PHYSICAL REVIEW B VOLUME 41, NUMBER 18 15 JUNE 1990-II

Donor levels and impurity-atom relaxation in nitrogen- and phosphorus-doped diamond

Koblar Jackson and Mark R. Pederson
Complex Systems Theory Branch, Condensed Matter and Radiation Science Division,
Naval Research Laboratory, Washington D.C. 20375-5000

Joseph G. Harrison
University of Alabama–Birmingham, Birmingham, Alabama 35294

(Received 11 December 1989; revised manuscript received 26 March 1990)

New fabrication techniques have generated interest in the use of impurity-doped diamond as an active material in electronic devices. In this paper we study the properties of the *n*-type impurities nitrogen and phosphorus in diamond, using a first-principles cluster approach based on the local-density approximation. We determine impurity-donor-level positions of 0.75 and 1.09 eV, respectively, for C:N and C:P, measured relative to the bottom of the conduction band. We also study the energetics of impurity-atom relaxation along the ⟨111⟩ direction in the diamond lattice. While experimental observations indicate a trigonal distortion about the impurity site, we find the on-center position for both impurity atoms to be stable against simple off-center relaxation.

I. INTRODUCTION

Recent advances in diamond-fabrication techniques have spawned an interest in the use of diamond as a semiconductor in electronic devices.[1] Diamond's unequaled hardness and thermal conductivity[1] make its use in devices subject to extreme conditions very attractive. With an indirect band gap of 5.4 eV, undoped diamond is a good insulator and practically useless as a semiconductor; however, diamond samples containing boron impurities show *p*-type conductivity with a hole activation energy of about 0.4 eV.[2] There is considerable interest in developing *n*-type–diamond semiconducting materials with similar or smaller activation energies, to make the *p*-*n* technologies of the conventional semiconductor industry applicable to future diamond-based devices. By studying the properties of the nitrogen and phosphorus impurities in diamond, we seek to better understand the nature of *n*-type–diamond systems.

Substitutional nitrogen and phosphorus, with five valence electrons, are prototype *n*-type impurities in diamond. While the isolated nitrogen impurity (C:N) is well characterized experimentally,[2–5] relatively little is known about the properties of phosphorous in diamond (C:P). In this paper we study the properties of C:N and C:P using a first-principles quantum-mechanical approach based on the Hobenberg-Kohn-Sham local-density approximation (LDA),[6] performing self-consistent LDA calculations on finite clusters of atoms. In these calculations we seek first to determine the positions of the impurity donor levels relative to the host conduction band (CB). A second issue of interest is the position of the impurity atom in the diamond lattice. Experimental evidence[7] clearly shows a distortion at the impurity site, lowering the point-group symmetry from tetrahedral (T_d) to trigonal (C_{3v}). A simple model for this distortion has the nitrogen atom relaxing off center in the ⟨111⟩ direction as a result of the Jahn-Teller effect. Four equivalent antibonding orbitals centered on the C—N bonds are available to the donor electron. Stretching one of the bonds lowers the energy of the corresponding antibonding orbital, and placing the donor electron in this state gives a nondegenerate ground state for the C:N system. From the point of view of a one-electron theory such as the LDA, however, such a picture is problematic. The lowest one-electron state available to the donor electron is a symmetric combination of the four antibonding orbitals. Any off-center relaxation must then be due to higher-order effects in these theories. We investigate the off-center relaxation of the impurity atom in the diamond lattice by performing total-energy calculations as the impurity atom is systematically moved off center.

In Sec. II we give a brief overview of our computational method, which employs a local-orbital basis to perform LDA calculations. In Sec. III we present results from calculations on perfect and defected hydrogen-terminated clusters (C_5H_{12} and $C_{17}H_{36}$). We show that the central atom is stable to simple distortions along the ⟨111⟩ direction and that Jahn-Teller or pseudo-Jahn-Teller distortions do not occur within the LDA framework. In Sec. IV we compare our results with other theoretical results and experiment.

II. COMPUTATIONAL METHOD

The local-density approximation[6] is the starting point for most current first-principles condensed-matter calculations. Assuming the Born-Oppenheimer approximation, the LDA total energy of a system of *N* electrons and *M* nuclei is written as a function of the nuclear coordinates and atomic numbers, and a functional of the electronic charge density:

$$E=\frac{1}{2}\sum_{\nu,\mu}{}'\frac{Z_\nu Z_\mu}{|\mathbf{R}_\nu-\mathbf{R}_\mu|}+2\sum_i\langle\psi_i|-\tfrac{1}{2}\nabla^2+V_{\mathrm{ext}}|\psi_i\rangle+\frac{1}{2}\int d\mathbf{r}\int d\mathbf{r}'\,\frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}+\int d\mathbf{r}\,\rho(\mathbf{r})\varepsilon_{\mathrm{xc}}[\rho]\ , \tag{1}$$

where

$$V_{\mathrm{ext}}=-\sum_\nu\frac{Z_\nu}{|\mathbf{r}-\mathbf{R}_\nu|} \tag{2}$$

and

$$\rho(r)=2\sum_{i=1}^{N}|\psi_i(\mathbf{r})|^2\ . \tag{3}$$

Here, $\rho(\mathbf{r})$ is the total electronic charge density, which is constructed from the occupied Kohn-Sham orbitals (ψ_i), and V_{ext} is the Coulomb attraction of the nuclei, with Z_ν the charge on the νth nucleus, centered at $\mathbf{R}_\nu$. The energy in Eq. (1) is a sum of the nucleus-nucleus repulsion, the electron kinetic energy, the electron-nucleus attraction, the electron-electron Coulomb interaction, and the exchange-correlation energy of the electrons, approximated in the LDA by a local functional of the electronic charge density, represented above by $\varepsilon_{\mathrm{xc}}[\rho(\mathbf{r})]$. In our calculations we employ the Kohn-Sham exchange functional, and the Ceperly-Alder correlation functional, as parametrized by Perdew and Zunger.[8] The energy expression in Eq. (1) is written without spin polarization for convenience. The corresponding spin-polarized expression is a simple generalization, and will not be discussed here.

