

Theoretical studies of native defects in cubic boron nitride

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We have studied the electronic and structural properties of native defects in cubic boron nitride (nitrogen vacancy, boron antisite, and oxygen substitutional) using all-electron first-principles total-energy calculations. We find that all defects introduce a deep state above the middle-energy gap. These defects present a C_{3v} -local symmetry. In the case of nitrogen vacancy the possibility of the F -center formation is discussed. [S0163-1829(97)02328-X]

Cubic boron nitride (c -BN), the lightest of III-V semiconductors, is a large-band-gap material (≈ 6.4 eV),¹ which has several similarities to diamond, such as crystal structure, wide energy band gap, extreme hardness, high thermal conductivity, high melting temperature, and low reactivity.² But while diamond is readily doped only p type, the c -BN can be doped p and n types when suitable impurities are added.³ Of the high-density forms, c -BN is unique among the group-III nitrides in that its zinc-blende structure is the most stable and characterized form. Although it could be an important material for devices at high temperature and high pressure, with many applications in industries in the future, the quality of the samples remains a major problem. If we compare with others III-V materials, c -BN has a very high concentration of native defects.

In this paper we report a theoretical calculation of the behavior of a native defect in c -BN. The electronic and structural properties of an N vacancy ($Vac_{[N]}$), a boron antisite ($B_{[N]}$), and an oxygen substitutional ($O_{[N]}$) are calculated. Although several calculations are available for pure materials,⁴ there are only a few works concerning the theoretical study of defects in c -BN.^{5,6} As far as we know, this is the first work to consider distortions induced by the defects in the calculation.

We have simulated the pure crystal through the molecular cluster with 71 atoms ($NB_4N_{12}B_{12}N_6H_{36}$)³⁺ initially in T_d

symmetry. The hydrogen atoms are introduced to saturate the dangling bonds at the cluster surface, as usual.^{7,8} The net charge 3+ at the cluster is necessary to get a neutral charge condition as in a crystal. Having defined the molecular cluster, the total energies are calculated using the all-electron Hartree-Fock method in the usual linear combination of atomic orbitals procedure. The atomic basis adopted here is the minimal split valence 3-21G basis set,⁹ which consists of $6s3p$ ($3s$) primitive Gaussian functions contracted in the $3s2p$ ($2s$) basis functions on each B and N (H) atom. The size of the set thus ranges from the smallest 242 (for the $Vac_{[N]}$) to 247 (for $O_{[N]}$ and $B_{[N]}$) contracted Gaussian-type functions. The calculations are performed using the program code GAMESS.¹⁰ Before calculating the distortions on geometric structure, when defects substitute the N central atom in the cluster, we first optimize the defect nearest-neighbor bond distances with respect to the A_1 vibrational mode. This is necessary to avoid spurious forces in the *defect cluster*. As we know from the literature,⁸ this cluster size is appropriate to study single-impurity distortions.

For the pure c -BN, the calculated eigenvalue separation between the highest occupied molecular orbital (HOMO) t_2 and the lowest unoccupied molecular orbital (LUMO) a_1 obtained is 8.07 eV. A better result for the band gap is obtained using the Mulliken correction $\Delta E(HOMO-LUMO) = \epsilon_{LUMO} - \epsilon_{HOMO} - J + 2K$, where J and K are the Coulomb

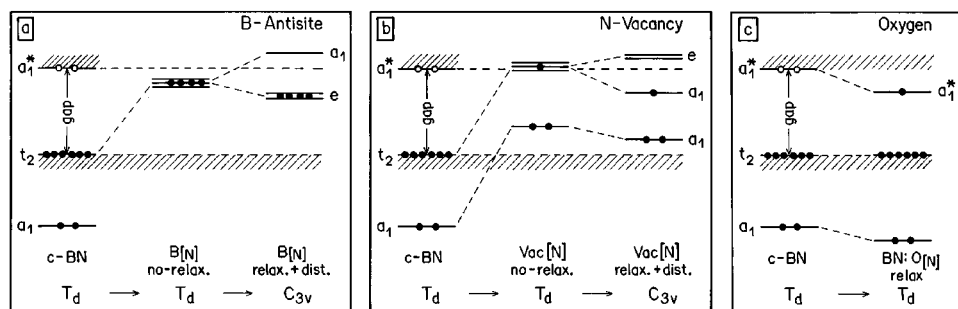


FIG. 1. Schematic representation of the energy levels in the gap region of c -BN for the (a) boron antisite, (b) nitrogen vacancy, and (c) oxygen substitutional.

