Crystal structures and metastability of carbon-boron compounds C_{3}B and C_{5}B

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The recent discovery of the diamondlike C_{3}B and C_{5}B compounds has raised hopes of revealing interesting properties and also elicits questions about the stability of such compounds. Using our implementation of the evolutionary global space-group optimization method, we have found ordered structural models for C_{3}B (layered hexagonal) and C_{5}B (diamondlike) with lower energies than previously obtained and revealing unusual layer-stacking sequences. The compounds are less stable than a mixture of freestanding lowest-energy phases of B, C, and C_{3}B, thus C_{3}B and C_{5}B are not ground-state structures. Nevertheless, disordered diamondlike C_{3}B and C_{5}B can be formed exothermically at high temperature in the reaction [graphitelike C_{3}B] + 2C → [diamondlike C_{5}B] and [graphitelike C_{3}B] → [diamondlike C_{3}B]. Thus, the disorder on the C and B sites of diamondlike C_{3}B and C_{5}B is responsible for the observed phases.

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Diamond has been the focus of attention for a very long time both because of its rare aesthetic appeal as well as for its unusual physical properties, including superhardness, thermal conductivity, wide band gap, and high hole mobility. Elemental boron has also held the scientific community in constant fascination because, among others, of its unusual polymorphism, showing a multitude of polyhedral crystal structures. Naturally, the reports that combine diamond and boron tend to stir much attention. Solid boron can accommodate as much as 20 atomic % of C in the stable C_{3}B_{12} (CB_{4}) phase, consisting of B_{12} icosahedra forming a hexagonal lattice surrounding a C-C-C chain located between the B_{12} icosahedra. In the opposite limit of carbon-rich phases, which are of interest here, boron has very low solid solubility, and B-doped diamond was predicted to attain a weakly p—type character. However, it was suggested that incorporation of large amounts of boron into diamond would result in extreme enhancement of superconductivity. B-doped diamond synthesized at 8–9 GPa and 2500–2800 K was reported to be a type-II superconductor with transition temperature $T_c = 5\text{ K}$, while $T_c$ of the heavily B-doped diamond (~20 at. % of B) was predicted, assuming simple hypothetical structural models, to rise to $T_c = 55\text{ K}$, prompting high-pressure experiments. However, most attempts to achieve high solubility of boron in diamond at extreme pressure ($P$) temperature ($T$) condition resulted in disordered C_{1−x}B_{x} alloys with B content around 1–2 at. %. The two exceptions, which are of interest here, are C_{3}B and C_{5}B as they represent claim stable phases.

C_{3}B was reported during chemical-vapor deposition (CVD) growth6–8 of boron trichloride and benzene around 1000 K. Its crystal structure has not been fully resolved, but C_{3}B was said to be graphite-like with uncertain distribution of C and B atoms. Later on, the C_{3}B was grown epitaxially on the NbB_{2} (0001) substrate. Several theoretical studies have attempted to propose the crystal structure for C_{3}B under using intuitive models for distributing of B atoms in graphite-type supercells. The most recent experimental study10 revealed another diamondlike phase with C_{3}B stoichiometry and unknown distribution of C and B atoms at 39 GPa and 2200 K. Theoretical study by Liu et al.11 predicted, using a swarm-optimization algorithm, which was combined with the first-principles structural relaxations, three metallic diamond-based structural arrangements, which had lower energies than all previously considered intuitive models.

C_{5}B was reported very recently by Solozhenko et al.12 in a course of the laser heating of samples in the diamond-anvil-cell and further quenching them from 24 GPa and ~2200 K to ambient conditions. This C_{5}B phase was said to be diamondlike, showing high bulk modulus of 335 GPa, high thermal stability (up to 1900 K), and exhibiting extreme Vickers hardness (71 GPa). Indeed, the analysis of the x-ray diffraction spectrum of C_{5}B showed that C_{5}B is similar to diamond though more certain information of the crystal structure has been lacking. Several theoretical works have proposed ordered structural candidates for C_{3}B,5,13–15 Two of the most stable structures were predicted by Li et al.15 by combining the evolutionary algorithm with first-principles calculations. Surprisingly, comparative analysis of the theoretical stability of the proposed C_{3}B and C_{5}B phases with respect to the known stable phases, namely elemental C, B, and CB_{4}, has not been performed.