One-electron, Schrödinger-like equations for the $\psi_i(\mathbf{r})$ are obtained variationally from E, and are written

$$[-\tfrac{1}{2}\nabla^2+V_{\mathrm{eff}}(\mathbf{r})]\psi_i(\mathbf{r})=\lambda_i\psi_i(\mathbf{r})\ , \tag{4}$$

where

$$V_{\mathrm{eff}}=V_{\mathrm{ext}}+\int d\mathbf{r}\,\frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}+\frac{\partial}{\partial\rho}(\rho\varepsilon_{\mathrm{xc}}[\rho])\ . \tag{5}$$

In this work we treat finite clusters of atoms. To solve Eq. (4) for these systems, we adopt a Gaussian-orbital-based, linear combination of atomic orbitals (LCAO) approach, solving Eq. (4) self-consistently in a fixed basis set consisting of contracted Gaussian orbitals obtained from calculations for the relevant free atoms, plus additional single Gaussian orbitals centered at the various nuclei to augment the variational freedom of the basis.[9] We have recently developed a variational mesh for the numerical integration of all Hamiltonian matrix elements. See Ref. 10 for details.

The cluster approach has a straightforward intuitive appeal in investigating localized impurities in solids, in that only the region of interest is included in the calculation. From a practical point of view, the cluster method allows for the investigation of impurity structural properties and the importance of geometrical relaxation in determining the impurity electronic properties. In addition, the method provides a direct and systematic means for determining the convergence of calculated properties with respect to cluster size.

To investigate impurity properties, we perform parallel calculations on clusters with and without an impurity atom replacing the central host atom. Electronic properties are taken from the LDA eigenvalues for the cluster eigenstates. The eigenvalues for the "pure" clusters are readily grouped into bands corresponding to the host-crystal energy bands. As larger clusters are treated, the "bands" are populated with increasing numbers of eigenvalues, and in the limit of very large clusters the cluster band structure coincides exactly with that of the full crystal. Properties corresponding to the bulk-crystal band gap and valence-band (VB) width are determined from the cluster results by taking the relevant one-electron—eigenvalue differences. These provide a measure of the extent to which a particular cluster reproduces the local electronic environment of the bulk crystal.

By comparing the self-consistent LDA eigenvalues for the pure and defect clusters, the positions of impurity-related electronic levels are identified. The orbital makeup of these states may be investigated by reference to the corresponding LCAO eigenvectors. Structural properties of a given cluster may be investigated by systematically minimizing the cluster total energy with respect to the appropriate nuclear coordinates. Since independent total-energy calculations are performed for each configuration, all effects of orbital relaxation are included self-consistently.

III. RESULTS

A. The pure cluster

Viewed as a semiconductor, diamond has a very large band gap (5.4 eV) and a small dielectric constant ($\epsilon=5.5$), implying that the valence electrons in diamond are tightly bound. This property makes diamond a good candidate for study using the cluster approach: Because the valence electrons are tightly bound, the local electronic properties of bulk diamond should be reproduced in a cluster calculation involving a relatively small number of atoms. Another key factor in studying diamond with the cluster method is the fact that dangling bonds on the cluster surface can be saturated with bonds to hydrogen atoms without disrupting the covalent bonding in the cluster interior, and without distorting the bulklike electronic properties. Dangling bonds from surface carbon atoms would appear as partially occupied states in what corresponds to the bulk band gap, and the presence of such gap states would complicate efforts to study impurity states lying in the gap. Capping the clusters with hydrogen atoms, placed at tetrahedral bond locations relative to surface carbon atoms with a fixed C—H bond length equal to the methane bond length (2.09 a.u.), transforms the dangling surface states into bonding states which lie in the VB and preserves the sp^3-bonding character of the C atoms.

The clusters used in our calculations consist of successive shells of nearest-neighbor (NN) carbon atoms around a central atomic site, with bond lengths set equal to the C-C distance in diamond, 2.92 a.u. As discussed above, fourfold coordination of surface carbons is achieved by adding hydrogen atoms at the appropriate tetrahedral sites, with a C-H distance of 2.09 a.u. The simplest cluster for studying substitutional impurities is C_5H_{12}, consisting of the impurity at (0,0,0), plus a NN shell of C atoms at the (1,1,1) positions and surface H atoms at appropriate sites corresponding to the (2,2,0) pure lattice shell. In $C_{17}H_{36}$, C atoms are placed on the (1,1,1) and (2,2,0) shells, with H atoms on the (3,3,1) and (3,1,-1) pure-crystal equivalents. The geometry of the central atoms of these clusters is shown in Fig. 1.

To provide a reference for the impurity calculations, and as a way of gauging the effects of cluster size on the impurity calculations, we performed a series of calculations on the "pure" clusters C_5H_{12} and $C_{17}H_{36}$. The energy-band gap and the VB width are convenient quantities for comparison of cluster and infinite crystal results. Bulk values for the band gap and VB width, obtained using a LCAO band-structure approach, are 4.2 and 22.1 eV, respectively.[11] In the cluster calculations we define the band gap to be the energy difference between the highest occupied VB state and the lowest unoccupied [conduction-band-(CB-) like] state. Similarly, the VB width is the energy difference between highest- and lowest-energy VB states. As shown in Table I, we found 7.5 and 12.6 eV, respectively, for the gap and VB width in the C_5H_{12} cluster, while for $C_{17}H_{36}$ we found 4.5 and 17.7 eV, respectively. In a separate calculation of a $C_{10}H_{22}$ cluster model of the diamond (111) surface, we found[12] 5.0 and 16.3 eV for the energy gap and VB width. These values are intermediate between the results for the two clusters treated here, and help to show the evolution of bulklike properties in successively larger clusters (see Table I). As expected, both the band gap and VB width approach the bulk-crystal values with increasing numbers of atoms in the clusters. We note that the band gap is within 10% of the bulk LDA value in the $C_{17}H_{22}$ cluster, suggesting that the electronic environment in this cluster is already reasonably bulklike.