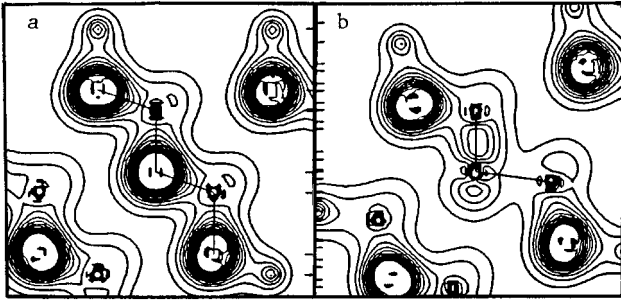


FIG. 2. Contour plot of the total-energy curves for displacements of the B antisite in the (110) plane for (a) pure *c*-BN and (b) the B antisite.

and exchange integrals, respectively. Using this correction, the result for the energy gap drops to 6.53 eV, in excellent agreement with the experimental results.¹

We show schematically in Figs. 1(a)–1(c) the electronic energy levels in the gap region for the $B_{[N]}$, $Vac_{[N]}$, and $O_{[N]}$, respectively, using a defect-molecule model. On the left-hand side is the pure system with the $a_1^2 t_2^6$ configuration. Our procedure to estimate the energy levels in the gap has been to compare the pure cluster and the defect clusters. The electronic energy levels shown in Fig. 1 are obtained as differences between the calculated Hartree-Fock eigenvalues. Fortunately, in all the defects studied here the density of states at the top of the valence band practically do not change. In this sense, the top of the valence, used as a reference for the calculated electronic levels, is fairly well defined.

As one can see in the middle of Fig. 1(a), the electronic effect of the $B_{[N]}$, before structural minimization, is to introduce a t_2 level occupied by four electrons in the gap region. This configuration presents a degenerate ground state and consequently is favorable for a Jahn-Teller distortion. The optimized geometric structure has a C_{3v} symmetry, where the t_2 orbital is split in a twofold-degenerate fully occupied e orbital and an empty a_1 orbital, as shown on the right-hand side of Fig. 1(a). The fully occupied e level, with ligand character (π type), is located 4.81 eV above the top of the valence band, resulting in a deep donor level. In Figs. 2(a) and 2(b) we show the total charge densities in the (110) plane for the *c*-BN and *c*-BN: $B_{[N]}$ systems, respectively. From Fig. 2(b) we see that the B antisite atom makes bonds with the B atoms in the σ_v plane of C_{3v} symmetry.

Concerning the structural properties for the $B_{[N]}$ defect, our results show that the antisite B atom is found in an off-center position. We first performed a breathing mode total-energy minimization that leads to a small inward relaxation of 5% in the bond length. Starting from this relaxed configuration we calculated the total-energy changes of the $B_{[N]}$ atom along the $\langle 111 \rangle$ and $\langle 100 \rangle$ directions, as shown in Fig. 3. For the distortion in the $\langle 111 \rangle$ direction, towards an interstitial position in a C_{3v} configuration, we find a stable position with an energy gain of 1.34 eV and a displacement of the B atom of 0.28 Å. In addition, the distortion in the $\langle 110 \rangle$ direction gives a metastable configuration with C_{2v} symmetry, where the energy gain is 0.65 eV and the displacement of the antisite B atom is 0.16 Å.

