Atomic Geometry and Energetics of Native Defects in Cubic Boron Nitride

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We use first-principles calculations to investigate the electronic structure, atomic geometries and formation energies of point vacancies (V_B, V_N), antisites (B_N, N_B) and interstitials (B_i, N_i) in cubic boron nitride (c-BN). We find that nitrogen and boron vacancies exhibit the lowest formation energies in nonstoichiometric c-BN for p-type and n-type conditions, respectively, showing intrinsic donor (V_B) and acceptor (V_N) characters. The equilibrium geometries show large outward breathing relaxations for both vacancies and for B_N, with slight Jahn-Teller distortions from T_d symmetry. For N_B we find an off-center distortion inducing a negative-U behavior in this center. For both interstitial centers we find stable configurations in which an atomic pair occupies a nitrogen site in the lattice, N-N for N_i and N-B for B_i. These systems are stable for the different charge states investigated.

Cubic boron nitride (c-BN) has recently emerged as an important material for semiconducting industry due to its interesting properties which make it ideal for ultraviolet optoelectronic and high-temperature devices. Despite the recent synthesis of high-quality c-BN single crystals[1], the high concentration of crystalline defects remains the central problem for experimental research in c-BN. Conductivities related to defects or impurities have been observed in doped c-BN.[2, 3] In fact, electron paramagnetic resonance (EPR) measurements[4, 5] for different allotropic forms of boron nitride ascribe to the nitrogen vacancy the dominant paramagnetic defect in this material.

There are few theoretical studies related to native defects in c-BN. Vacancies and/or antisites have been studied with pseudopotential,[6] tight-binding,[7] cluster[8] and LAPW[9] methods. However, in most of these calculations the atomic relaxation is restricted to the first-neighbor atoms[8, 9] or simply not considered[7].

In this work we present a comparative study of the electronic structure and energetics of native defecs in c-BN, using first-principles total energy calculations. For each defect, we have determined the fully-relaxed atomic geometry in all relevant charge states. Our calculations are based on the density-functional theory,[10] using the supercell approach with 64 atoms per cell, a plane-wave basis set with a kinetic energy cutoff of 60 Ry, and norm-conserved soft Troullier-Martins pseudopotentials.[11] For the exchange-correlation functional, we use the generalized gradient approximation (GGA).[12] The integration over the Brillouin zone is performed with one special **k**-point (the , point). The geometry optimization is obtained by calculating Hellmann-Feynman forces on the nuclei. The atomic positions are supposed to converge when the forces on the atoms are less than 0.05 eV/Å.

The formation energies of native defects in c-BN are calculated as a function of the chemical potentials of nitrogen and boron. For charged systems, the formation energy also depends on the position of the Fermi level. Thus, for a defect in the charge state q, the formation energy is given by [13]

$$E_{form}(q) = E_t(q) - n_N\,\mu_N - n_B\,\mu_B + q\,(\mu_e + E_v),\ (1)$$

where E_t is the total energy of the defect derived from the supercell calculation, n_N (n_B) is the number of N (B) atoms in the supercell, and μ_N (μ_B) is the corresponding chemical potential, μ_e is the electronic chemical potential or the position of the Fermi level relative to the valence band edge, and E_v is the energy of the top of the valence band for bulk c-BN. The atomic chemical potentials can vary over a range given by the heat

of formation of c-BN, which we calculated as 3.0 eV. Additionally, they are constrained by the equilibrium condition, $\mu_N+\mu_B=\mu_{cBN(bulk)}$. Upper bounds for μ_N and μ_B are the precipitation limits on bulk phases, $\mu_N < \mu_{N(bulk)}$ and $\mu_B < \mu_{B(bulk)}$, which are calculated from solid nitrogen (α-N$_2$) and metallic boron (α-B), respectively.

Our results for the equilibrium geometries and relaxation energies of both vacancies in different charge states are summarized in Table 1. The vacancies in the neutral charge state show large outward breathing relaxations of the nearest-neighbor atoms, with slight distortions from the T_d symmetry. For neutral V$_B$ (V$_N$), the distance from the center of the vacancy to its N (B) first-neighbor atoms is found to be 10.5 % (7.7 %) larger than in the unrelaxed system, while the distance between the first and second neighbors is 4.3 % (2.9 %) shorter. The relaxation energies, calculated from the difference between the relaxed and the unrelaxed systems, show that V$_N$ suffers a more drastic relaxation with changes in the charge states as compared with V$_B$. This suggests a stronger interaction among the dangling bonds on the neighboring atoms of V$_N$ than the corresponding for V$_B$.

Table 1. Change in the atomic geometry with respect to the unrelaxed system (in percent) for boron and nitrogen vacancies in c-BN. Δd_1 is the change in the distance between the vacancy center and the first-neighbor atoms. Δd_2 is the change in the distance between first and second-neighbor atoms. E_r is the relaxation energy, in eV.

