The current interest in the research on cubic boron nitride (c-BN) resides in its extraordinary thermomechanical properties, ideal for visible as well as ultraviolet optoelectronic and high-temperature devices. c-BN is a wide-bandgap semiconductor which can easily be doped to obtain p-type and n-type materials.\(^1\) This led, ten years ago, to the successful fabrication of a \( p-n \)-junction diode,\(^2\) functional up to 600 °C, and later to an ultraviolet light-emitting diode.\(^3\) However, the presence of recombination centers associated with native defects or impurities, coupled with the lack of an appropriate technology to achieve high-quality semiconducting samples, have prevented the practical use of c-BN devices.

The high concentration of crystalline defects remains the central problem in the growth methods of BN. Commonly, n-type and p-type conductivities related to defects or impurities have been observed in doped c-BN.\(^2,3\) In fact, electron paramagnetic resonance (EPR) measurements,\(^4,5\) made in different allotropic form of boron nitride ascribe to the nitrogen vacancy the dominant paramagnetic defect in this material.

There are a 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 linear augmented plane wave (LAPW)\(^9\) methods. However, in most of these calculations, the atomic relaxation is restricted to the first-neighbor atoms\(^5,9\) or simply not considered.\(^7\)

The aim of this work is to present a comparative study of the electronic structure and energetics of antisites and vacancies 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-conserving 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 \( \Gamma \) point). The geometry optimization is obtained by calculating Hellmann–Feynman forces on the nuclei. The atomic positions are considered converged when the forces on the atoms are less than 0.05 eV/Å. A detailed description of the computational method is given in Ref. 13.

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\(^14\)

\[
E_{\text{form}}(q) = E_f(q) - n_{\text{N}}\mu_{\text{N}} - n_{\text{B}}\mu_{\text{B}} + q(\mu_e + E_v),
\]

where \( E_f \) is the total energy of the defect derived from the supercell calculation, \( n_{\text{N}} \) (\( n_{\text{B}} \)) is the number of N (B) atoms in the supercell, and \( \mu_{\text{N}} (\mu_{\text{B}}) \) is the corresponding chemical potential. \( \mu_e \) 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, defined as

\[
H_f = E_{\text{BN}}(\text{bulk}) + E_N(\text{bulk}) - E_{\text{BN}}(\text{bulk}),
\]

which we calculated in 3.0 eV. Additionally, they are constrained by the equilibrium condition: \( \mu_{\text{N}} + \mu_{\text{B}} = \mu_{\text{c-BN}}(\text{bulk}) \). Upper bounds for \( \mu_{\text{N}} \) and \( \mu_{\text{B}} \) are the precipitation limits on bulk phases: \( \mu_{\text{N}} < \mu_{\text{N}}(\text{bulk}) \) and \( \mu_{\text{B}} < \mu_{\text{B}}(\text{bulk}) \), which are calculated from solid nitrogen (\( \alpha - \text{N}_2 \)) and metallic boron (\( \alpha - \text{B} \)), respectively. For bulk c-BN, we find an equilibrium lattice constant \( a_0 = 3.617 \text{ Å} \) and a bulk modulus \( B = 3.80 \text{ Mbar} \),\(^15\) which are in good agreement with the experimental values \( (a_0 = 3.615 \text{ Å} \text{ and } B = 3.69 \text{ Mbar}) \).\(^16\) For the band structure, we obtain an indirect gap \( (\Gamma_0 - X_1') \) of 4.8 eV. \( \alpha - \text{N}_2 \) has a face-centered-cubic (fcc) structure with four \( \text{N}_2 \) molecules per unit cell. We find an equilibrium lattice constant \( a_0 = 5.934 \text{ Å} \), within 5% of the experimental value \( (5.65 \text{ Å}) \).\(^17\) \( \alpha - \text{boron} \) has a rhombohedral structure formed by \( \text{B}_2 \) icosahedra which can be represented by a 36-atoms hexagonal unit cell. To calculate \( \alpha - \text{B} \), we fix the \( c/a \) ratio of the hexagonal cell to its experi-

\[^{a}\text{Electronic mail: wmomunoz@fisica.ufmg.br}\]
TABLE I. Change in the defects geometry with charge state for boron and nitrogen vacancies. Units are in percent with respect to the unrelaxed defects. $\Delta d_1$ is the mean variation on the distance between the vacancy center and the first-neighbor atoms. $\Delta d_2$ is the mean variation on the distance between first- and second-neighbor atoms. $E_r$ is the relaxation energy, in eV.