With respect to the $Vac_{[N]}$, the calculated breathing

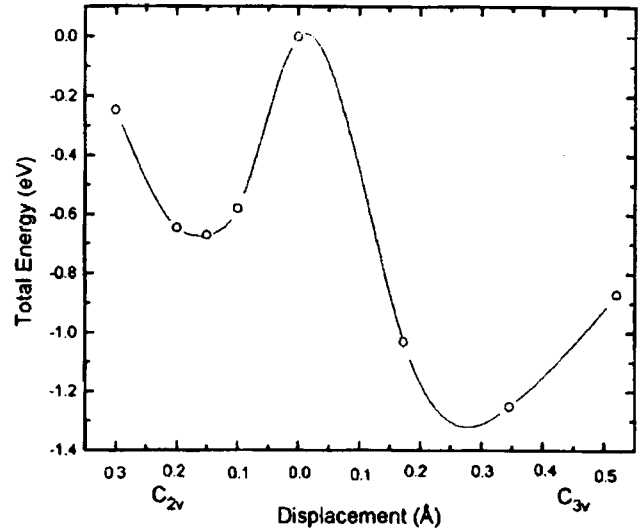


FIG. 3. Calculated total-energy curves for displacement of the B antisite in the $\langle 100 \rangle$ (C_{2v}) and $\langle 111 \rangle$ (C_{3v}) directions (see the text).

mode relaxation of the nearest-neighbor boron atoms gives an outward displacement of 0.31 Å for these atoms, as shown in Fig. 4. A subsequent C_{3v} mode distortion was observed with one boron atom B_1 following a $\langle 111 \rangle$ direction and the three others B_2 , B_3 , and B_4 , getting closer to form a triangle.

As shown in the middle of Fig. 1(b), the removal of a N atom, $Vac_{[N]}$, results in a strong perturbation in the electronic configuration of the system with two orbitals: an a_1 fully occupied in the gap region and a t_2 singly occupied resonant in the conduction band, in agreement with Gubanov *et al.*⁶ After the total-energy minimization a C_{3v} configuration is obtained. The t_2 orbital splits into an a_1 plus an e orbital, as shown on the right-hand side of Fig. 1(b). In the gap region there are two levels with a_1 character ($1a_1^2 2a_1^1$) located 1.76 eV and 4.90 eV above the top of the valence band, respectively.

In Fig. 5 the wave functions for the two highest occupied orbitals ($1a_1 2a_1$) of the neutral vacancy are presented. In the figure the (a) and (c) planes contain the B_1 - Vac - B_3 cen-

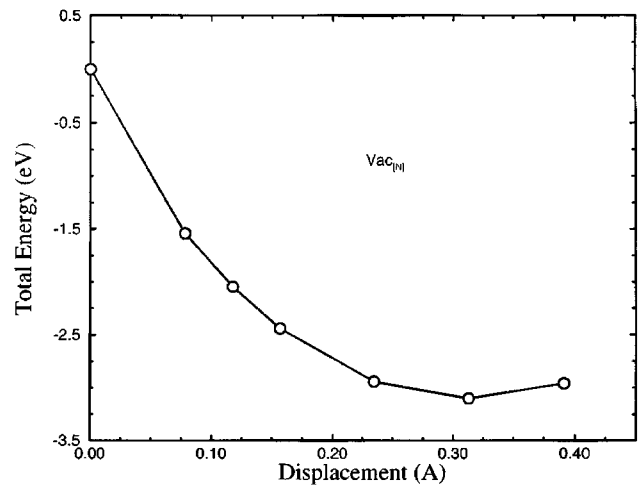


FIG. 4. Calculated total-energy curve for outward lattice relaxation (A_1 mode) for the nitrogen vacancy in *c*-BN.

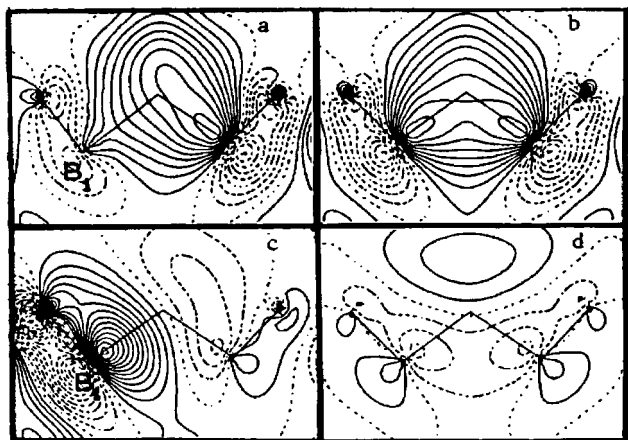


FIG. 5. Contour plot of the (a) and (b) $1a_1$ and (c) and (d) $2a_1$ orbitals. The (a) and (c) planes contain the B_1 -Vac- B_3 centers and the (b) and (d) planes the B_2 -Vac- B_4 centers (see the text).