	V$_N$			V$_B$		
Charge	Δd_1	Δd_2	E_r	Δd_1	Δd_2	E_r
3+	19.8	−5.7	2.79			
2+	15.4	−4.8	1.79			
1+	7.6	−2.9	0.72	10.8	−4.0	1.83
0	7.7	−2.9	1.19	10.5	−4.3	2.14
1−				10.4	−4.9	2.29
2−				10.3	−5.8	2.57
3−				10.3	−6.5	2.70

The electronic structure of the native defects in c-BN is presented schematically in Fig. 1. In the figure, we show the positions of the defect-induced one-electron states in the band gap, for the neutral vacancies, antisites and interstitials. For V$_N^0$, we find a fully-occupied s-like a_1 state in the band gap close to the valence band edge, and a doublet state slightly split into singlets, lying as an e-like resonance in the bottom of the conduction band. Because this resonance is singly occupied,

the neutral charge state is unstable, and V$_N$ only exists in donor states. For V$_B^0$, we find a p-like t_2 state in the lower part of the band gap, which also shows a slightly split into singlet states. This t_2 state is half occupied, thus acting as a triple acceptor. The small splitting of the partially filled degenerate levels indicates a very small Jahn-Teller (JT) effect in the neutral vacancies. The difference in energy between split levels is less than 10 meV.
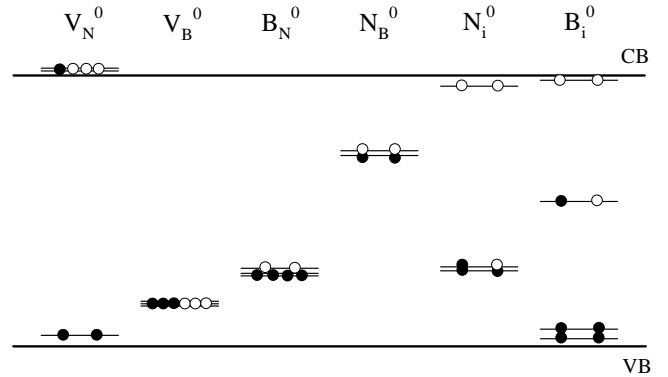

Figure 1. Schematic representation of the position of one-electron levels in the band gap induced by native defects in c-BN in neutral charge states. The filled circles indicate electrons and the open circles indicate holes.

The equilibrium geometry for B$_N^0$ shows an outward breathing relaxation of the neighboring B atoms, with a small distortion of the B antisite along the [100] direction (about 0.03 Å from the N site). The distance between B$_N$ and its first-neighbor atoms is 5.2 % larger than in the unrelaxed system, while the distances between first and second neighbors are 0.2 % shorter. No distortion along the [111] direction has been detected. We observe only small distortions of the B antisite for other charge states investigated. The electronic structure for B$_N^0$ (Fig.1) shows a p-like t_2 state in the gap, occupied with four electrons. This state also splits into singlet states, due to the small JT distortion.

For N$_B^0$, we observe an off-center distortion of the N antisite along the [100] direction, with a minimum at 0.35 Å from the B-site. The N antisite binds to two neighboring N atoms, forming a bridge structure with equal N-N bond lengths of 1.41 Å, and an angle of 122° between the bonds. For N$_B$ in negative charge states, we also find the same distortions which are characterized by large lattice relaxations. However, for positive charge states we observe a breathing relaxation, preserving the T_d symmetry. In Table 2, we summarize our results for the stable geometries and relaxation energies of the N antisite for different charge states.

Table II. Stable geometry for the nitrogen antisite in c-BN. d is the distance between the antisite and their first-neighbor N atoms, and θ is the angle between them. E_r is the relaxation energy.

Charge	Symmetry	d [Å]	θ [°]	E_r [eV]
2+	T_d	1.528	109.5	0.51
1+	T_d	1.628	109.5	0.60
0	C_{2v}	1.408	122.0	2.41
1−	C_{2v}	1.412	122.7	3.92
2−	C_{2v}	1.425	123.7	4.96

Considering that previous calculations[14] have reported an off-center stable geometry for N_B^0 with C_{3v} symmetry, we have calculated the total energy surface as a function of the nitrogen displacement along the [100] and [111] directions. This is done by placing the N antisite in various positions along these directions, allowing the neighbor atoms to relax. These calculation are performed by considering four special $\mathbf{k}$-points[15], instead the , point of our early calculation, in order to ensure the convergence with respect to the Brillouin zone integration. Our results are shown in Fig.2, where we see that the stable configuration has the N atom displaced along the [100] direction with respect to the substitutional site, lowering the total energy by about 0.5 eV. No distortion along the [111] direction has been detected. This result agrees with our calculation with one $\mathbf{k}$-point. We also note that the N antisite can occupy a metastable position with T_d symmetry. We attribute the discrepancy between our results and the calculation of Ref. 14 to the small supercell here used (16 atoms), implying in restrictions on the atomic relaxation.