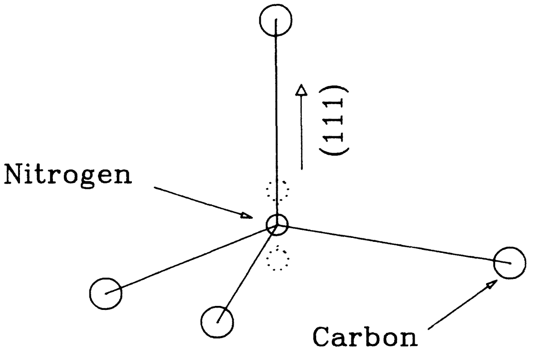

FIG. 1. Geometry of central five atoms for the clusters studied in this work. The ⟨111⟩ trigonal axis is indicated, and relaxation of the central atom along this axis is shown schematically.

TABLE I. Calculated values for the band gap and valence-band width of diamond taken from hydrogen-terminated carbon-cluster calculations.

System	Band gap (eV)	VB width (eV)
C_5H_{12}	7.5	12.6
$C_{10}H_{22}^{a}$	5.0	16.0
$C_{17}H_{36}$	4.5	17.7
C(bulk)[b]	4.2	22.1

[a] Diamond-film calculations of Ref. 12.

[b] Bulk band-structure calculations of Ref. 11.

In Fig. 2(a) we show a contour plot of the full charge density of the C_5H_{12} cluster in a plane containing the central C atom, two of the first NN C atoms, and two of the surface H atoms. It is interesting to note the similarity in the density at the central atom compared with one of the NN atoms. The surface H atoms apparently do little to disrupt the bonding (as reflected by the density plot) in the cluster interior.

Anticipating our interest in the position of an impurity atom in the diamond lattice, we calculated the total energy of the "pure" cluster while moving the central carbon atom off the tetrahedral site in the ⟨111⟩ direction, as indicated in Fig. 1. The total-energy–versus–distortion plot for this series of calculations is given in Fig. 3(a), where the distortion is given as a percentage of the C-C bond length. Positive values correspond to bond-shrinking distortions and negative values to a stretching of the C-C bond. As would be expected for the bulk system, the ideal tetrahedral site is found to be stable.

B. The N substitutional impurity

When the central atom in the C_5H_{12} and $C_{17}H_{36}$ clusters is replaced by N, two impurity-related states appear in the vicinity of the host band gap. First, a donor state of A_1 (s-like) symmetry in the tetrahedral (T_d) group appears in the band gap just below the CB. As shown in Table II, the position of this level with respect to the CB is very similar in the two clusters studied, at $E_c - 0.91$ eV and $E_c - 0.75$ eV in the smaller and larger clusters, respectively, where E_c is the bottom of the CB. While the donor level is not completely converged in the two clusters studied, the convergence of the pure-cluster properties as a function of cluster size (see Table I) suggests that the result from the larger cluster is a good approximation of the corresponding bulk-system value. The lowest CB state is also of A_1 symmetry in both clusters. A second impurity level of T_2 (p-like) symmetry is found just above the CB edge, 1.4 eV above the donor level in C_5H_{12}:N and 1.2 eV above the donor level in the larger cluster. A third, much deeper impurity-related state is also found in these clusters. The state has A_1 symmetry and lies just below the VB in both clusters, at 24.63 and 25.31 eV below the CB in the smaller and larger cluster, respectively. This level has been called the "hyperdeep" impurity state elsewhere,[13] and is a highly localized bonding combination of N and NN C orbitals.

From our self-consistent solution, we determine the nature and extent of the donor-state wave function. The donor state is an antibonding combination of states, centered around the N and first-NN C atoms. In Fig. 2(b) we show a contour plot of the full cluster charge density, and in Fig. 2(d) that of the donor-state charge density. The antibonding character of the donor state is clearly seen in Fig. 2(d). The plot of the full cluster charge density for C_5H_{12}:N indicates that the presence of the N impurity atom only mildly disrupts the covalent bonding of

