

***Ab initio* calculation of structural properties of  $C_3B$  and  $C_5B$  compounds**

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The structural properties of three-dimensional ordered phases of  $C_3B$  and  $C_5B$  compounds were studied using the *ab initio* pseudopotential method. Two different stacking sequences, BC and BB, of graphite layers were considered. Results indicate that for  $C_3B$ , the structure with hexagonally symmetric distribution of B atoms and BC stacking is stable, whereas for  $C_5B$ , both BC and BB stackings are possible with BC stacking being more stable. In the case of  $C_3B$ , the interlayer spacing is 3.43–3.45 Å, while for  $C_5B$ , the interlayer spacing is 3.00 Å. [S0163-1829(97)05102-3]

Since the discovery of oxidation-inhabitation effect of boron in graphite,<sup>1–6</sup> the synthesis, geometric structures, and electronic band structures of  $C_{1-x}B_x$  ( $x \leq 0.25$ ) compounds have been extensively studied both experimentally<sup>7–10</sup> and theoretically.<sup>11–15</sup> Based on experimental observation, it was suggested that the  $C_3B$  compound has a graphitelike structure and an ordered distribution of B atoms within a graphite layer as shown in Fig. 1. Both *ab initio*<sup>11,14</sup> and extended Huckel<sup>12</sup> calculations confirmed that the ordered structure with the hexagonal symmetry within the layer is the most stable structure for the  $C_3B$  compound and predicted the bond lengths within the layer are 1.42 Å for C-C and 1.55 Å for C-B. It has also been suggested experimentally that<sup>7</sup> there exists the  $C_5B$  compound as shown in Fig. 2, and that the interlayer distance is about 0.10 Å smaller compared to pure graphite. However, how the graphite layers are stacked up along the direction normal to the layer is still not clear. For example, two types of stacking are possible: BC stacking in which B atoms are directly on top of C atoms or vice versa; and BB stacking in which some of the B atoms are on top each other. Therefore, the main objective of this paper is to determine the relative stability of BC and BB stackings in the  $C_3B$  and  $C_5B$  compounds using the *ab initio* pseudopotential method. The total energies of structures were calculated by relaxing the unit-cell lattice parameters, including both in-plane and  $z$  directions, and the atomic positions.

Our first-principles approach for calculating the ground-state charge density and energy is based on the local-density-functional theory. The exchange and correlation energy was calculated using the Perdew-Wang's expression.<sup>16</sup> Nonlocal pseudopotentials are employed for both C and B atoms.<sup>17,18</sup> We used a plane-wave basis set with kinetic energy cutoff at 71 Ry and sample the first Brillouin zone of each structure with four special  $k$  points according to the scheme of Monkhorst and Pack.<sup>19</sup> The minimization of the total energy  $E$  was carried out by a preconditioned conjugate-gradient method in two steps.<sup>20,21</sup> At first, the in-plane cell parameter (i.e., lattice constant  $a$ ) was optimized with atom positions fixed and  $c = 6.70$  Å. Then, the atom positions were relaxed using the steepest-descent method with the cell parameter  $a$  fixed at its optimized value and  $c$  fixed at 6.70 Å. The opti-

mization with respect to atom positions was carried out until the difference in total energies between two consecutive iterations is less than 0.01 eV (i.e., the relative error is less than  $10^{-5}$ ). With the optimized atomic positions and in-

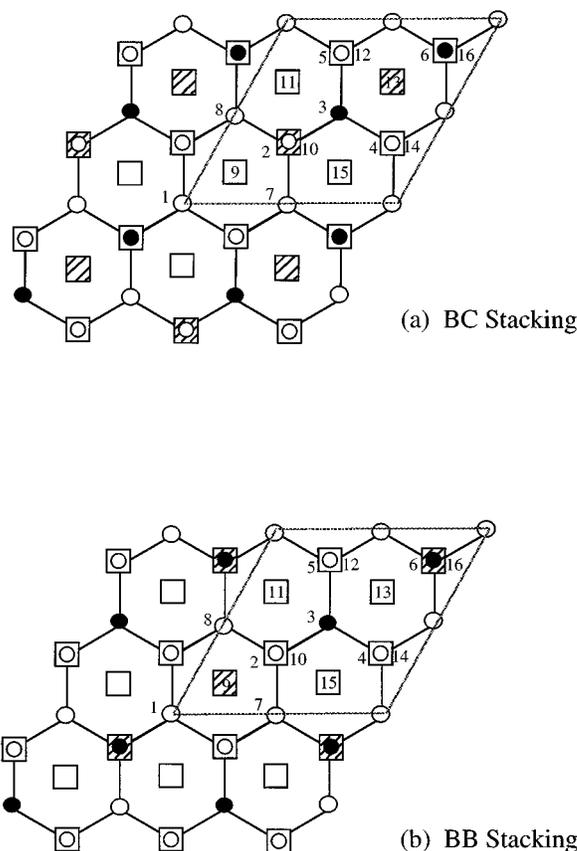


FIG. 1. The atomic arrangements of  $C_3B$  ordered structure with (a) BC stacking and (b) BB stacking, where two layers are included, the circles representing the atoms on the top layer and the squares representing those on the bottom: open circles or squares for carbon sites and shaded circles or squares for boron sites. The dashed lines give the unit cell which includes two layers with 16 atoms (12 carbons and 4 borons).