<table>
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<th>Charge</th>
<th>$\Delta d_1$</th>
<th>$\Delta d_2$</th>
<th>$E_r$</th>
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<th>$\Delta d_2$</th>
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</tr>
</tbody>
</table>

mental value ($\approx 2.56$). We find an equilibrium lattice constant $a = 5.122$ Å, within 5% of the experimental value (4.908 Å).\(^{18}\)

Our results for the equilibrium geometries and relaxation energies of boron and nitrogen vacancies in different charge states are summarized in Table I. In both vacancies, we find large outward breathing relaxations of the nearest-neighbor atoms, with slight distortions from the $T_d$ symmetry for every charge state investigated. We also note that $V_N$ suffers a more drastic relaxation with the charge state as compared with $V_B$. The electronic structure of 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 and antisites. 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 single 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.

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 neighbors 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 every charge state investigated. The electronic structure for $B_N^0$ (Fig. 1) shows a $p$-like $t_2$ state in the gap, which is 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 the 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. 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 $t_2$ gap state of the defect in $T_d$ symmetry.

The distortions observed in the $B_N^0$ and $N_B^0$ defects were checked with calculations including four special $k$ points.\(^{19}\) No additional distortions or changes in the equilibrium positions with respect to the calculation with one $k$ point were found. Moreover, the difference in total energy between the two $k$-point samples is less than 0.07 eV/B–N pair.

In Fig. 2(a), we show our results for the formation energies of native defects as a function of the Fermi energy ($\mu_e$) for nitrogen-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. The range of variation for $\mu_e$ is chosen to be the value of the experimental gap (6.4 eV).\(^{20}\) We observe that for $p$-type conditions (Fermi energy close to the top of the valence band), $V_N^{+1}$ has the lowest formation energy and can be considered as the dominant defect. $N_B^{2+}$ also exhibits low formation energies, comparable to those of $V_N^{3+}$. On the other hand, for semi-insulating and $n$-type conditions (Fermi energy near the middle of the gap and close to the bottom of the conduction band, respectively), $V_B^{1/2}$ exhibits the lowest formation energy, and hence is a dominant defect in c-BN.

The formation energies for boron-rich conditions are shown in Fig. 2(b). Similar to the $N$-rich case, the vacancies are the dominant defects. $V_N^{3+}$ and $V_B^{1/2}$ have the lowest formation energies in $p$-type and $n$-type conditions, respectively. 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, $B_B$ has the lowest formation energy for $2.4 < \mu_e < 3.8$ eV. Therefore, the boron antisite should also be considered as a dominant defect in B-rich c-BN.

Recent core-level photoabsorption studies on hexagonal BN thin films\(^{21}\) indicate that ion bombardment produces $sp^3$-bonded material with the presence of nitrogen intersti-
distals, while the remaining $sp^2$ material exhibits nitrogen vacancies. However, no evidence of boron vacancies is found. The relevant energetics for the defect production by ion bombardment can be obtained by the comparison between the formation energy $E_1$ of a $V_N + B$ distant pair and the formation energy $E_2$ of a $V_N + N$ distant pair. We obtain $E_1 > E_2$ for $p$-type condition and $E_1 < E_2$ for $n$-type condition. Therefore, we predict that if experiments similar to those of Ref. 21 are made for cubic BN, nitrogen vacancies would be produced in $p$-type materials and boron vacancies would be produced in $n$-type materials, unless the cross section for nitrogen–boron collisions is too small.

We now turn our attention to other 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 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 for $V_N$ in GaN.

Additionally, our results show that $N^+_B$ is never stable, which characterizes a negative-$U$ behavior for this defect, where $U = E^{(+B)} - E^{(+/)} \approx -0.7$ eV. The origin of this 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 of about 2 eV.

Finally, EPR measurements have reported paramagnetic defects in bulk and thin-film 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 of $V_N^0$, 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. According to our calculation the high formation energies observed for $V_N$ in $n$-type conditions exclude it as a source of $n$-type conductivity.

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15. Determined by fitting the total energy to the Murnaghan’s equation of state.