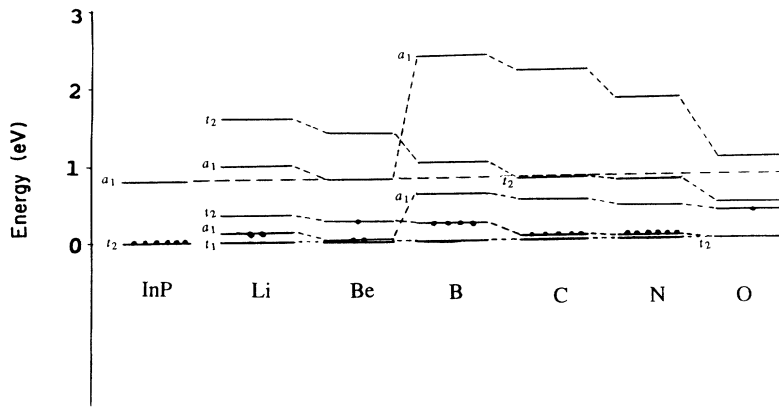


FIG. 2. One-electron self-consistent energy bands in the gap region for (a) host, (b) Li, (c) Be, (d) B, (e) C, (f) N, and (g) O for an impurity occupying the P site in InP.

passivated the dangling bonds in InP: a behavior seen in hydrogen-doped Si,²⁵ Ge,²⁶ and GaAs.²⁷ In the present DV- $X\alpha$ study, we calculate the electronic structure of Li in InP by placing the impurity first at an In site and then at the P site. A fraction of Li is thought to occupy the Ga site (Li_{Ga}) and form pairs with Li in the interstitial sites²⁴ (Li_I) when Li was diffused in GaAs at high temperatures. Li has a smaller ionic radius of 1.01 Å as compared to In and P, and can thus substitute for the element with larger atomic radius.

Table I shows the Mulliken population analysis for Li_{In} and Li_{P} . The initially vacant Li $2p$ state picks up more charge for Li_{In} as compared to Li_{P} along with a redistribution in the s shell after reaching self-consistency. Since the direction of flow of charge is from In to P and Li, Li_{P} , having In as nearest neighbors, accumulates a larger charge as compared to Li_{In} , where In occupies the second neighboring shell. In general, Li is an acceptor with a charge of $-0.13e$ and $-0.25e$ transferred from the indium atom in both configurations. The MS- $X\alpha$ calculation finds the Li_{In} site to be an acceptor with a net charge of $-0.04e$ as some charge from the ligands goes into the interatomic region.⁵

The Li_{In} impurity introduces a level of t_2 character composed of 64% P $3p$, 29% In $5p$, and 6% Li $2p$ located just 0.16 eV above the valence-band edge [Fig. 1(b)]. This is consistent with the multiple-scattering calculation,⁵ where a level at $E_v + 0.29$ eV ($E_g = 1.08$ eV) is reported. On the other hand, from our numerical calculations we find levels of t_2 (77% P $3p$, 16% In $5p$, and 6% Li $2p$) and a_1 character (14% Li $2s$, 15% In $5s$, 9% In $5p$, and 62% P $3p$) at 0.36 and 0.13 eV [Fig. 2(b)], respectively, above the valence-band edge when the impurity occupies

the P site. In other III-V compounds like GaSb, an increase in hole concentration but a decrease in mobility is observed, with the increase of Li concentration, to a critical value of 3×10^{19} atoms/cm³. Above this critical value, the impurity levels merge with the valence band of GaSb and an increase in width of the optically forbidden zone is noticed.²⁸ Increase of the Li concentration in our calculation may result in additional levels arising from the $2s$ and $2p$ states of Li hybridized with the host and forming an s band centered on the a_1 state close to the valence-band edge. Considering the diffuse states involved, this impurity band could rapidly become broad enough to overlap the host valence band. Also, the t_2 level deep in the gap acts as a trapping center and may be related to the reduction of mobility seen in GaSb:Li up to the critical concentration range.

A fraction of Li was thought to occupy the Ga site (Li_{Ga}) and form pairs with Li in the interstitial sites (Li_I) when Li was diffused in GaAs at high temperatures. Li has a smaller ionic radius of 1.01 Å as compared to In and P, and can substitute either site in InP. The present binding energy calculations reveal that Li_{In} site is favored as compared to the occupancy at the P site by approximately 0.22 eV (see Table II). However, this does not rule out the possibility of an energetically favored interstitial position. Translation of the impurity atoms to an interstitial position lowers the symmetry of the system, posing greater computational difficulty and will not be considered in this paper.