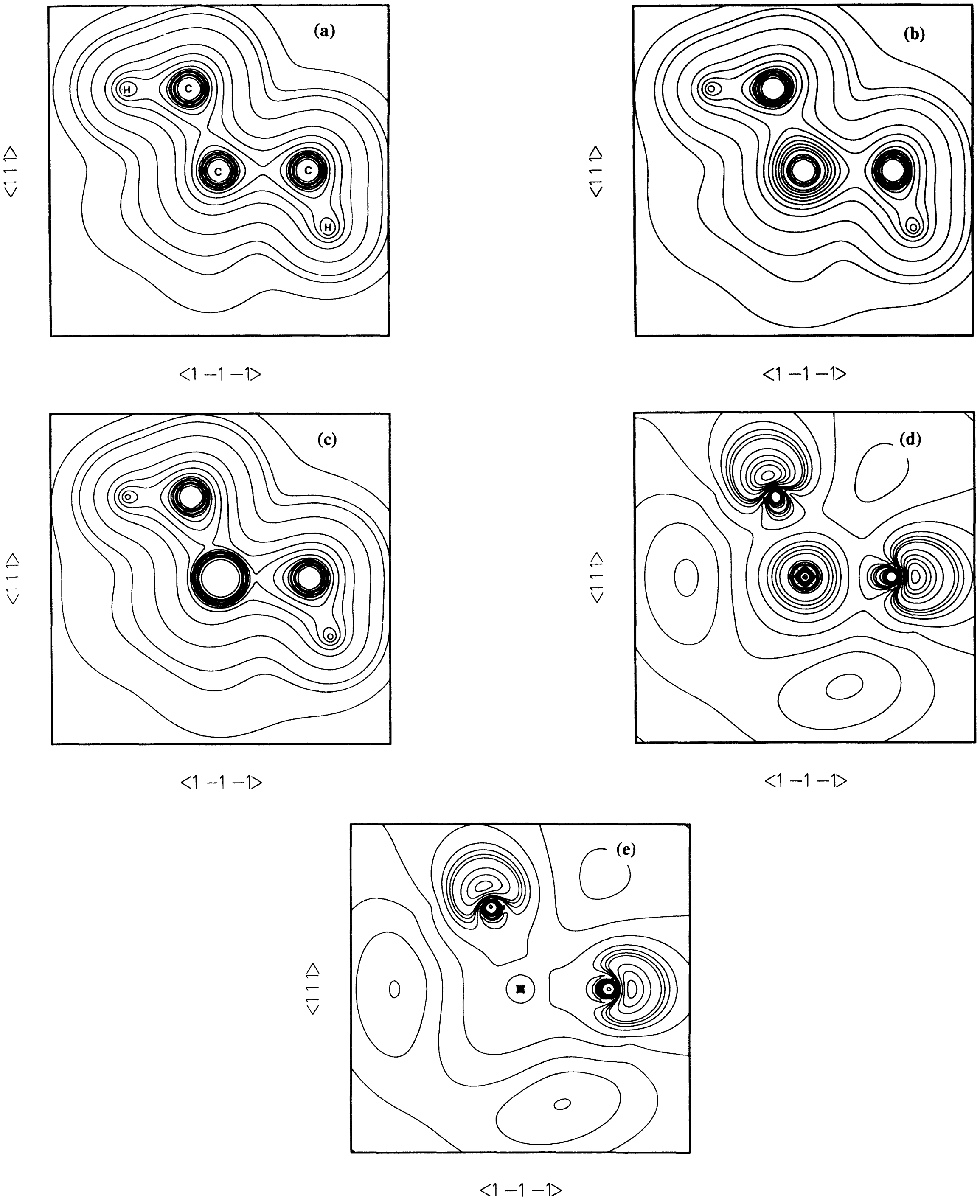

FIG. 2. Contour plots of various cluster charge densities in a plane containing a bonding chain consisting of two surface H atoms, two near-neighbor C atoms, and the central atom in the cluster. The atoms are labeled in (a) for clarity. (a) Full charge density of the pure C_5H_{12} cluster. (b) Full charge density of the C_5H_{12}:N impurity cluster. (c) Full charge density of the C_5H_{12}:P impurity cluster. (d) Charge density of the C_5H_{12}:N donor state. (e) Charge density of the C_5H_{12}:P donor state.

the system.

To determine the stable position of the N impurity in the diamond lattice, we calculated the total energy of the C_5H_{12}:N cluster as the impurity atom was moved off the perfect substitutional site in the ⟨111⟩ direction. (See Fig. 1.) Figure 3(b) is a plot of the total energy versus off-center distortion, again given in percent of the C—C bond length in diamond (2.92 a.u.). Figure 3(b) shows the on-center substitutional site to be stable against simple impurity-atom relaxation in C_5H_{12}:N.