ters while the (b) and (d) planes contain the B_2 -Vac- B_4 ones. The fully occupied $1a_1$ defect orbital in the gap region has π character with a charge density shared among the three equivalent (B_2 , B_3 , and B_4) boron atoms near the vacancy. This trapped charge resembles the F centers that arise in anion vacancies in alkali-halide crystals.¹¹ In particular, the formation of F centers in wurtzite BN (h -BN), due to a nitrogen vacancy, was proposed by Zunger and Katzir using an extended Huckel method.¹² The singly occupied $2a_1$ orbital above the middle gap has an electronic distribution strongly localized on B_1 with π character. Although there are some similarities between the highest occupied orbitals in c -BN and h -BN, such as the π character and charge confinement, a very important difference in the energetic ordering of the electronic levels is remarkable. Differently from h -BN, c -BN could present an F center only for the doubly ionized nitrogen vacancy (Vac^{++}). The essential role played by carbon doping for the formation of F centers in h -BN (Ref. 13) could also be seen in the case of c -BN, at least for high concentrations of these impurities when a recombination occurs between the electron localized at the $2a_1$ orbital and the hole introduced by the carbon atoms. It is in agreement with experimental electron paramagnetic resonance (EPR) results by Fanciulli and Moustakas.¹⁴

In Fig. 6 the total-energy curve for the A_1 mode relaxation of the $O_{[N]}$ in the neutral charge state is shown. We obtain the energy minimum when the nearest neighbors relax ≈ 0.16 Å outward (10% in the bond length). But if we look carefully at the total-energy surface we observe that the system distorts from the T_d symmetry towards a C_{3v} configuration, with the oxygen and the boron atoms moving oppo-

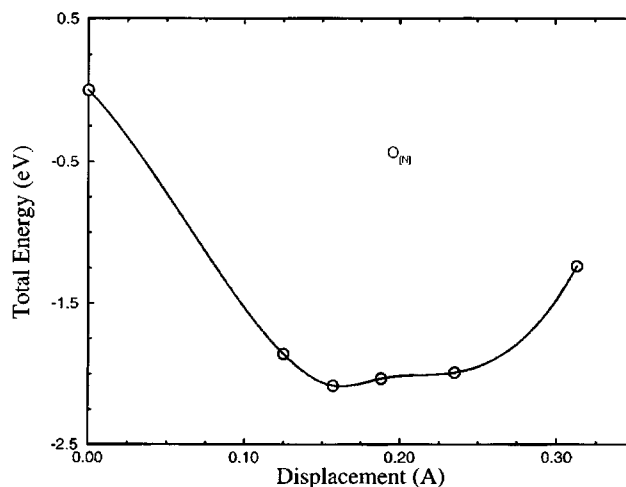


FIG. 6. Calculated total-energy curve for outward lattice relaxation (A_1 mode) for the oxygen substitutional in c -BN.

sitely in the $\langle 111 \rangle$ direction. The oxygen and boron displacements are 0.03 Å and 0.18 Å, respectively.

The electronic energy levels for the relaxed (right) and unrelaxed (left) configurations at T_d symmetry for the $O_{[N]}$ system are shown schematically in Fig. 1(c). We obtain a singly occupied a_1 level with antibonding character that comes from the conduction band, 4.70 eV above the top of the valence band. Also a super-deep a_1 state below the top of the valence band and a resonant p -type state in the valence band are obtained. By this analysis we see that substitutional oxygen impurity introduces an a_1 antibonding state in the gap region.

In conclusion, we have discussed the role played by the native defects in c -BN using an *ab initio* Hartree-Fock method within the cluster approach. For the neutral isolated boron antisite, a Jahn-Teller distortion in the $\langle 111 \rangle$ direction is observed. For the neutral N vacancy a strong relaxation is found. A highly localized a_1 orbital in the vacancy region (F -center precursor) and a t_2 orbital resonant in the conduction band appear before the lattice relaxation. The relaxation (plus distortion) splits the t_2 orbital leading to a half-occupied a_1 level, close to the conduction band. Our calculations enable us to suggest that the strong EPR signal seen in c -BN (Ref. 14) could be provided by the trapping of two electrons by acceptor levels introduced by carbon doping. For the neutral $O_{[N]}$ we found that an a_1 orbital, half occupied, is introduced above the middle of the valence band after lattice relaxation.

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