### Atomic arrangement and electronic structure of BC<sub>2</sub>N

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The results of a pseudopotential local-orbital calculation on the recently synthesized hybrid of graphite and hexagonal BN,  $BC_2N$ , are presented. Three possible atomic arrangements in the  $BC_2N$  monolayer, representing a variety of nearest-neighbor environments, are studied. For the monolayer structures considered, the one which maximizes chemical bond strength has the lowest total energy. The electronic structures of the three models are also investigated, and a correlation between the structural symmetries and the conducting properties of the models is found. In particular, the two structures which lack inversion symmetry are found to have semiconducting gaps, while the one with inversion symmetry is found to be metallic. This behavior is similar to the relation of graphite to BN. Of the inspected structures, the one with the lowest energy displays a local-density-approximation (LDA) gap of about 1.6 eV, which is expected to decrease upon stacking of the semiconducting monolayers.

### I. INTRODUCTION

The structural similarity between graphite and hexagonal BN has motivated the synthesis of alloys of these two materials. It is expected that the conducting and intercalation properties of such hybrids may be intermediate between those of graphite, which is semimetallic and forms many intercalation compounds, and BN, which is an insulator with a very limited intercalation chemistry. In the past, there have been several attempts to synthesize such a hybrid, the first of which was reported by Badzian et al.<sup>1</sup> In that report, the chemical-vapordeposition method (CVD), with BCl<sub>3</sub>, CCl<sub>4</sub>, N<sub>2</sub>, and H<sub>2</sub> as starting materials, was used to synthesize various compounds which were characterized as substitutional solid solutions in the graphite-BN system. Although the composition of these materials was not known quantitatively, it was assumed to be of the form  $(BN)_x C_{1-x}$ . Since that first effort, similar hybrids have been synthesized both by nitriding a mixture of amorphous boron and carbon black<sup>2</sup> and by CVD using  $BCl_3$ ,  $C_2H_2$ , and  $NH_3$  as the starting materials.<sup>3</sup> In all of these cases, the products have been characterized as having graphitelike layered structures, but there has been uncertainty regarding the degree of order and homogeneity in the samples.

Recently a hybrid of composition  $BC_2N$  has been synthesized using CVD with  $BCl_3$  and  $CH_3CN$  as the starting materials.<sup>4</sup> The use of only two starting materials reduces problems of inhomogeneities in the product. Xray diffraction indicates that this new material consists of irregularly stacked hexagonal sheets with an intralayer lattice constant (a = 2.44 Å) and an interlayer distance (c = 3.40 Å) (Ref. 4) very close to the values in graphite. Although the x-ray data do not yield the atomic arrangement within the planes, the fine structure in the electronenergy-loss core edges show that all three atomic species in  $BC_2N$  participate in  $sp^2$ -type bonding.<sup>4</sup> Hence the atoms are expected to be arranged in planes of graphitelike hexagonal rings, with weak interplanar interactions. At this time, it is unclear whether  $BC_2N$  is a semiconductor or a semimetal. While conductivity measurements<sup>4</sup> indicate that it is semiconducting with a small gap of about 0.03 eV, x-ray photoemission experiments<sup>5</sup> suggest that it is metallic.

In this paper, we investigate three possible geometries for the  $BC_2N$  monolayer. The three models are chosen to display some different basic features of the bonding such as nearest-neighbor environments and symmetry properties. These are introduced and discussed in detail in the next section. There is an apparent competition between structural stress and chemical bond strength in determining the preferred structure of the BC<sub>2</sub>N monolayer. We investigate this competition by calculating the total energies of the different structural models using a firstprinciples pseudopotential local-orbital approach. A brief description of the methods used in this calculation is given in Sec. III. In Sec. IV, the results for the total energies and electronic structures of the three models are presented and discussed. Of the monolayer structures considered, the one with the lowest total energy has the highest chemical bond energy. It is semiconducting with a local-density-approximation (LDA) gap of approximately 1.6 eV. The calculated density of states is given for the lowest-energy model. This curve may be useful in interpreting the electron-energy-loss spectra of BC<sub>2</sub>N. Section V contains some concluding remarks.