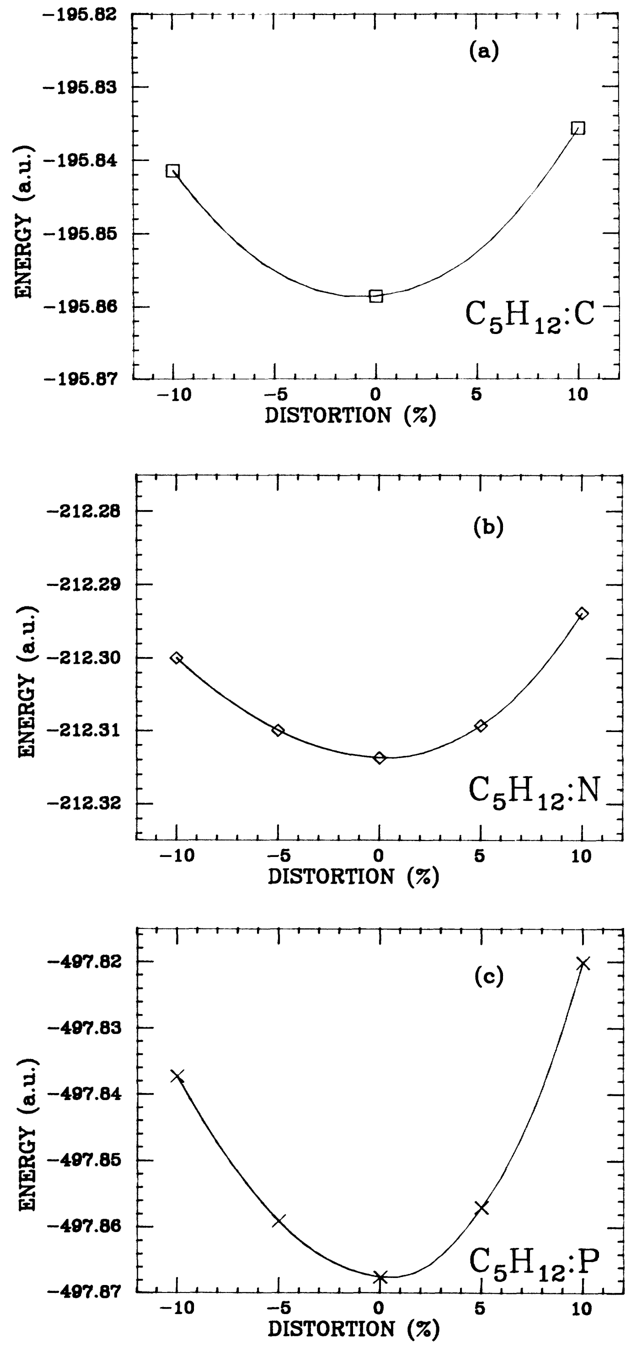

FIG. 3. Total energy vs distortion curves for relaxation of the central atom off the ideal tetrahedral site in the ⟨111⟩ direction for the indicated clusters. The distortion is expressed as a percentage of the C—C bond length in diamond (2.91 a.u.). Positive values correspond to bond-shrinking distortions and negative values to bond-stretching distortions. (a) C_5H_{12}, (b) C_5H_{12}:N, and (c) C_5H_{12}:P.

TABLE II. The defect levels for on-site substitutional nitrogen and phosphorus defects in hydrogen-terminated clusters are presented as a function of cluster size. Energies are with respect to the lowest unoccupied state.

System	Energy (eV)
C_5H_{12}:N	0.91
$C_{17}H_{36}$:N	0.75
C_5H_{12}:P	1.17
$C_{17}H_{36}$:P	1.09

To test the result shown in Fig. 3(b) for the effects of spin polarization, we performed a separate self-consistent spin-polarized total-energy calculation at each of the points shown in the figure. Including spin polarization causes a small, essentially rigid downward shift of the curve in Fig. 3(b), leaving the position of the minimum unchanged.

C. Substitutional P

Isovalent with nitrogen, the phosphorus atom is also a donor impurity in diamond. One significant difference exists between the P and N impurities, however; the P atom is significantly larger than C, with atomic radii of 1.28 and 0.91 Å, respectively, whereas the atomic radius of N is 0.92 Å. Consequently, we expect lattice relaxation around the P impurity in diamond to be important, whereas such relaxation was assumed unimportant in C:N and was not investigated. The large size of the P atom also suggests that the P-impurity system may be more sensitive to cluster-size effects than the clusters containing N.

We studied C:P first assuming no lattice relaxation. We placed the P atom at the central substitutional site in the C_5H_{12} and $C_{17}H_{36}$ clusters, freezing the near-neighbor C atoms at their bulk-crystal positions. As with the N impurity, we found the hyperdeep and donor impurity levels of A_1 symmetry. The donor state is again antibonding and centered about the P and NN C atoms. Contour plots of the C_5H_{12}:P cluster charge density and that of the C:P donor state are shown in Figs. 2(c) and 2(e), respectively. As was the case for the C_5H_{12}:N cluster, the presence of the P-impurity atom introduces additional charge in the region around the impurity. One result of this is the disruption of the approximate symmetry of the charge contours along the bonding chain. In the pure cluster the charge contours around the near-neighbor carbon atoms exhibit an approximate symmetry along the bonding chain, demonstrating that terminating the cluster with H atoms does not seriously alter the covalent bonding between the interior C atoms. In the impurity-containing clusters, there is a distinct asymmetry in the contours in the C-impurity bond direction as compared to those in the C—H bond direction, as the density around the near neighbors adjusts to accommodate the increase in charge around the impurity atom.

The donor state in the C:P system is seen to have less density at the central impurity site than the C:N donor state. As shown in Table II, the P donor level lies at 1.17 and 1.09 eV below the CB, respectively, in the two clusters studied, indicating again some sensitivity of the donor-level result to cluster size. In C:P the unoccupied T_2 impurity state is lower in energy than the corresponding state in C:N, and is essentially degenerate with the lowest CB state.

We investigated the on-center stability of the P substitutional impurity by moving the P atom off center in the C_5H_{12}:P cluster, holding the neighboring atoms fixed at their unrelaxed positions. The energy-versus-distortion curve for this process is shown in Fig. 3(c). As in the case of C_5H_{12}:N, P has a stable on-center position in the unrelaxed cluster.

To address the issue of lattice relaxation around the P impurity, we allowed the first-NN C atoms to relax symmetrically outward from the impurity atom in the $C_{17}H_{36}$ cluster, holding the remaining atoms in the cluster fixed at their ideal lattice positions. By calculating the total energy of the cluster versus this relaxation, we find that the first shell of atoms around the impurity relaxes outward by 6% of the C—C bond length, making the relaxed NN C-P distance 3.10 a.u. The position of the donor level is fairly insensitive to the NN relaxation. With no relaxation, the P donor level is at 1.09 eV below the CB in $C_{17}H_{36}$. Relaxing the carbon neighbors outward by 5% and 10%, respectively, changes the donor level to 1.09 and 1.13 eV below the CB. The A_1 impurity state remains well below the T_2 state in all these calculations.

IV. COMPARISON WITH OTHER WORK AND DISCUSSION

A. Theory

Both *ab initio*[13] and semiempirical[14–18] calculations of the properties of C:N have appeared in the literature. Here we compare and contrast our results first with a first-principles LDA calculation using a Green's-function approach,[13] and then with cluster calculations using the semiempirical, extended Hückel theory (EHT).[14] Other semiempirical calculations give results which are generally similar to those in Ref. 14, and will not be discussed here.

Bachelet, Baraff, and Schlüter[13] investigated the properties of C:N using the LDA in a self-consistent, pseudopotential Green's-function formulation, using Gaussian orbitals to represent the valence states. Their calculation also included an approximate self-energy operator to adjust the LDA single-particle energies to correct for the tendency of the LDA to underestimate the host-crystal band gap. (A discussion of this point regarding the present calculation will be given later.) The N impurity was positioned at the ideal substitutional site.

