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Energetic and electronic structure of BC_2N compounds

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Abstract. The stability and electronic structure of BC_2N compounds are studied using first-principle calculations. The investigated structures have the topology of graphite layers with either carbon, nitrogen or boron atoms at each site. The calculations show that stabler structures are obtained by increasing the number of C-C and B-N bonds. On the other hand, less stable structures result from increasing the number of N-N and B-B bonds. The energy gap of the stablest compounds varies from 0.0 to 1.62 eV, depending on the distribution of B, C, and N atoms in the unit cell. The electronic properties of BC_2N layered materials strongly depend on their atomic arrangements. The observed changes in energy gaps do not simply follow a symmetry-based argument proposed earlier.

PACS. 71.20.Tx Fullerenes and related materials; intercalation compounds – 71.15.Mb Density functional theory, local density approximation, gradient and other corrections – 81.05.Zx New materials: theory, design, and fabrication

1 Introduction

The structural similarity between graphite and hexagonal BN motivated the synthesis of alloys of these materials. One expects that the conduction and intercalation properties of such hybrids could be intermediate between these of semi-metallic graphite and insulating BN. Also, their mechanical properties could be similar to these of diamond and cubic BN, providing new super-hard materials [1–4]. Hence, B-C-N compounds are of potential technological interest. In the past, B-C-N thin films of various chemical compositions were prepared by chemical vapor deposition (CVD), using boron trichloride, N_2, H_2, and either CCl_4 or acetylene as starting materials [5–7]. These films were characterized as semiconductors, having graphite-like layered structures and various band-gap energies [8,9]. Amorphous BC_2N powders were also obtained by mechanical milling hexagonal boron nitride together with graphite [10]. Conductivity measurements of such bulk amorphous BC_2N showed that it behaves as a semiconductor of band-gap energy ~0.11 eV. Recently, Chen et al. [11] investigated with high resolution electron energy-loss spectroscopy the band gap of semiconducting BC_2N, measuring electronic excitations from the valence band to the conduction band. The BC_2N thin films used in the latter study were prepared by CVD from boron trichloride BCl_3 and acetronitrile CH_3CN. Theoretical research on the atomic arrangements and structural stability of these compounds were developed from first-principle, based on pseudo-potential local-orbital, semi-empirical and semi-classical methods [12–14]. In [1], three BC_2N structures were studied using a first-principle pseudopotential local-orbital approach. One metallic and two semiconducting systems were found and a symmetry-based explanation for the band-gap change was proposed. It was concluded that structures maximizing the bond strength have the lowest energy. In another work [14], a semi-classical method was applied to examine the dependence of the structural stability of monolayers on their atomic arrangement. It was found that stabler structures are formed by increasing the number of both C-C and B-B bounds. Both works used eight-atom unit cells with the same model.

In this work, first-principle calculations are applied to investigate the relative stability and the electronic structure of BC_2N compounds with eight-atom unit cells, using models different from these described in [12–14]. For the calculation of the formation energy, we adopt an approach based on the prior determination of chemical potentials, as described in detail in [15–18]. Besides, we also investigated the possible correlation between structural symmetries and conducting properties proposed in [1]. To study the relative stability of various atomic configurations, we first determine the corresponding molecular formation energy. Thereafter, we obtain the total density of states (DOS) for the six stablest structures – among the sixteen polymorphs that are investigated – and we study the band-gap changes of these compounds. Our first-principle calculations indicate a separation of C and BN for the

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stablest structures. We also find that the stablest compounds are semiconducting with either indirect or direct gaps. Besides, we find that our models do not follow the proposal based on symmetry, which leads us to conclude that the wide range of electronic structures observed is due to a strong dependence on the atomic arrangements.

Our ab initio method is based on the density functional theory [19] as implemented in the SIESTA program [20]. We use norm-conserving Troullier Martins pseudo-potentials [21] in the Kleinman-Bylander factorized form [22], and a double ζ basis set composed of numerical atomic orbitals of finite range. Polarization orbitals are included for all atoms, and we make use of the generalized gradient approximation (GGA) [23] for the exchange-correlation potential. The structures were obtained by minimization of the total energy using Hellmann-Feynman forces. The structural optimization was performed using a conjugate gradient procedure until the residual forces reached values smaller than 0.05 eV/Å. We used GGA rather than the local density approximation (LDA) which is well established for BC_2N, in order to verify the performance of the former for such structures. SIESTA can be used with either approximation.