C. Beryllium

The control of residual impurities is essential for growing high-purity material. At temperatures 1.7–20 K, photoluminescence measurements on epitaxial and bulk samples with low doses (10^9 – 10^{11} cm⁻²) of Be were carried out by Skromme *et al.*²⁹ to identify the residual acceptors in high-purity InP. Also, deliberate doping of beryllium can result in high quality p - n junctions.³⁰ Doping concentration in GaAs (easily controlled by varying the Be oven temperature) has been achieved³¹ to about 10^9 cm⁻³. The Be-ion implantation technique used in preparing uniform p layers in III-V compounds is now well recognized for its high activation and low radiation-induced damage.³²

The self-consistent charge distributions are presented

TABLE II. Energy preference of the impurities occupying either the In or P sites in InP semiconductor.

Impurity	In site	P site
Li		0.22 eV
Be	0.44 eV	
B	0.24 eV	
C		0.03 eV
N		0.40 eV
O		0.20 eV

in Table I for Be_{In} and Be_{P} . The impurity retains its atomic character when substituted at the In site. It picks up a minimal charge equivalent to $0.01\text{--}0.02e$ to become a nominal acceptor. This is consistent with the Pauli electronegativity scale as no charge transfer with neighboring phosphorus atoms is expected due to their identical electronegativities. But when the impurity is placed at the P site, it gathers a larger charge: $0.32\text{--}0.37e$ to become an active acceptor. Thus Be, in general, behaves like an acceptor in InP. Our calculations reveal an acceptor level of t_2 symmetry (7% Be $2p$, 29% In $5p$, and 62% P $3p$) at 0.12 eV for Be_{In} [Fig. 1(c)], in fair agreement with photoluminescence experiments³³ where an acceptor level is identified at 0.04 eV. But for the Be_{P} site, we identify two gap levels: one at $E_v + 0.03$ eV of a_1 character (8% Be $2s$, 15% In $5s$, and 77% P $3p$), and the other at 0.28 eV below the conduction band-edge of t_2 character (8% Be $2p$, 10% In $5p$, and 80% P $3p$) as shown in Fig. 2(c). Low-temperature-grown (130–480 °C) InP was investigated³⁴ using photoluminescence spectroscopy with changes of excitation intensity and temperature. Two deep broad photoluminescence bands at approximately 0.8 and 1.06 eV are found in undoped and Be-doped materials, and their formation strongly depends on the growth temperature. These levels are due to $\text{P}_{\text{In}}\text{V}_{\text{In}}$.

It is not known for certain if Be occupies the In site. At about 600 °C Be atoms go to the substitutional Ga site in GaAs. The binding energy for Be at both the In and P sites is calculated. The binding-energy preferences are shown in Table II. The energies calculated in the present model for Be_{In} exceeds the binding energy of the Be_{P} site by 0.44 eV, suggesting that Be tends to occupy the In site. However, from packing fraction considerations Be, with an atomic radius (1.06 Å) less than both In and P, can substitute for either site in InP.

D. Boron

Boron is a residual contaminant in the liquid encapsulation Czochralski (LEC)-grown (B_2O_3)-InP crystal. The content of boron contamination has been proved³⁵ to be 10^{16} cm^{-3} . We present, in Table I, the self-consistent charge distribution for the isoelectronic B impurity in InP. The net charge on the impurity increases from $0.01e$ to $0.33e$ when the impurity is switched from the In to the P site. Boron and In belong to the same group in the Periodic Table, and therefore a similar ionicity to that of In in InP was expected when substituted at the In site. B is thought to occupy the In site, assuming that metals substitute at the metallic sites. When at the In site, it introduces an a_1 level at 0.3 eV below the conduction-band edge [Fig. 1(d)]. In GaAs, with a low boron content, Ta, Hobgood, and Thomas³⁶ find no residual acceptors but a low conductivity n -type material. Elliott³⁷ describes a model of the defect chemistry of double acceptors in GaAs and confirms the p -type material to be unaffected by boron at a low concentration of 10^{16} cm^{-1} , but for a higher B content a greater number of B_{As} defects is formed. As the impurity is placed at the P site in InP, two levels at 0.21 and 0.61 eV of t_2 and a_1 symmetries,

respectively, are predicted above the valence-band edge [Fig. 2(d)] in the gap of the host semiconductor.

Our calculations as shown in Table II reveal that B tends to go to the In site. The binding energy of B_{In} exceeds B_{P} by 0.24 eV. The atomic radius of B is known to be 0.88 Å, so by packing arguments either site is acceptable.

E. Carbon

Carbon is a residual impurity in InP. Traces of carbon enter the material when vitreous carbon boats are used for liquid-phase epitaxial (LPE) layers in growing crystal³⁸ or from carbon hydrides in metal-organic vapor-phase epitaxial (VPE) InP films.³⁹

The carbon impurity in III-V semiconductors is likely to behave as an amphoteric dopant. When in a group-III site (or group-V site), it is expected to act as a donor (or acceptor). The tendency is to substitute for the element with larger atomic radii. Carbon with a smaller radius (0.774 Å) as compared to indium or phosphorus can occupy either site; moreover, the possibility of its going into the interstitial site still remains.