Because of the use of pseudopotentials and the self-energy operator in the Green's-function calculation, a direct quantitative comparison of our results with the impurity levels found in Ref. 13 is not very useful. Bachelet *et al.* find an impurity state of A_1 symmetry to lie in the host band gap at $E_c - 0.15$ eV, where E_c is the conduction-band edge, and a second impurity state of T_2 symmetry is found to lie about 2 eV higher. This ordering of the impurity states, with the symmetric A_1 state at lower energy, matches the result of our calculation, although our donor level is much deeper, at $E_c - 0.75$ eV, and the splitting between the impurity levels in our calculation is somewhat smaller at 1.2 eV. The character of the N donor state is similar in the two calculations. Bachelet *et al.* also describe the donor level as a symmetric, antibonding state well localized at the impurity site and first-NN shell, with 60% of the donor electron charge concentrated about the central five atoms. Off-center positions for the impurity atom were not investigated in Ref. 13.

Messmer and Watkins[14] used extended-Hückel-theory cluster calculations to determine the properties of substitutional N and the neutral diamond vacancy. In their comprehensive study, they treated clusters of up to 71 atoms, investigating structural as well as electronic properties as a function of cluster size. The results of the EHT and our LDA calculations differ in two significant ways. First, in contrast to our results, the EHT results were sensitive to cluster size, with the position of the donor level relative to the CB varying over a 1-eV range in the 35-, 47-, and 71-atom clusters, with no trend toward convergence. The lack of convergence of the donor level in the EHT calculation is probably due to the nature of the theory. In EHT the Hamiltonian matrix elements are based on empirically chosen parameters, with charge relaxation and other self-consistency effects playing no role.

Also in contrast to our results is the ordering of the A_1 and T_2 impurity states for the on-center C:N system in the EHT calculation, a difference between the LDA and EHT noted by Bachelet *et al.*[13] Messmer and Watkins found the T_2 state to have lower energy, making the donor level in the EHT calculations orbitally degenerate, and the corresponding cluster ground state unstable to Jahn-Teller (JT) distortions. Messmer and Watkins investigated several possible distortion modes of the N atom and NN C atoms, finding a minimum-energy configuration corresponding to a 26% increase of the C—N bond length in the ⟨111⟩ direction. It has been argued[16] that the T_2 level appears at lower energy than the symmetric A_1 donor level in the EHT calculation because of the choice of parameters representing the bonding of *s* and *p* orbitals. Appropriate changes to the parameters reverse the ordering of A_1 and T_2 levels, making the A_1 state lower in energy. Charge self-consistency effects may also play a role in the ordering of the impurity levels in the semiempircal calculations.[17]

With the symmetric A_1 state at lower energy than the T_2 state, the ground state of C:N is nondegenerate, and not a candidate for a Jahn-Teller distortion, and alternative models, including the pseudo-Jahn-Teller effect (PJTE) to be discussed later in this paper, have been put forth[19] to explain the experimentally observed trigonal distortion of C:N.

We are unaware of previous published calculations of the properties of C:P.

B. Experiment and discussion

As mentioned above, experiments have identified a C:N donor level with an activation energy of 1.7 eV.[2] Our result of 0.75 eV is somewhat smaller, but clearly indicates that the N donor level in diamond is "deep." The discrepancy between our result and the experimental activation energy is not surprising. LDA eigenvalues are known to be only rough approximations of electron-removal energies;[8] it is known, for example, that insulator and semiconductor band gaps in the LDA are underestimated by 20–50%. It is interesting to note that our underestimate of the donor activation energy, $1.7-0.75=0.95$ eV, is similar in magnitude to the LDA underestimate of the diamond band gap, $5.5-4.2=1.3$ eV. Several techniques proposed to address the band-gap problem in LDA, including the self-energy operator used in the calculation of Bachelet *et al.*[13] mentioned earlier and the self-interaction correction (SIC),[8] improve the LDA band-gap result by shifting the VB levels down with respect to the CB, thereby increasing the value of the band gap over the uncorrected LDA,[20] and bringing it into close agreement with experiment. Since the donor level in C:N is well removed from the CB, these correction procedures would likely lower the position of the donor level relative to the unoccupied states by an amount comparable to the shift of the VB levels. This would bring the calculated result into better agreement with experiment. Our uncorrected LDA results for C:N are instructive in analyzing the C:P results. The donor level for C:P was found to lie at $E_c-1.09$ eV, so that the C:P donor level is therefore also "deep." Based on the C:N results, we expect this LDA result to underestimate the experimental activation energy for the C:P donor. By assuming that the LDA underestimate of the C:P donor activation energy is similar to that found for C:N, we could expect the C:P donor level to be observed in the neighborhood of $E_c-2.0$ eV. We know of no published experimental value for the C:P donor level.

Experimental studies of C:N show a trigonal distortion of the lattice at the impurity site.[7] This has been understood as a lengthening of one of the C—N bonds to accommodate the donor electron in a bond-centered, antibonding state. Estimates of this bond-stretching relaxation range from 5% to 35% of the diamond C—C bond length.[2] Our calculations suggest that the simple picture of the N atom relaxing along the $\langle 111 \rangle$ direction is not energetically favorable. The results illustrated in Fig. 3 indicate that the tetrahedral site is stable against this relaxation mode in the C_5H_{12} cluster.

While we have not investigated off-center relaxation of impurity atoms in clusters larger than C_5H_{12}, we believe the LDA result for the simple impurity-atom relaxation in those clusters would be the same as seen for the smaller clusters. The donor state in the LDA calculation is a symmetric, nondegenerate A_1 state, making the overall symmetry of the system also A_1, and the system ground state nondegenerate, ruling out a Jahn-Teller instability. The A_1 symmetry of the donor state can be expected on general grounds in the LDA, independent of cluster size, as the symmetric (*s*-like) state is expected to fall at lower energy in an attractive, symmetric potential than the (*p*-like) T_2 state. Bachelet *et al.*[13] find this ordering of the impurity levels in their Green's function calculation, which, in principle, treats the infinite C:N system.