No detailed experimental crystal structure of BC_2N is available. In particular, the size of the unit cell is not known owing to the lack of BC_2N samples of sufficient quality. Thus, we investigate unit-cell models that have been calculated previously [1,14]. If eight constituent atoms are allowed in the unit cell, sixteen polymorphic structures of BC_2N of different atomic arrangements are possible when the structural model is restricted to monolayer unit cells. These sixteen different geometries are illustrated in Figure 1. We develop the calculation for an isolated monolayer, since the main properties are expected to be dominated by the atomic arrangements in the graphite-like layers. In addition, the layer stacking along the y-axis is a difficult problem from the viewpoint of total energy considerations [1,13,14]. The BC_2N compounds studied are thus composed of periodically repeated $x-z$ plane layers, with an interlayer distance $d = 15$ Å along the y-axis so that neighboring layers do not interact.

The lattice parameter was optimized for each structure. From the calculations, we obtain 2.49 Å for the stablest structures, whereas 2.70 Å is found in structures with B-B bonds, owing to the larger size of this bound compared to other bonds. The bond lengths in the relaxed structures are $d_{BB} = 1.70$ Å, $d_{BC} = 1.50$ Å, $d_{CC} = 1.44$ Å, $d_{CN} = 1.44$ Å, $d_{NN} = 1.42$ Å, and $d_{BN} = 1.45$ Å.

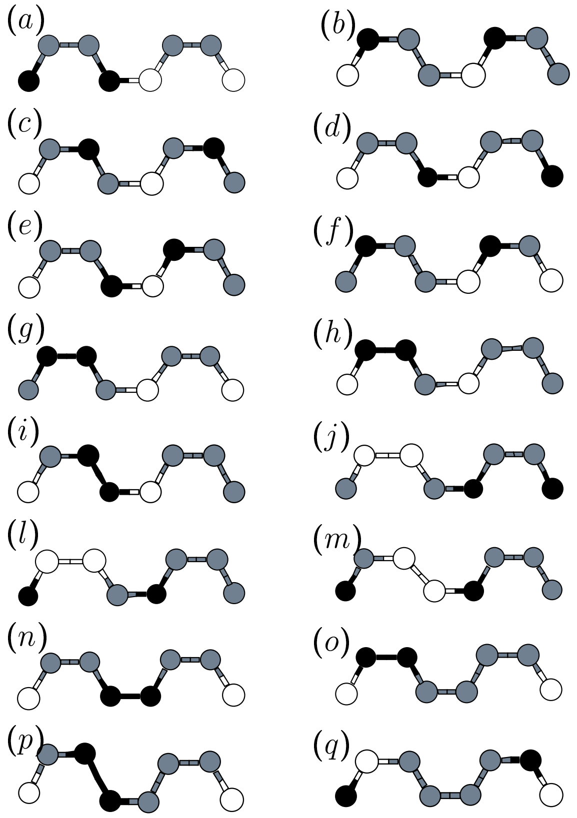

Fig. 1. Sixteen BC_2N structures. Boron, carbon and nitrogen atoms are represented in white, gray, and black, respectively. The compounds (*b*) and (*q*) are the stablest ones.

2 Relative stability and electronic structure

We now proceed with a comparative analysis of the energetic stability of all the structures illustrated in Figure 1. A zero-temperature thermodynamic approach based on the prior determination of chemical potentials has been proposed to address this issue [18]. This is done by defining the theoretically calculated chemical potentials μ_{BN}^{layer} and μ_{CC}^{layer}, for pure BN and CC, respectively. The chemical potential $\mu_{BN}^{\text{layer}} = -350.17$ eV is obtained for BN pairs in an infinite planar BN sheet. The chemical potential for a graphene sheet calculation is $\mu_{CC}^{\text{layer}} = -309.72$ eV. The formation energy for BC_2N structures can be written

$$E_{\text{form}} = E_{\text{tot}} - 2\mu_B - 2\mu_N - 4\mu_C, \tag{1}$$

where E_{tot} is the total energy of a monolayer derived from a supercell calculation of eight atoms. The factors 2, 2, and 4 are the numbers of B, N, and C atoms in the unit cell, respectively.

We use the thermodynamic constraint [18] that

$$\mu_N + \mu_B = \mu_{BN}^{\text{layer}}. \tag{2}$$

This constraint corresponds to situations in which the nanostructures are formed in equilibrium with BN layers. For the chemical potential of carbon we have

$$\mu_C + \mu_C = \mu_{CC}^{\text{layer}}, \tag{3}$$

where μ_{CC}^{layer} is obtained from the total energy calculation of a graphene sheet.

Table 1. Formation energies (in eV/molecule), second column, and number of bonds, from third to eighth column, of the BC_2N structures shown in Figure 1. The underlined figures in the second column indicate the six stablest structures.