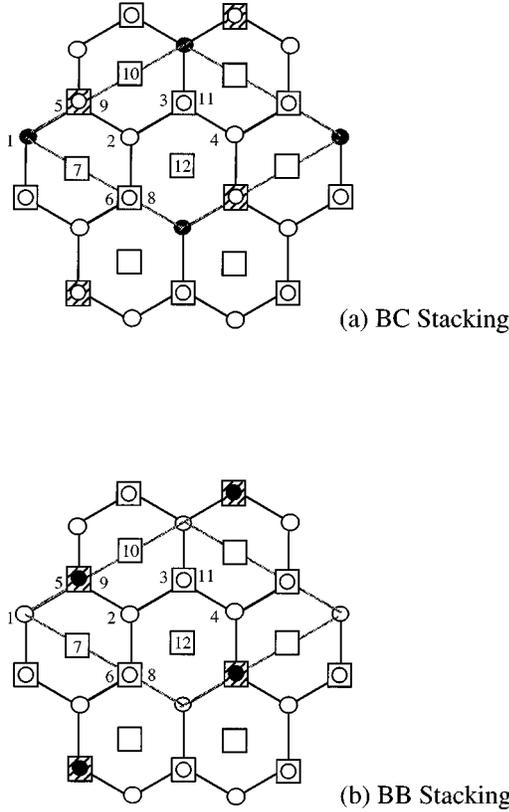


FIG. 2. The atomic arrangements of  $C_3B$  ordered structure with (a) BC stacking and (b) BB stacking. The unit cell includes two layers with 12 atoms (10 carbons and 2 borons).

plane cell parameter fixed, the cell parameter  $c$  was optimized.

We first calculated the structural properties of graphite carbon as a test for the  $C$  pseudopotential. The optimized in-plane lattice constant was found to be 2.453 Å and the interlayer distance  $c/2$  was approximately 3.30–3.35 Å, which compare very well with the experimental values [ $a=2.456$  Å and  $c=6.674$  Å (Ref. 22)]. The cohesive energy of the graphite was found to be 8.59 eV/atom, which is in reasonable agreement with the experimental value, 7.374 eV/atom.<sup>23</sup>

The unit cell of the  $C_3B$  structure was shown in Fig. 1, where two layers are included, the circles representing the atoms on the top layer and the squares representing those on the bottom. Each layer contains eight atoms within the unit cell, with six being carbon atoms (open circles or squares) and two being boron atoms (shaded circles or squares). Figures 1(a) and 1(b) represent the BC and BB stackings, respectively.

For both stacking sequences, the relaxation was carried out with respect to cell parameters  $a$  and  $c$  and atomic positions within the unit cell. The lengths of the in-plane C-C and B-B bonds were found to be 1.42 and 1.55 Å, respectively, which are consistent with our calculations on a single layer<sup>14</sup> and those given in Refs. 11 and 12. Therefore, there seems to be very little effect of interlayer interactions on the bond lengths within the layers. The total energies of  $C_3B$  per unit cell as a function of lattice parameter  $c$  are shown in

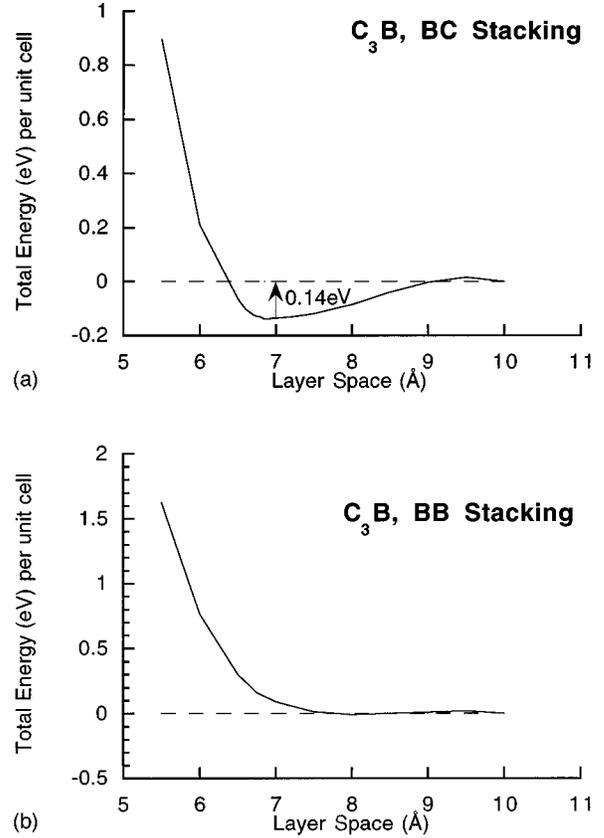


FIG. 3. The total energies (eV)/per unit cell vs parameter  $c$  (Å) for  $C_3B$  ordered structures, (a) for BC stacking and (b) for BB stacking.