It has been suggested[18] that a pseudo-Jahn-Teller effect (PJTE) is responsible for driving N off center in diamond. The PJTE examines the effect of distortion on both the occupied nondegenerate impurity level, $A_1(T_d)$, and the unoccupied triply-degenerate impurity level, $T_2(T_d)$. While the occupied $A_1(T_d)$ state cannot be split by a distortion, the $T_2(T_d)$ level is split by a trigonal distortion into a higher twofold degenerate state, $E(C_{3v})$, and a lower, nondegenerate state, $A(C_{3v})$. In C_{3v} symmetry, matrix elements can connect the $A(C_{3v})$ state with the $A_1(T_d)$ state, and the resultant mixing of these states, for a sufficiently strong coupling, could lower the energy of the occupied state enough to stabilize the trigonal distortion. Since our total-energy calculations include all effects of this sort of mixing self-consistently, it is clear that the coupling between impurity states is not sufficient to stabilize the trigonal distortion in C_5H_{12}:N, probably because of the large energy difference between the A_1 and T_2 levels (1.2 eV) in the LDA calculation. (We note that this energy difference changes by only about 0.1 eV for a 5% stretching of the C—N bond.) It is unlikely that the distortion-induced coupling of impurity levels would change significantly with additional shells added to the cluster.

The PJTE was invoked to explain the results of a MNDO (modified neglect of differential overlap) calculation[21] in which the position of the N impurity in silicon was studied. In that calculation, the on-center position was found to be metastable, and a deeper minimum was found with the impurity atom off center in the $\langle 111 \rangle$ direction (bond stretching) by 25% of the bulk Si-Si distance. To investigate such large relaxations for C:N and C:P, we performed two additional calculations, one with the N atom off center by 25%, and the P atom off center by 30% of the C—C bond length. These calculations show no tendency for larger distortions to lower the energy of these systems. The results are illustrated in Fig. 4.

How do we reconcile our results with the observed off-center position of isolated nitrogen in diamond? First, it is possible that the experimentally observed distortion involves a more complicated mode than the simple relaxation of the N atom studied here. The experiments indicate only the local symmetry at the impurity site and not the positions of the various atoms. Distortions involving the relaxation of the NN C atoms as well as the impurity may correspond to the stable ground state. Such distortions cannot be reasonably treated in the small cluster used in this work.

A second, somewhat more speculative possibility is that the ideal tetrahedral site is simply the lowest energy state in the LDA, i.e., that the LDA does not predict the observed symmetry-breaking distortion. The LDA is generally very successful in determining structural prop-

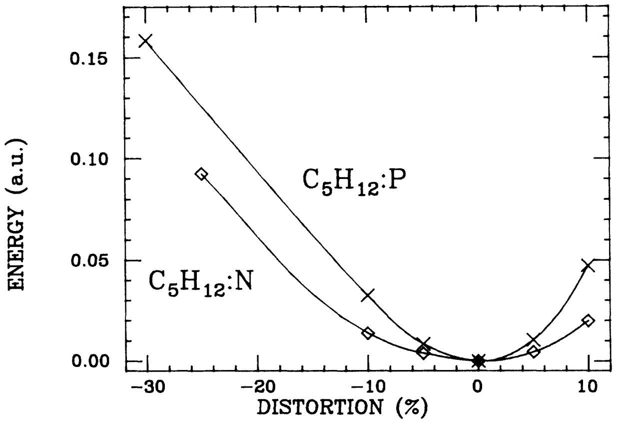

FIG. 4. Total energy vs distortion curves for impurity relaxation off the tetrahedral site in the ⟨111⟩ direction including very large distortions. Energies are given relative to the energy for the on-center configuration for each system.

erties including bond lengths and vibrational frequencies,[22] yet well-known problems associated with the LDA eigenvalues may be responsible for the on-center result for the N impurity in diamond. The self-interaction correction of Perdew and Zunger[8] (SIC) was introduced into the LDA to remove the effects of electronic self-interaction from the LDA total energy, and from the LDA eigenvalues. The resulting SIC-LDA eigenvalues[8,23] are much better approximations of electron-removal energies than the uncorrected counterparts. One feature of the SIC-LDA particularly relevant to the present discussion is that localized one-electron states tend to be favored in the SIC-LDA over delocalized states, the correction preferentially lowering the energy of localized states. In C:N such a tendency could cause a donor state relatively localized on a single C—N bond to fall at lower energy relative to a symmetric state spread out over the four equivalent C—N bonds, compared to the same states in the uncorrected LDA. For atomic nitrogen, for example, using sp^3-hybridized orbitals in place of less localized Cartesian orbitals (s,p_x,p_y,p_z) for the valence electrons lowers the SIC-LDA total energy of the N atom by about 2.0 eV, or about 0.4 eV per valence electron.[24] This tendency could stabilize the off-center placement of the N impurity, since the distortion picks out a particular bond direction for localization, and linear combinations of the $A_1(T_d)$ and $T_2(T_d)$ impurity states can be taken to construct a state localized along a single C—N bond. Note that the energy differences separating the on- and off-center configurations in Fig. 3(b) are only a few tenths of an eV.

Our results also show the P atom to be stable on the ideal tetrahedral site in the small cluster. As with the C:N calculation above, we expect this result to be indicative of the simple relaxation of a P atom in the bulk crystal. We have seen in C:P, however, that lattice relaxation around the impurity site is important, and such relaxation may influence the on-site stability of the impurity. Further calculations using a larger cluster are needed to investigate effects of NN relaxation on the trigonal distortion of C:P.