Structure	E_{form}(eV)/mol.	B-N	C-C	B-B	N-N	B-C	N-C
a	0.69	2	2	0	0	4	4
b	$\underline{0.22}$	4	4	0	0	2	2
c	0.79	0	0	0	0	6	6
d	$\underline{0.52}$	2	2	0	0	4	4
e	$\underline{0.42}$	3	3	0	0	3	3
f	$\underline{0.54}$	2	2	0	0	4	4
g	1.04	0	1	0	1	6	4
h	0.71	2	3	0	1	4	2
i	1.00	1	3	0	2	5	1
j	1.03	0	1	1	0	4	6
l	$\underline{0.67}$	2	3	1	0	2	4
m	0.85	1	3	2	0	1	5
n	1.10	0	2	1	1	4	4
o	0.79	2	4	1	1	2	2
p	1.20	0	3	1	2	4	2
q	$\underline{0.14}$	5	5	0	0	1	1

Considering expressions (2) and (3), equation (1) can be rewritten as

$$E_{\mathrm{form}} = E_{\mathrm{tot}} - 2\left(\mu_{BN}^{\mathrm{layer}} + \mu_{CC}^{\mathrm{layer}}\right). \qquad (4)$$

The details of this approach are described in [15–17].

The results obtained for the formation of the BC_2N structures of Figure 1, using the above procedure, are summarized in Table 1. The underlined figures in Table 1 indicate the most stable structures. We find that structure (*q*), which has the maximum number of C-C and B-N bonds and no B-B or N-N bonds, is the stablest. This result agrees with these in [12,14,13]. The second stablest structure, compound (*b*), is the one which has the second largest number of C-C and B-N bonds. However, structures (*e*) and (*o*) both exhibit six B-N or C-C bonds, but the former is stabler. This is probably due to the fact that the former does not have any B-B or N-N bonds, while the latter has two such bonds. Thus, we conclude that B-B and N-N are unstable bonds. This is already known and these bonds have been described as “wrong” bonds in [24]. It is also confirmed *a contrario* from structure (*p*), the least stable one, which has the largest number of B-B or N-N bonds. Hence, from our results we conclude that, besides structure II described in [12], structure (*q*) is also a good candidate to study the stability and electronic properties of BC_2N nanotubes. Besides, we observe from Table 1 that compounds with the same distribution of bonds, like models (*a*) and (*d*), can display different values of their formation energy.

We verify that the stablest configurations (*b*) and (*q*) shown in Figure 1 alternate one chain of BN with one chain of CC, in a so-called strip-like pattern. Hence, there exists the possibility that some sort of “phase separation” occurs in stable structures of BC_2N. This could occur once B and N aggregate alternately and h-BN-like regions appear. Then, carbon atoms could segregate from B and N atoms and graphite-like structures would form. If such a phase separation occurs, the number of C-C and B-N bonds increases and the number of B-B and N-N bonds decreases, lowering the formation energy. One sees from Table 1 that structures (*b*) and (*q*) do not display any wrong bonds. In addition to the strip-like models investigated here, there exist island-like ones. Owing to the required size of the unit cell, we have not investigated these so far. However, we intend to study island formation processes in the future, using a much larger unit cell with at least 32 atoms.

Now, we proceed with the investigation of the electronic structure of these BC_2N compounds. In Figure 2, we show the DOS of the six stablest structures. One sees that BC_2N sheets can exhibit a wide range of electronic behavior, the energy gap varying from 0.0 to 1.62 eV, at the GGA level. The stablest structure, among the six exhibited in Figure 2, has a band gap of 1.1 eV. The second stablest one has a gap of 1.6 eV. The third, fourth, fifth, and sixth ones have gaps of 0.65, 1.62, 0.0, and 0.0 eV, respectively. This suggests that, at least from the electronic energy point of view, stoichiometric BC_2N structures can have widely different optical behavior, in this case semiconductor or metallic, depending on the atomic distribution in the unit cell. This suggests that different atomic arrangements can strongly affect the optical properties of BC_2N layered materials.

In our first-principle calculation we find that structure (*i*), which does not display inversion symmetry, is metallic with a gap of 0.0 eV. On the other hand, structure (*n*), which presents inversion symmetry, has a gap

