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Structural and electronic properties of crystalline graphite-like BC_3

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ABSTRACT

We investigated the crystalline stacking and electronic properties of graphite-like layered BC_3 using van der Waals density functional theory calculations. By exploring the energy landscape with respect to the stacking morphology, we identified two different stackings as the most stable structures which we investigated further in detail. Our calculations show that the electronic structure of this material dramatically changes from a semiconductor to a metal through the most likely direction of layer gliding between the energetically favored *AB*-stacking and an aligned *AA*-like stacked structure where B atoms sit on top of C atoms. These results could provide an explanation for the semimetallic character found in the experiments for the turbostratic form and open a venue for engineering the electronic properties of this material through the control of its crystalline structure.

1. Introduction

Layered materials have attracted significant attention lately due to their vast variety of tunable properties which can be engineered for practical applications such as electronics, optoelectronics, and battery technologies. A member of the family of layered structures, graphite-like BC_3 (g-BC_3) has been recently synthesized and its structural and electronic properties investigated experimentally and computationally [1–5]. Experimental work presented by Bartlett et al. indicated that B atoms reside inside the layers of BC_3 for samples synthesized at 800 °C [1]. According to experimental observation, at low B concentrations, in-plane boron atoms tend to avoid each other producing a relatively low number of directly bonded B pairs, however upon increasing boron content, existence of boron-to-boron connected structures are suggested for the material synthesized at a temperature of 1140 °C [6]. However, experimental investigations have not been able to determine the relative arrangement of atoms between consecutive layers, i.e. the stacking of layers, as synthesized materials seem to present randomly rotated and shifted layers (turbostratic form) [1,3,7]. Therefore, the interlayer distance has been found to be slightly dependent on the synthesis temperature with measured values around 3.4 Å [1,3,6,7]. This disordered form of BC_3 has been observed to be a semi-metal and exhibits a higher basal-plane electrical conductivity than highly oriented pyrolytic graphite [4,8].

Density functional theory (DFT) studies of the crystalline form of BC_3 carried out by Sun et al. [2] using the local density approximation (LDA) shows that the most stable stacking corresponds to the *AB*-stacking type, as in graphite, and presents a semiconductor character. Although a limited number of *AB*-stacked structures were investigated, the authors found that a proportional shift of the third consecutive layer corresponds to a less stable stacking structure with a metallic character (*ABC*-stacking).

It is well known that in layered materials, such as graphite or g-BC_3, the layers interact with each other via weak long-range van der Waals forces [9–11]. However, local and semi-local functionals, like LDA and GGA, do not properly take into account this kind of interactions producing, oftentimes, spurious minima [12]. In order to treat dispersion interactions within DFT, semi-empirical corrections such as that presented by Grimme [13] have been introduced. However, although successful in known systems close to the fitting set, this approach might not capture all the physics of unknown systems. Other improvements in this regard have been recently presented, for instance, the so called vdW-DF functional, where a first-principles interaction kernel for the correlation functional that is able to capture non-local effects is constructed [14–18]. Among these dispersion corrected functionals, vdW-DF2 and vdW-DF2-C09 predict the interlayer distance and binding energy of graphite in better agreement with experiment than others [9] and they are thus adopted in this work for the study of g-BC_3.

In this work, we analyze the in-plane arrangement of boron atoms, the stability, and the electronic structure of a variety of stackings for g-BC_3 by means of first-principles calculations using the vdW-DF2 [17] and vdW-DF2-C09 [18] exchange–correlation functionals and we also discuss how the electronic properties of the system depend on the specific interlayer stacking.

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2. Method

Self-consistent DFT calculations are carried out using the Quantum-Espresso software [19]. Two different forms of the dispersion corrected density functionals are used, vdW-DF2 (PW86 exchange) [17] and vdW-DF2-C09 [18] which uses gradient-expansion approximation in the slowly varying/high density limit and asymptotically reaches revPBE [20] in the rapidly varying/low density limit [18]. Ultrasoft pseudopotentials generated with the semilocal PBE exchange–correlation functional are used to replace the core electrons of B and C atoms in the electronic configurations of [He] $2s^2$ $2p^1$ and [He] $2s^2$ $2p^2$, respectively. Calculations are performed using plane-wave basis set with kinetic energy cutoffs of 80 Ry and 320 Ry for the wavefunctions and charge densities, respectively. The Brillouin zone is sampled using Monkhorst–Pack [21] scheme with $14 \times 14 \times 14$ mesh for the bulk systems and $14 \times 14 \times 1$ mesh for the isolated layers. Structure relaxations are carried out using the Broyden–Fletcher–Goldfarb–Shanno algorithm with force convergence threshold of 10^{-3} Ry/Bohr. Band structures are calculated along the path including high symmetry points of the hexagonal unit cell.

Inter-layer binding energy of the monoatomic layers of the bulk is calculated from the energy difference between the bulk and the isolated layers, and averaged over the number of atoms inside the unit cell of the bulk:

$$E_b = -(E_{bulk} - NE_{layer})/N_{tot}, \quad (1)$$

where E_b is the atom-averaged layer binding energy, E_{bulk} is the energy of the bulk system, E_{layer} is the energy of the single isolated layer, N is the number of layers in the unit cell of the bulk system, and N_{tot} is the total number of atoms inside the unit cell in the bulk system.