The gap levels for N_B^0 shown in Fig.1 correspond to the off-center configuration with C_{2v} symmetry. We find a fully-occupied s-like a_1 state in the upper part of the band gap, close to an empty a_1 state. The difference in energy between these states is 0.07 eV. The empty a_1 state originates from the split of a t_2 state localized close the bottom of the conduction band for the defect in T_d symmetry. The empty and occupied a_1 states move toward one another while the N antisite moves along the [100] direction to its stable configuration.

For the self interstitial defects in c-BN (N_i and B_i), we consider different interstitial sites in the lattice as a starting positions for N and B atoms in the molecular dynamic calculation. These sites are: *bonding* (between a B-N bond), *antibonding* (opposite to the bonding site with respect to a lattice atom), *tetrahedral* and *hexagonal*. This procedure is necessary in order to avoid possible metastable positions for the interstitial atoms. Our results for the minimum energy configuration of N_i^0

show the formation of a N-N pair occuping a nitrogen site in the lattice, where each atom of the pair binds to two neighboring B atoms. The N-N bond distance is found in 1.28 Å, which is 16 % larger than that of the N_2 molecule (1.1 Å). The bond distance between one nitrogen of the pair and the boron first neighbors is 1.42 Å, with a B-N-B angle of 141°. This same configuration is also obtained for the N_i center in other charge states. The electronic structure of N_i^0 (Fig.1) shows two midgap singlet states, one fully occupied and the other one half occupied, and a empty singlet state close to the bottom of the conduction band. The midgap levels correspond to two p_z-like dangling bonds located at each N atom of the pair, which are oriented normal to the plane formed by the B-N-B atoms.
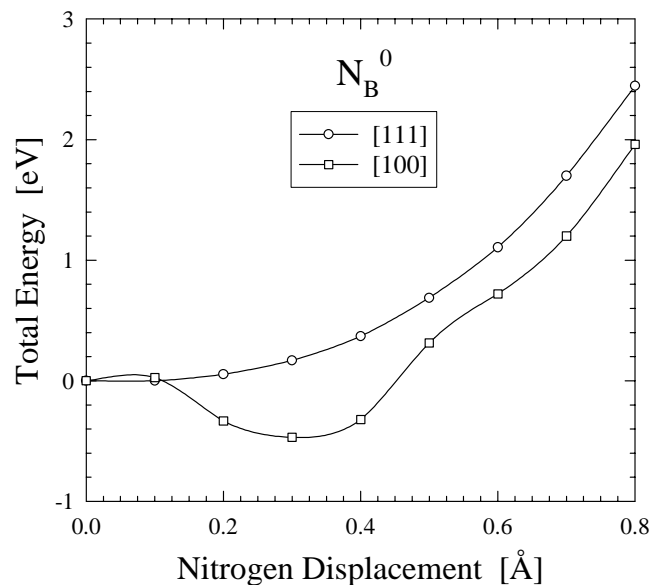

Figure 2. Total energy as a function of the nitrogen displacement along the [111] and [100] directions for the neutral N_B in c-BN. The zero energy refers to the total energy with nitrogen at the substitutional site.

For the B_i^0 defect we find a minimum energy configuration in which a N-B pair substitutes a nitrogen atom in the lattice. The N-B bond distance is 1.32 Å, which is 15 % shorter than the N-B bond of bulk c-BN. The nitrogen of the N-B pair binds to two neighboring B atoms, with bond distance of 1.42 Å and B-N-B angle of 140°. The boron of the pair binds to the other two neighboring B atoms, with bond distance of 1.52 Å and B-B-B angle of 141°. This configuration is stable for different charge states. The electronic structure of B_i^0 (Fig.1) shows a half-ocuppied singlet states in the middle of the gap and two fully-occupied singlet states close to the edge of the valence band. We also find a empty singlet state close to the bottom of the conduction band. Similarly to the N_i center, the midgap