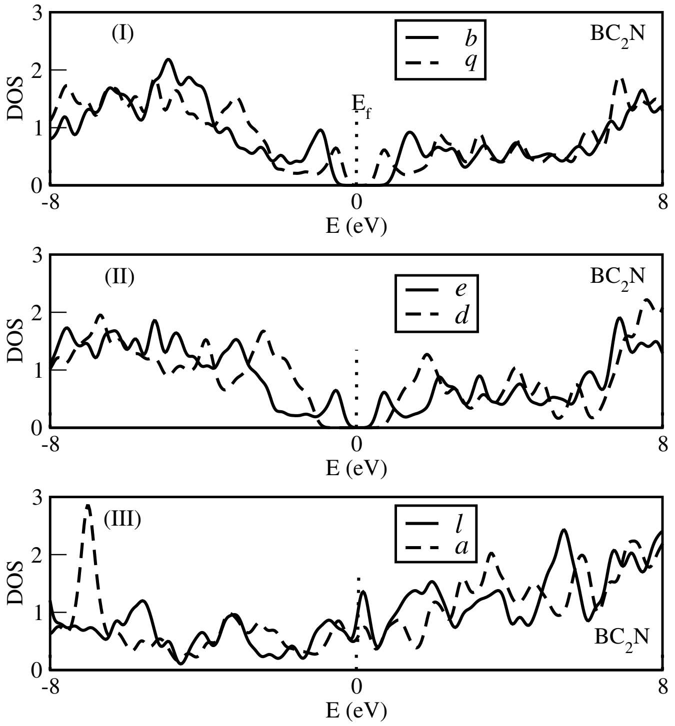

Fig. 2. The total density of states of the six stablest structures. The stability of these compounds is listed in Table 1 while the geometry is shown in Figure 1.

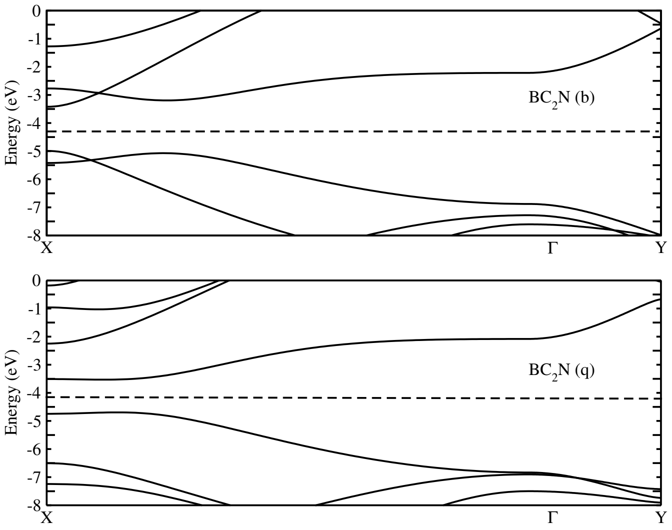

Fig. 3. The calculated band structure of the two stablest structures. These BC$_2$N compounds are shown in Figure 1. The dashed horizontal line indicates the Fermi level.

of 0.6 eV. Therefore, in the models investigated here, we find BC$_2$N compounds for which the gaps do not follow the symmetry-based rules proposed in [12]. From this we conclude that the symmetry-based arguments of [12] cannot be used for these model structures. The trends in these compounds strongly depend on the particular atomic arrangements.

The calculated electronic band structures of the two stablest structures, (*b*) and (*q*) in Figure 1, are displayed in Figure 3. In both cases, the bands are plotted in the Brillouin zone corresponding to the eight-atom unit cell. It is seen that both compounds are semiconducting, with a direct gap of 1.6 eV for (*b*), and an indirect gap of ∼1.1 eV for (*q*).

3 Conclusions

In summary, we investigated the energetic stability and electronic structure of sixteen polymorphic BC$_2$N compounds using first-principle calculations. It is found that the stabler structures have a maximum number of C-C and B-N bonds, that is, that they are closest to the strip-like configuration. The trend towards this type of configuration which is found here agrees with results obtained in [12,14] using another approach. We find that less stable structures exhibit a maximum number of N-N or B-B bonds, similarly to previous works [12,14]. Thus, BC$_2$N compounds experience a phase separation between C and BN, which is the configuration that maximizes the number of B-N and C-C bonds, while it minimizes the number of B-B and N-N bonds. Besides, we verify that, in spite of the BC$_2$N stoichiometry of all sixteen structures, the band gap varies from 0.0 to 1.62 eV for the six stablest compounds, depending on the atomic configuration in the unit cell. From these results, we conclude that BC$_2$N monolayers can behave either as metal or as semiconductor, at least from the energetic point of view studied here. Therefore, this suggests that the atomic configuration in BC$_2$N monolayers strongly affects the optical properties of such systems. In addition, we find that the two stablest structures behave as semiconductors with either indirect or direct gaps. Symmetry based arguments do not work for some of the models presented here. Namely, there exist structures of different band gaps, which cannot be argued on the basis of inversion symmetry. Thus, the models described here lead us to conclude that the strong changes in the electronic properties of these compounds essentially depend on their atomic arrangements.

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