# **II. STRUCTURAL MODELS**

As described above, the structure of  $BC_2N$  is expected to consist of graphitelike layers with an irregular stacking pattern. The similarity of the scattering factors of B, C, and N makes x-ray diffraction techniques ineffective for determining the intraplanar distribution of the different atomic species. However, it is likely that the C—C and C—N bonds in the starting materials are never broken in

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the synthesis process, suggesting atomic arrangements in the product which preserve the integrity of  $C_2$  and BN molecules.<sup>4</sup> In the present investigation, three monolayer models are chosen. These have up to two formula units per cell and consist of units of B—N—C—C laid down in graphitic layers. These models, selected from a systematically generated set,<sup>4</sup> were chosen because they illustrate different basic features of interest such as nearestneighbor environments. The three structural models are shown in Fig. 1.

In model I, each C atom has a C, B, and N nearest neighbor, while each B (N) has two C's and one N (B) as nearest neighbors. The unit cell contains eight atoms, and the structure has inversion symmetry. This model is particularly attractive because it allows all the bond lengths to be relaxed, i.e., to be written as summations of well-defined atomic radii, while maintaining all the hexagonal angles equal to  $120^{\circ}$ . Therefore, structural stress, which has recently been recognized to be an important factor in the stabilization of ordered pseudobinary compounds,<sup>6</sup> is likely to be minimized in this model.

In model II, each C atom is joined to two other C's and either one B or one N. Every B (N) atom has two N (B) and one C nearest neighbors. This type of nearestneighbor coordination leads to chains of C and chains of BN which extend throughout the plane. Since the C—C bond length is about 1% shorter than the B—N bond length, this model for the BC<sub>2</sub>N monolayer probably contains some structural stress. The primitive cell of this structure contains only one formula unit, but for the sake



FIG. 1. Three structural models for the  $BC_2N$  monolayer. In each case, the unit cell shown contains eight atoms. Also shown is the two-dimensional Brillouin zone corresponding to the  $BC_2N$  monolayer viewed from the perspective of an eight-atom cell.

of comparison with model I, it is convenient to consider structure II with a supercell containing two formula units (eight atoms).

In model III, each C atom has one C and two B's or two N's as nearest neighbors, while each B (N) has two C's and one N (B) as nearest neighbors. As in the case of  $BC_2N$ -II, this structure has a four-atom primitive cell. In fact, these models are the only two possible four-atomper-cell atomic arrangements which preserve the integrity of  $C_2$  and BN molecules while avoiding the formation of energetically unfavorable B-B and N-N bonds. From the point of view of the eight-atom supercell,  $BC_2N$ -III is similar to  $BC_2N$ -I, except that the inversion symmetry has been broken by flipping one of the two BN molecules in each supercell. Since this model consists of C-N and C-B chains which must be lined up, and since the C-B bond length is about 15% larger than the C-N bond length, there appears to be a considerable amount of structural stress in this model.

By assigning chemical energies to the formation of the different types of bonds (C-C, C-N, etc.), Sasaki and Bartlett<sup>4</sup> have concluded that nearest-neighbor environments like those of structure II are the most favorable from the point of view of chemical bond strength. This is understandable since environments like those in model II seem to optimize the number of C-C and B-N bonds, which are the strongest ones. The same bookkeeping procedure indicates that models I and III should have equal chemical bond energies. However, because of the difference in internal stresses, their structural energies may differ considerably. It is this apparent competition between what can be phenomenologically described as structural stress and chemical bond strength that can be clarified by calculating the total internal energies of these three atomic arrangements. In Table I, the three structural models are compared in terms of the two competing factors of structural stress and chemical bond energy: while the former favors model I, the latter favors model II.