singlet state of the B_i center correspond to a p_z-like dangling bond located at the N atom normal to the plane formed by the B-N-B atoms. In this configuration the N atom is bound to three B atoms in a sp^2 hybridization showing a p_z-like dangling bond. This structure resembles the hexagonal phase of boron nitride. However, the boron of the N-B pair is bound to three neighboring B atoms forming metallic bonds.
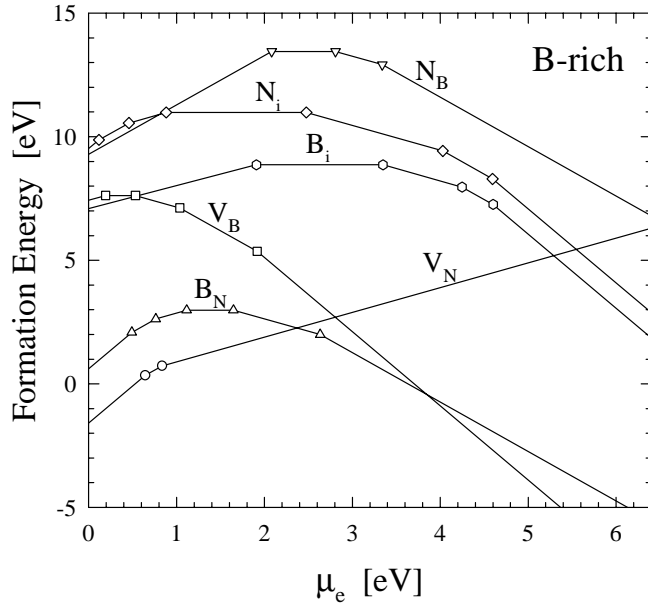

Figure 3. Formation energies as a function of the electronic chemical potential (Fermi level), of native defects in c-BN for nitrogen-rich conditions, $\mu_B = \mu_{B(bulk)}$. The slopes of the line segments characterize to defects charge states, and the symbols characterize transition states.

In Fig. 3, we show our results for the formation energies of native defects as a function of the Fermi energy (μ_e) for boron-rich conditions. In this figure, the slopes of the line segments correspond to the charge states of the defects. Changes in the slopes indicate transition states, which are represented by symbols. We observe that for p-type conditions (Fermi energy close to the top of the valence band), V_N^{3+} has the lowest formation energies among the native defects and can be considered as the dominant defect in p-type c-BN. On the other hand, for n-type conditions (Fermi energy close to the bottom of the conduction band), V_B^{3-} exhibits the lowest formation energy, and hence dominantes in n-type c-BN. We also note that the boron antisite exhibits low formation energies in the entire range of the band gap, which are comparable to those of the vacancies. In fact, B_N has the lowest formation energy for 2.4 eV $< \mu_e <$ 3.8 eV, and thus can be considered a dominant defect for semi-insulating c-BN. Another

defects that show low formation energies in n-type conditions are the interstitials. N_i^{3-} and B_i^{3-} exhibit low formation energies which can be readily incorporated in n-type c-BN. Because the relatively low formation energies found for V_N^{3+} in p-type condition and for V_B^{3-} for n-type condition, we believe they could act as a compensation centers in doped c-BN.

We now turn our attention to important subjects derived from our calculations. We find that the nitrogen vacancy in n-type c-BN shows high formation energies ($>$ 6 eV). Therefore, the observed n-type conductivity[3] usually associated to the nitrogen vacancy would imply either in a nonequilibrium incorporation of this defect or in the incorporation of a donor-like impurity with lower formation energy. According to our equilibrium calculation, the nitrogen vacancy should not be responsible for the n-type conductivity. The same picture has also been suggested fo V_N in GaN.[16]

Additionally, our results show that N_B^+ is never stable, which characterizes a negative-U behavior for this defect. From the $(2+/+)$ and $(+/0)$ transition states we obtain U = E$(+/0)$ $-$ E$(2+/+)$ $\approx$ -0.7 eV. The origin of the negative-U behavior is related to the off-center distortion of the nitrogen antisite in the neutral charge state. The $(2+/0)$ transition, located at 2.1 eV from the top of the valence band, is characterized by a large lattice relaxation, with an energy gain by about 2 eV.

Finally, EPR measurements have reported paramagnetic defects in bulk[4] and thin-film[5] boron nitride, which are commonly associated to V_N in neutral charge state. Our results show that V_N only exists in positive charge states, supporting that V_N^{2+}, instead V_N^0, should be the paramagnetic center associated to the nitrogen vacancy in c-BN.

In summary, we have found, based on first-principles calculations, that nitrogen and boron vacancies are the dominant defects in nonstoichiometric c-BN for p-type and n-type conditions, respectively. The vacancies also show intrinsic donor (V_N) and acceptor (V_B) characters which makes them the main candidates for the experimentally observed dopant compensation. Moreover, according to our calculations the high formation energies observed for V_N in n-type conditions exclude this vacancy as a source of n-type conductivity. For N_B we find a negative-U behavior originates in an off-center distortion of the N antisite along [100] direction. Finally, for the interstitial centers we find configurations

in which the interstitial atom forms an atomic pair with a lattice atom occuping a nitrogen site, N-N for N_i and N-B for B_i. These systems show midgap levels in the band gap and are stable for different charge states.

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