Figs. 3(a) and 3(b) for BC and BB stackings, respectively. The values of those total energies are relative to that for  $c=10.00$  Å. It is clear that there is a minimum in Fig. 3(a) although the energy well is relatively smooth and shallow with the well depth 0.14 eV per unit cell. By carefully checking the values of the total energies, we found that the minimum corresponds to  $c=6.85$ – $6.90$  Å. Therefore, the BC stacking is a possible, stable three-dimensional structure with an interlayer distance  $c/2=3.43$ – $3.45$  Å, which expands slightly from 3.30–3.35 Å of pure graphite due to the effect of boron substitution in the  $C_3B$  compound. The indication of expansion along the  $z$  direction of the  $C_3B$  compound is in agreement with the experimental observation.<sup>10</sup> However, it should be pointed out that since the depth of the energy well is only about 0.14 eV per unit cell, the BC stacking might be disordered at relative low temperatures. The corresponding total energies as a function of  $c$  for the BB stacking is shown in Fig. 3(b), which shows that there is no minimum and hence the BB stacking is unstable.

Similar calculations were performed for the  $C_5B$  compound. The corresponding BC and BB stackings for the  $C_5B$  compound is shown in Figs. 2(a) and 2(b), respectively. The unit cell includes two layers of six atoms each (five carbon and a boron atom). The curves of total energies vs lattice parameter  $c$  are shown in Figs. 4(a) and 4(b) for BC and BB stacking, respectively. The cohesive energies and depth of the energy well are 8.04 eV/atom and 1.40 eV/unit

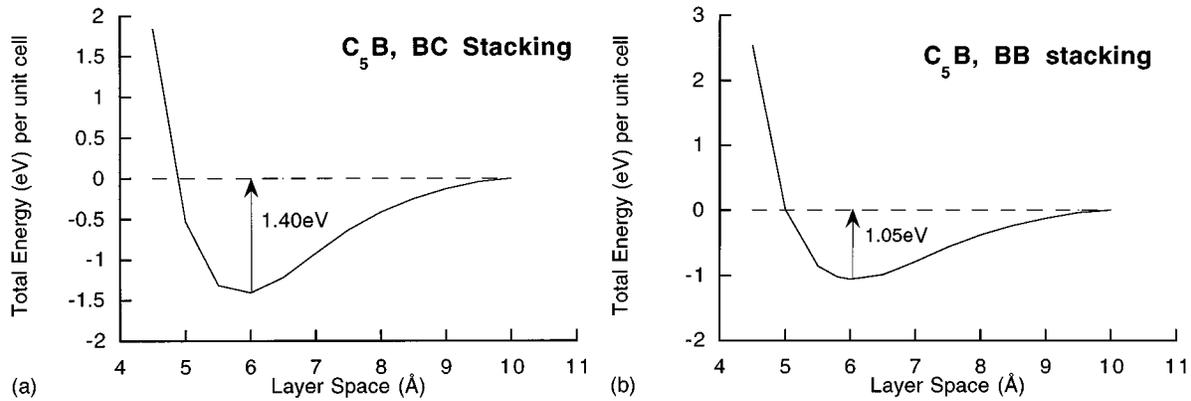


FIG. 4. The total energies (eV)/per unit cell vs parameter  $c$  (Å) for  $C_5B$  ordered structures, (a) for BC stacking and (b) for BB stacking.

cell for BC stacking, and 8.00 eV/atom and 1.05 eV/unit cell for BB stacking. Therefore, it seems that both stacking sequences could be stable with the BC stacking having higher stability. The optimized parameter  $c$  corresponding to the minimum is about 6.00 Å for both stackings, which is significantly smaller than 6.60–6.70 Å in pure graphite. However, this decrease in the  $c$  lattice parameter is much larger than experimental observation<sup>7</sup> (i.e., 0.10 Å) for the  $C_{1-x}B_x$  compound with  $x=0.17$ . A possible explanation for the smaller shrinkage in the experimental observation is that the lattice parameter  $c$  might be the average value of graphite and  $C_5B$  ordered structure, which implies that the  $C_{1-x}B_x$  with  $x=0.17$  compound might be a mixture of  $C_5B$  ordered phase and graphite.

In summary, based on our *ab initio* pseudopotential calculations, it is shown that (1) the ordered structure of the  $C_3B$  compound with the hexagonal symmetry within the layer and BC stacking sequence along the normal to the layer is stable with a  $c$ -lattice parameter 6.85–6.90 Å, while the structure with BB stacking is unstable; and (2) the ordered structures of  $C_5B$  can be stable in both stacking sequences with the  $c$ -lattice parameter 6.00 Å, which is significantly smaller compared with 6.60–6.70 Å of pure graphite.

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