It should be pointed out that the in-plane anisotropy under 120° rotations found in all of these models is typical of ordered structures of  $BC_2N$ . This can be seen by recalling that the honeycomb lattice is formed by a twoatom basis placed on the sites of a triangular lattice. To form a plane of  $BC_2N$ , one of two possible kinds of basis (C—C or B—N) is placed on each point of the triangular lattice, which frustrates the ordering of the two bases unless the anisotropy constraint is relaxed.

TABLE I. Comparison of three structural models for the  $BC_2N$  monolayer in terms of structural stress, chemical bond strength, and cohesive energy. Structural stress is measured qualitatively as discussed in the text, and chemical bond energies are from Ref. 4.

	Structural stress	E <sub>bond</sub> (eV/molecule)	$E_{\rm coh}$ (eV/molecule)
I	none	23.7	20.0
II	some	24.7	21.2
Ш	most	23.7	18.5

#### **III. CALCULATIONAL METHOD**

The calculations are done using the first-principles pseudopotential local-orbital method.<sup>7</sup> The pseudopotentials used to describe the interaction between the valence electrons and the ion cores have been used successfully in previous studies of graphite<sup>8</sup> and BN.<sup>9</sup> The local-density approximation (LDA) is used, and we employ the Wigner form<sup>10</sup> of the exchange and correlation functional. The electronic wave function is expanded in a linear combination of Bloch sums of orbitals localized on the atomic sites. Orbitals of *s* and *p* character are used. Three, four, and five Gaussian decay constants are used to describe the radial part of the orbitals localized on B, C, and N sites, respectively.

Because of the weak interplanar interactions, we have performed our calculations on isolated monolayers. The electronic structure of the three-dimensional solid is likely to have features which are less sharp than that of a monolayer because extra band dispersions are introduced by interlayer interactions. However, the prominent features of the monolayer results are expected to be present in the bulk, and hence our results provide a basis for understanding the electronic structure of bulk samples.

As discussed previously, models II and III have smaller primitive cells than model I. However, to facilitate comparison of the models, all of our calculations have been performed using an eight-atom basis. In addition, the same set of six  $\mathbf{k}$  points in the two-dimensional Brillouin zone (Fig. 1) has been used for each model. Because of the large number of structural degrees of freedom available to minimize the total energy, we have chosen to set the bond lengths equal to those found in graphite, BN, and BC<sub>3</sub> (Ref. 11):  $d_{CC} = 1.42$  Å,  $d_{BC} = 1.55$  Å,  $d_{BN} = 1.45$  Å,  $d_{CN} = 1.32$  Å. These values are consistent to within a few percent with the Slater radii<sup>12</sup> of B, C, and N atoms. For each of the structural models investigated, the total energy has been minimized by allowing the angles in the hexagonal rings to vary while keeping the bond lengths fixed. The angles of the resulting hexagonal rings are a measure of the stress present in each structure. For model I, the energy is found to be minimized when all the interior angles are 120°, while in models II and III, the angles deviate from 120° by as much as  $\pm 2^{\circ}$  and  $\pm 18^{\circ}$ , respectively.

### IV. RESULTS AND DISCUSSION

The cohesive energies of the three monolayer structures investigated are listed in Table I. These values are obtained by taking the difference between the total energy of the solids and the ground-state energies of the isolated spin-polarized<sup>13</sup> atoms. No correction for zero-point motion in the solids has been made. BC<sub>2</sub>N-II is seen to be the most energetically favorable of the three structures. Not surprisingly, BC<sub>2</sub>N-III, which is the least favorable from both the chemical and structural points of view, has the smallest cohesive energy. The cohesive energy of BC<sub>2</sub>N-II (21.2 eV per molecule) corresponds to an average value of 5.3 eV per atom, which is considerably smaller than the graphitic value of about 7.4 eV per atom (Ref. 14).