The Mulliken population is indicated in Table I. When C is placed at the In site, a tenth of an electron is released to the neighboring P. Again, switching sites leads to a slightly lower ionicity for the impurity, thereby making it more atomiclike with a charge reorganization in the neighboring P and In atoms. The volume-integrated charge, however, is in opposite phase with respect to the Mulliken population analysis. This calculated donor character is surprising, since an acceptorlike behavior for carbon has been observed by many experimental researchers,^{7,40,41} in other semiconductors. A thermodynamical approach⁴² indicates that C in GaAs is the most acceptorlike impurity, but that all the group-IV impurities, including C, are unlikely to be acceptors in InAs or InP. Again, photoluminescence studies on vapor-phase epitaxial GaAs (Ref. 43) indicate C (assumed to be at the Ga site) to be a shallow donor.

The C impurity at the In site introduces a level of a_1 character, composed of 45% C $2p$, 2% P $3s$, 8% P $3p$, and 45% In $5p$, in the gap region at 0.39 eV above the valence-band edge, as shown in Fig. 1(e). This is in excellent agreement with experimentally predominant shallow levels at $E_v + 0.4$ eV,³⁸ and at $E_v + 0.044$ eV.³³ At the P site, however, the impurity leads to two gap states: a t_2 level composed of 18% C $2p$, 3% In $5p$, and 75% P $3p$, and an a_1 level arising from 11% In $5s$, 8% In $5p$, and 80% P $3p$ with a negligible C $2s$ contribution [Fig. 2(e)]. The t_2 state is a shallow level with a binding energy of 70 meV with respect to the valence band, and is in fair agreement with the photoluminescence measurement of 45 meV.³³ The a_1 level at $E_v + 0.54$ eV is a deep level. Experimentally C-related deep donors were predicted⁴⁴ to compensate for the acceptor levels in order to explain the independency of carrier concentration with CH_4 doping. Simultaneous shallow and deep levels are predicted⁴⁵ theoretically using Koster-Slater linear combination of atomic orbitals (LCAO) interpretation theory. The main C-related levels as detected experimentally⁴⁴ in deep-level

transient spectroscopy (DLTS) are at $E_v+0.4$ and $E_c-0.45$ eV, respectively. C was thought to introduce shallow levels in other semiconductors like GaAs and GaP, but recent calculations assert the presence of deep levels at $E_v+0.12$ and $E_c-0.4$ eV in GaAs,⁴⁶ and at $E_c-1.0$ and $E_c-1.3$ eV, in GaP.⁴⁷

The calculated difference in the binding energies (see Table II) of C at the P and In sites is very small (0.33 eV), suggesting that C can substitute at either In or P sites in InP, and is indeed an amphoteric dopant here.

F. Nitrogen

Being the first member of the group-V elements, nitrogen is an isoelectronic impurity in III-V compound semiconductors. It enters as a residual impurity in the vapor-grown material. Technologically, GaP:N and GaAs:N are used in the production of light-emitting diodes.

When placed at the In site, we find that N is atomiclike with a configuration $2s^2 2p^{2.97}$; see Table I. The $2p$ state picks up a total charge of 3.34 eV when substituted at the P site. Nitrogen acts as a donor at the In site and as an acceptor at the P site: an amphoteric behavior similar to that of group-IV elements here.

In GaP:N, one trap level at 0.44 eV below the conduction-band edge is usually detected⁴⁸ for both majority and minority carrier injection conditions. Two other levels occasionally detected are at $E_c-0.39$ and $E_v+0.60$ eV, respectively. Other authors⁴⁹ predict levels at $E_c-0.42$ and $E_c-0.28$ eV, respectively.

Replacing the central indium by N results in a deep level at $E_v+0.45$ eV of t_2 character [Fig. 1(f)] in the midgap region. N at the P site introduces a deep level of a_1 character at 0.62 eV [Fig. 2(f)], above the valence-band edge. Apart from the calculated deep level, two shallow levels of t_2 character are detected close to the band edges. The filled t_2 state is 60 meV above the valence-band edge, while the empty t_2 state is 45 meV below the conduction-band edge. In principle, due to the isoelectronic nature, minimal changes in conductivity should occur when N is substituted at the P site. But experimentally,⁴⁴ the net carrier concentration was found to decrease with NH_3 doping. The principal defect levels assigned to N from deep-level transient spectroscopy (DLTS) measurements⁴⁴ are at 0.21 and 0.3 eV above the valence-band edge. The same experiments carried out under minority-carrier concentration indicated levels at 0.41 and 0.51 eV below the conduction-band edge.⁴⁴ These deep levels act as strong recombination centers and thereby make the material highly resistive. In GaP:N, one trap level at 0.44 eV below the conduction-band edge is usually detected for both majority- and minority-carrier injection conditions. Two other levels occasionally detected are at $E_c-0.39$ and $E_v+0.60$ eV, respectively. Other authors predict levels at $E_c-0.42$ and $E_c-0.28$ eV, respectively.