3. Results & discussion

In order to find the energetically favored in-plane arrangement of B atoms, three possible structures of mono-layer BC_3 are considered as shown in Fig. 1. Our calculations show that after full relaxation both BC_3-2 and BC_3-3 structures are less stable than BC_3-1. The energy difference between BC_3-2 and BC_3-1, ΔE, is 1.13 eV/cell and 0.99 eV/cell calculated with the vdW-DF2 and vdW-DF2-C09 functionals, respectively. The structure presenting boron pairs, BC_3-3, is again less favored than BC_3-1 by ΔE = 1.82 eV/cell and ΔE = 1.56 eV/cell as obtained with vdW-DF2 and vdW-DF2-C09, respectively. These results support the proposed structure initially reported in experiments for the in-plane arrangement of boron atoms, BC_3-1 [1].

In search for the most favorable stacking, several possible structures derived from the *AB* stacking of BC_3 are obtained by shifting one of the layers with respect to the other in the region enclosed by the red parallelogram shown in Fig. 2a and b. In this scheme, the structure labeled *C* corresponds to the *AB*-stacking without any shifting and structures labeled as A, A', E, and E' are obtained by gliding one of the two layers inside the cell. In structure *C*, one boron atom resides right on top of a carbon atom while the other boron atom resides on the center of an hexagon of the adjacent layer. The structure labeled as *A* (BC_3-*A*) corresponds to the *AA*-stacking with boron on top of boron and carbon on top of carbon atoms. BC_3-A' corresponds to an *AA*-like stacking where atoms are aligned along the *c*-axis as in the *AA*-stacking but all the B atoms are on top of C atoms. For all structures, energies are obtained after force optimization by varying the lattice constant *c* but keeping all the interatomic distances within each layer fixed using the calculated in-plane lattice constant a_0 of BC_3-*C*. Resulting vdW-DF2-C09 energies are linearly interpolated and color coded to generate the stacking energy landscape shown in Fig. 2c. The only stable *AB*-stacked structure reported so far in the literature is BC_3-*E* which has been obtained with LDA [2]. Here, energy of BC_3-*E* corresponds to the point at the crossing of the line connecting *A* and A' with the line connecting *B* and *C* on the energy landscape. Besides BC_3-*E*, we have found two possible stable structures labeled as BC_3-E' and BC_3-A' represented by deep blue color in Fig. 2c. We note that the energy differences between stable structures is small (less than 5 meV/atom) and therefore interatomic rearrangement within the layers could impact the energy landscape presented in Fig. 2c. Upon complete optimization (in all crystal directions and relative positions of the atoms within the planes) the stacking of BC_3-E' becomes equivalent to the structure of BC_3-*E* which becomes slightly favored over all the other structures. When fully relaxed, the energy difference between BC_3-*E* and BC_3-A' becomes −4.9 meV/atom and −1.2 meV/atom obtained with the vdW-DF2-C09 and vdW-DF2 functionals, respectively (Table 1). A better account of the energy variation upon gliding one layer is needed for the particular path connecting BC_3-*E* and BC_3-A' to better understand the stability of these structures and detect any possible energy barrier, if present. The energy variation corresponding to the transformation of the optimized BC_3-A' structure into the BC_3-*E* structure is obtained by a linear interpolation of the atomic coordinates of the two structures; BC_3-$\alpha = \alpha BC_3$-$E + (1-\alpha)BC_3$-A' where α is a parameter between 0 and 1. Each structure BC_3-α is further optimized with respect to the lattice parameter *c* only and the resulting energy variation with respect to α is presented in Fig. 3. We find no energy barrier for the transformation of BC_3-A' into BC_3-*E* indicating that the structure BC_3-A' is at the energy maximum of this path.

For comparison purposes, we have additionally calculated the energy difference between *AA* and *AB* stackings in graphite and found that the *AB* stacking is favored by 14 meV/atom using the vdW-DF2-C09 functional. This difference is about 3 times larger than the corresponding difference between BC_3-A' and BC_3-*E*. *AB*

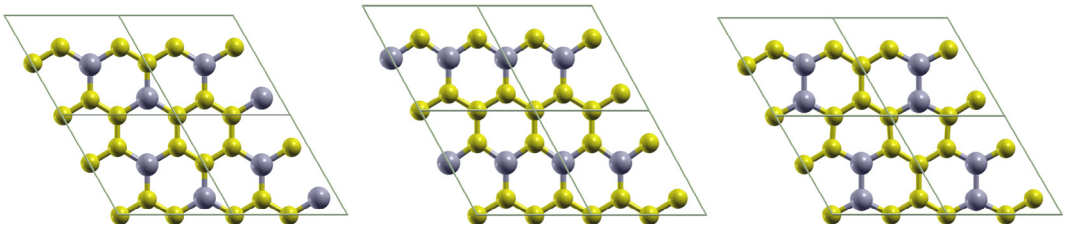

Fig. 1. Single layer BC_3 structures: (a) BC_3-1, the boron configuration proposed experimentally by Bartlett et al. [1], (b) BC_3-2 is less stable than BC_3-1 by $\Delta E \simeq 1$ eV/cell, and (c) BC_3-3 is less stable than BC_3-1 by $\Delta E \simeq 1.5$ eV/cell. Gray and yellow balls represent boron and carbon atoms, respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)