The calculated electronic band structures of the three models are displayed in Figs. 2–4. In all cases, the bands are plotted in the Brillouin zone (BZ) corresponding to an eight-atom unit cell, and therefore the bands of structures II and III are folded and contain many degeneracies which are introduced because of the use of larger unit cells. The  $\pi$  bands are indicated by the set of heavier lines. It is seen that models II and III are semiconducting with indirect gaps of 1.6 and 0.5 eV, respectively, while model I is a metal.

An intimate correlation between the electronic structure and the structural model can be shown at this point. Recall in particular that the monolayer of hexagonal BN (with space-group symmetry  $D_{3h}^1$ ) differs structurally from that of the graphite monolayer  $(D_{6h}^1)$  by the lack of inversion symmetry. This basic difference in symmetry is responsible for the difference in the conducting character of both the monolayers as well as the bulk materials. In the graphite monolayer the Fermi level lies on a twofolddegenerate state at the K point of the BZ, which makes the monolayer the reduction of symmetry lifts the degeneracy at the K point and opens a semiconducting gap.

In what follows we show that the conducting character of the inspected structures of  $BC_2N$  can be justified by us-



FIG. 2. The calculated band structure of the BC<sub>2</sub>N-I monolayer, plotted in the Brillouin zone corresponding to an eightatom unit cell. The heavier lines indicate  $\pi$  bands, and the dashed horizontal line marks the Fermi level.

ing similar symmetry arguments. This task can be simplified by using the detailed interpretation of the band structure<sup>15</sup> of another new layered material  $BC_3$  which has an atomic arrangement that resembles that of  $BC_2N$ -I.

The atomic arrangement of a BC<sub>3</sub> monolayer (symmetry  $D_{6h}^1$ ) can be envisioned by replacing the two N atoms in BC<sub>2</sub>N-I ( $D_{2h}^{19}$ ) by two C atoms. The conclusions of the symmetry analyses of the band structure of BC<sub>3</sub> can therefore be applied to BC<sub>2</sub>N-I if we introduce an extra reduction of symmetry from  $D_{6h}^1$  to  $D_{2h}^{19}$  for the electronic states of BC<sub>3</sub>. This procedure, together with an inspection of the orbital character of the states, gives the classification of the states<sup>16</sup> in Fig. 2.

The BZ (Fig. 1) of the single-face-centered orthorhombic structures of BC<sub>2</sub>N differs from that of BC<sub>3</sub> because the hexagonal symmetry no longer exists and one of the directions is inequivalent to the other two. Comparing the bands of BC<sub>2</sub>N-I in Fig. 2 to those of BC<sub>3</sub>, we find that the substitution of two C's by two N's lifts the remaining degeneracies of the  $\pi$  bands at points  $\Gamma$ , Y (M in BC<sub>3</sub>), and K. However, because the two relevant bands around the Fermi level along the  $\Sigma$  line (with group  $C_{2\nu}$ ),  $\Sigma^{(3)}$  and  $\Sigma^{(4)}$ , have different symmetries, they are allowed to cross and close the gap. This crossing can be prohibited if we further reduce the symmetry of the space group of  $BC_2N$ , in particular the group of  $\Sigma$ , and force these particular bands to acquire the same symmetry.

In BC<sub>2</sub>N-II and III, with eight atoms per cell, the space group is reduced to  $C_{2v}^{11}$  (with the twofold axis lying in the plane) by eliminating the inversion operation, and the group of  $\Sigma$  is reduced to  $C_{1h}$ , which forces the  $\pi$  states along the  $\Sigma$  line to have the same symmetry,  $\Sigma^{(2)}$ . The band crossings (or touchings) along the  $\Sigma$  line displayed in Figs. 3 and 4 by  $\pi$  bands are accidental from the point of view of the unit cell containing eight atoms. They originate from the fact that the primitive cell in these structures contains four atoms and the bands in Figs. 3 and 4 are actually folded from a larger BZ. From the perspective of the smaller cell these crossing bands have different symmetries (more specifically, they correspond to different k points).