The atomic radius of N (0.7 Å) is smaller than both In and P, so it can substitute at either site. From the amphoteric nature it might seem that the energy difference between the two configurations would be small, but the

calculated binding energies (Table II) show that the P site is favored by 0.40 eV.

G. Oxygen

Being highly reactive, oxygen can easily contaminate the material at various stages of growth and processing. Experimentally deep donors in melt-grown crystal^{50,51} and shallow donors in LPE-grown crystal⁵² are observed in GaAs doped with oxygen. However, electronic and structural properties have not been studied in detail in InP.

The Mulliken population analysis [see Table I] shows that O is an acceptor in general. In the O_{In} configuration, however, O tends to remain neutral in the host. Earlier calculations^{53,54} for GaP:O were used to work out a quantitative approach to the problem of deep levels. According to the Green-function calculation by Jaros and Dean, a filled O $2p$ state is contained within the valence band in contradiction to Morgan's nearly free atomic model. In InP, our calculations show that O is atomiclike with its $2p$ state lying in the valence band, close to the band edge. A similar situation is seen in the MS- $X\alpha$ calculation of da Silva, Makinchi, and Leite⁵⁵ for GaP:O.

O_{In} doping leads to a defect level at $E_v+0.24$ eV of t_2 character, as shown in Fig. 1(e). This level is formed by mixing 29% O $2p$, 2% P $3s$, 26% P $3p$, and 42% In $5p$. At the P site [Fig. 1(f)], the impurity introduces two levels at $E_v+0.36$ and $E_v+0.47$ eV of a_1 and t_2 characters, respectively. These levels are composed of 11% In $5p$ and 80% P $3p$ for a_1 , and 8% O $2p$, 10% In $5s$, and 82% P $3p$ for t_2 , respectively. Experimentally determined trap levels of a vapor-phase epitaxial (VPE)-grown material are at $E_v+0.17$ and $E_c-0.66$ eV.⁴⁴ The main trap in conducting and semi-insulating⁵⁶ GaAs is at $E_c-0.75$ eV. It is not known if the trap is due to the oxygen impurity or an intrinsic defect. Huleer *et al.*,⁵⁷ from their secondary-ion-mass spectroscopy (SIMS) and DLTS experiments, concluded that O is not involved in producing this trap responsible for the semi-insulating properties. In contrast, a later work by Kaminska *et al.*⁵⁸ pointed out that O was responsible for introducing the impurity by suppressing the inherent Si impurity level introduced in the process of growth as a contamination. Ikoma, Takikawa, and Taniguchi⁵⁹ also reported independently that the center is O related.

The atomic radius of O (0.8 Å) is less than both In and P. Our theoretical calculations reveal that O tends to occupy the P site over that of the In site by approximately 0.20 eV (Table II). This is consistent with the chemical valence picture, where nonmetal atoms are assumed to substitute at the P site in InP.

IV. CONCLUSIONS

We have carried out detailed electronic structure calculations of the substitutional impurities Li, Be, B, C, N, and O in InP, using the embedded-cluster DV-LCAO-SCF self-consistent field method. The calculated band gap of 0.8 eV is in fair agreement with the experimental value. The impurities were first substituted at the In site, forming a $\text{Imp}_4\text{In}_{12}$ cluster, and then at the P site form-

ing $\text{ImIn}_4\text{P}_{12}$ clusters. In general, Li, Be, and O are found to be acceptors, whereas B and C are donors. N, on the other hand, is a donor at the In site and an acceptor at the P site. Apart from the expected shallow levels for these light elements as dopants, deep levels were also identified as is seen in other III-V compound semiconductors. The impurity $2s$ state close to the cluster Fermi energy for Li is pulled down gradually to the bottom of the valence band. Again following the same path, the impurity $2p$ states formally in the conduction band cross the Fermi level and enter the valence band due to the increasingly attractive potential of the central impurity atom. Hence an ascending order in charge accumulation is observed (see Table I) for impurity states. Binding-energy comparisons at two different sites of the impurity leads to

predictions of stable configurations in these systems. According to our calculations, Li, Be, and B tend to go to the In site and N and O to the P site. C, on the other hand, can occupy either site, but tends toward P by a slight margin.

The effect of lattice relaxation, which has not been accounted for in our model, may alter the electronic structure and energies appreciably. Studies of lattice relaxation effects, interstitial site energetics, and formation of binary defect complexes are needed for a complete understanding of impurities in III-V semiconductors.

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