V. SUMMARY

In this work we have performed self-consistent LDA cluster calculations on the C:N and C:P impurity systems. We found the donor levels in both systems to be deep levels, lying well below the conductionlike states. We find the activation energy for the C:P donor state (1.09 eV) to be similar to that for the C:N donor (0.75 eV), suggesting that other group-V elements such as As are also likely to have deep donor levels in diamond.

We have also investigated the structural properties of the N and P impurity atoms in the diamond lattice. For both C:N and C:P we found the ideal tetrahedral substitutional impurity site to be stable against simple off-center relaxation of the impurity atom in the ⟨111⟩ direction. This suggests that the experimentally observed trigonal distortion at the impurity site in C:N is due to a more complicated relaxation mode than the simple relaxation of the impurity atom off the ideal substitutional site. We also discuss the possibility that the self-interaction correction[8] to the LDA could alter the LDA result for the stable impurity position, favoring an off-center placement for the impurity. For C:P we investigated the relaxation of the NN carbon atoms around the impurity, and found an outward relaxation of 6% of the C—C bond length. Additional calculations are necessary to investigate trigonal distortion modes in these systems involving more than the impurity atom. We are currently implementing a force algorithm into our codes, to calculate the Hellmann-Feynman forces (including basis-set corrections) (Refs. 25–27) on the atomic nuclei in the clusters. Forces will be a key addition in structure calculations, allowing the simultaneous optimization of many structural degrees of freedom. Applied to C:N, we plan to use forces to locate the minimum of the $C_{17}H_{36}$:N cluster with respect to relaxation of the impurity and first-NN atoms, and determine whether the experimentally observed trigonal distortion at the impurity site is reproduced by the LDA.

ACKNOWLEDGMENTS

This work was supported in part by the Office of Naval Research. One of us (K.A.J.) acknowledges partial support from the National Research Council. The calculations were carried out on Cray Research, Inc. supercomputers at the Pittsburgh Supercomputer Center (K.A.J.), at the Naval Research Laboratory (M.R.P.) and at the Alabama Supercomputer Center (J.G.H.). We thank Dr. W. E. Pickett for helpful comments on this work and Dr. S. C. Erwin for computer-programming assistance.

---

[1] J. C. Angus and C. C. Hayman, Science **241**, 913 (1988); J. C. Angus, F. A. Buck, M. Sunkara, T. F. Groth, C. C. Hayman, and R. Gat, Mater. Res. Soc. Bull. **14**, 38 (1989).

[2] J. Walker, Rep. Prog. Phys. **42**, 108 (1979).

[3] G. Davies, Rep. Prog. Phys. **44**, 787 (1981).

[4] J. Loubser and J. A. van Wyk, Rep. Prog. Phys. **41**, 1201 (1978).

[5] C. A. J. Ammerlaan and E. A. Burgemeister, Phys. Rev. Lett. **47**, 954 (1981).

[6] P. Hohenberg and W. Kohn, Phys. Rev. **136**, B864 (1964); W. Kohn and L. J. Sham, *ibid.* **140**, A1133 (1965).

[7] W. V. Smith, P. P. Sorokin, I. L. Gelles, and G. J. Lasher, Phys. Rev. **115**, 1546 (1959).

[8] J. P. Perdew and A. Zunger, Phys. Rev. B **23**, 5048.

[9] E. E. Lafon and C. C. Lin, Phys. Rev. **152**, 579 (1966).

[10] M. R. Pederson and K. A. Jackson, Phys. Rev. B **41**, 7453 (1990).

[11] S. C. Erwin (private communication).

[12] M. R. Pederson, K. A. Jackson, and W. E. Pickett, in *Technology Update on Diamond Films,* edited by R. P. H. Chang, D. Nelson, and A. Hiraki (Materials Research Society, Pittsburgh, 1989).

[13] G. B. Bachelet, G. A. Baraff, and M. Schlüter, Phys. Rev. B **24**, 4736 (1981).

[14] R. P. Messmer and G. D. Watkins, Phys. Rev. B **7**, 2568 (1973).

[15] A. Mainwood, J. Phys. C **11**, 2703 (1979); **12**, 2543 (1979).

[16] M. Lanoo, Phys. Rev. B **25**, 2987 (1982).

[17] H. W. L. Alves, A. N. Borges, J. L. A. Alves, J. R. Leite, and A. Dal Pinto, Solid State Commun. **51**, 939 (1984).

[18] S. J. Sferco and M. C. G. Paseggi, Solid State Commun. **62**, 517 (1987).

[19] J. Koppitz, O. F. Schirmer, and M. Seal, J. Phys. C **19**, 1123 (1986).

[20] R. A. Heaton and C. C. Lin, J. Phys. C **17**, 1853 (1987); S. C. Erwin and C. C. Lin, *ibid.* **21**, 4285 (1988).

[21] G. D. Watkins, G. G. Deleo, and W. B. Fowler, Physica B+C (Amsterdam) **116B**, 28 (1983).

[22] M. L. Cohen, Phys. Scr. **T1**, 5 (1982), and references therein.

[23] J. G. Harrison, R. A. Heaton, and C. C. Lin, J. Phys. B **16**, 2079 (1983).

[24] M. R. Pederson and C. C. Lin, J. Chem. Phys. **88**, 1807 (1988).

[25] P. Pulay, in *Modern Theoretical Chemistry,* edited by H. F. Schaefer (Plenum, New York, 1977), Vol. 4, pp. 153–185.

[26] F. W. Averill and G. S. Painter, Phys. Rev. B **34**, 2088 (1986); **32**, 2141 (1985).

[27] P. J. Feibelman, Phys. Rev. B **35**, 2626 (1987).