Before comparison between the calculated and experimental results can be made, two factors should be considered. First, the calculated monolayer gaps are probably underestimates since the local-density approximation is used. In addition, the interactions between layers need to be included since the present results are for monolayers of  $BC_2N$  without stacking. To estimate the effects of interlayer interactions, we look to previous cal-





FIG. 3. The calculated band structure of the BC<sub>2</sub>N-II monolayer, plotted in the Brillouin zone corresponding to an eightatom unit cell. The heavier lines indicate  $\pi$  bands, and the dashed horizontal line marks the Fermi level.

FIG. 4. The calculated band structure of the BC<sub>2</sub>N-III monolayer, plotted in the Brillouin zone corresponding to an eight-atom unit cell. The heavier lines indicate  $\pi$  bands, and the dashed horizontal line marks the Fermi level.



FIG. 5. The calculated partial density of states of  $BC_2N$ -II. The Fermi level is indicated by the dashed line.

culations on graphite relatives. In both graphite and hexagonal BN, the interlayer interactions lead to  $\pi$ -band dispersions in the *c* direction on the order of 1 eV (Ref. 17). Since the graphite monolayer is calculated to be semiconducting with zero gap, graphite becomes a semimetal upon stacking of the layers. BN, on the other hand, remains an insulator since the stacking-induced dispersion is not large enough to close the monolayer gap. Similar behavior has been observed in calculations of BC<sub>3</sub>, where the monolayer displays semiconducting behavior, while the bulk is semimetallic.<sup>11</sup> Although the details of the dispersion in BC<sub>2</sub>N will depend on the stacking sequence, it is expected that upon stacking of layers, the semiconducting gaps of models II and III will be reduced by an amount on the order of 1 eV.

The calculated density of states (DOS) for  $BC_2N$ -II is shown in Fig. 5. The DOS of the other two structures are not displayed since they have features similar to the one shown. From the integrated partial DOS, we find that there are on the average approximately 2.1 electrons occupying each B site, 4.3 electrons on each C site, and 5.2 electrons per N site. The low occupation number of B orbitals is a reflection of the fact that of the three atomic species, B has the least bound atomic states. There is thus a transfer of electrons from the higher-energy B orbitals to C and N orbitals.

The structure of peaks in the DOS above the Fermi level can be compared to electron-energy-loss spectra (EELS). Peaks 1 and 2 in Fig. 5 are composed of  $\pi$  states, while peak 3, which is about 6 eV higher in energy than peak 1, corresponds to the lowest-energy  $\sigma$  states above the Fermi level. Of the two  $\pi$  peaks, the lower-energy one contains mainly N and C states; the higher-energy one contains mostly B and C states. These features are at least qualitatively consistent with the EELS data<sup>4</sup> which show  $\pi^*$  and  $\sigma^*$  peaks separated by about 6, 7.5, and 5.5 eV in the B, C, and N K edges, respectively. Good quantitative agreement between our results and the experimental data is not expected because the use of the LDA limits the accuracy of the calculated conduction states.

#### **V. CONCLUSIONS**

Using a first-principles pseudopotential approach with a localized basis for the wave functions, we have investigated three possible atomic arrangements for the monolayer of the recently synthesized graphite-BN hybrid,  $BC_2N$ . The three structures were chosen for displaying different basic features such as a variety of nearestneighbor environments. We have found that the structure with the lowest total energy has a nearest-neighbor environment which seems to optimize the chemical bond energy by maximizing the number of C—C and B—N bonds.

In addition, we find an intimate relation between the symmetry properties and the conducting behavior of the monolayer structures. While inversion symmetry allows metallic behavior, the lack of inversion symmetry forces a gap to open. Of the three structures considered, the one with the highest cohesive energy lacks inversion symmetry and has a LDA monolayer gap of about 1.6 eV; the one metallic structure has a slightly lower cohesive energy.

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