This paper reports a structure search with the evolutionary method called global space-group optimization (GSFO), using first-principles calculations. Starting from a set of randomly generated structures, we find ordered structures for C_{3}B (layered hexagonal) and C_{5}B (diamondlike), which have lower total energies than all previously proposed structural models. We perform a systematic analysis of thermodynamics for bulk C_{3}B and C_{5}B phases, finding that at low temperature they are not ground state structures (i.e., would decompose to the stable phases C, B, and CB_{4}). However, disordered diamondlike phases of C_{3}B and C_{5}B can be formed exothermically at high temperature in the reaction [graphitelike C_{3}B] + 2C → [diamondlike C_{5}B] and [graphitelike C_{3}B] → [diamondlike C_{3}B].
Method of calculations. We have performed an evolutionary search of the structures for the C$_3$B and C$_5$B phases using implementation to the GSGO method, which determines the lowest-energy structure starting from unbiased random lattice vectors and random atomic positions in a supercell of given maximal size. A comparative discussion of different optimization approaches can be found in Ref. 17. To minimize the risk of getting trapped into high-energy local minima, we restarted the evolutionary search a few times, starting from independent sets of random structures. The electronic-structure calculations were performed in the framework of the density functional theory (DFT), using the projector augmented wave (PAW) method with exchange and correlation treated within the generalized gradient approximation (GGA) as implemented in the VASP code (previous studies Refs. 11 and 15, which predicted the lowest-energy structures for C$_3$B and C$_5$B, respectively, also used GGA). The structural search for the C$_5$B candidates was done at pressure of 20 GPa since the synthesis of the phase was reported at similar pressure conditions. The search for the C$_3$B candidates was done at the same pressure. For more details see Supplemental Material.

Results of the evolutionary structural search. C$_3$B: The GSGO procedure identifies a structural candidate for the ordered C$_3$B [see Fig. 1(b)], which has positive formation enthalpy, yet lower than all other structural candidates known in the literature [see Figs. 1(c)–1(e)]. Figure 1(a) shows the results of the calculated formation enthalpies ($\Delta H_{\text{form}}$) vs pressure for our best candidate and for the most competitive structural models of Ref. 11, using the same GGA calculation parameters. Remarkably, all previously suggested structures from Ref. 11 represent diamondlike carbon networks with different substitutions of C by B. In contrast, our best candidate for the C$_3$B phase represents a layered hexagonal structure with unusual stacking along the close-packed [111] direction. It has a hexagonal unit cell, which consists of 12 atoms (coordinates are listed in Ref. 23). Three bilayers of C and three bilayers of C/B form the structure. The central C-B bilayer has graphitelike environment with 3-coordinated B and C in plane. The adjacent bilayer of C/B and other C bilayers have diamondlike environment and with fourfold coordination. The stacking of the fourfold coordinated bilayers of C/B and C differs from diamond. Our C$_3$B model can be viewed as tetrahedral-based with the tetrahedra oriented along (111) direction. Interestingly, the tetrahedra are oriented opposite from both sides of the graphitelike C/B bilayer. The C$_3$B structure represents a semimetal with rather low occupancy of the density of states (DOS) at the Fermi level [see Fig. (S1)]. Experimentally the crystal structure of C$_3$B has not been resolved. By assumption from Ref. 6 C$_3$B may have a graphitelike structure with unknown distribution of C and B atoms, and, in principle, our structural model would fit such description. However, complete structural refinement requires further experimental analysis.

C$_5$B: Our best candidate for the C$_5$B structure obtained with the GSGO is shown in Fig. 2(b). Its formation enthalpy is positive, but lower than the best candidates from the literature, shown in Figs. 2(c)–2(d). The crystal structure of our best candidate is diamondlike unlike the case we find for C$_3$B. C$_5$B has fourfold coordination [see Fig. 2(a)] with 10 layers of C and two nearby B layers stacked along [111] direction.

FIG. 1. (Color online) (a) The formation enthalpy $\Delta H_{\text{form}}$ of the structural models of C$_3$B with respect to freestanding diamond plus $\alpha$-boron (3C + B) as a function of pressure. The structural models show carbon as red and boron as green spheres. The models include (b) the lowest-energy crystal structure, obtained with GSGO; (c)–(e), respectively, the Liu (S1), Liu (S2), and Liu (S3) structures proposed in Ref. 11, which were considered as most stable in previous studies.
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diamond direction (12 atoms per unit cell; coordinates are listed in Ref. 24). The structure forms tetrahedra, oriented along [111] diamond direction in such a way that they produce twin chain with a period of three tetrahedra. The bonds are separated in three groups. The B-B bonds are ∼1.79 Å, the C-B bonds are ∼1.58–1.59 Å, and the C-C bonds are ∼1.54 Å. Both structures from Ref. 15 have also diamond–based structures [see Figs. 2(b)–2(b)]. However, in contrast to our model, they have layer stacking along the [100] diamond direction. C5B is found here to be semimetallic. The electron deficiency in the C5B diamondlike structure results in small occupancy of the DOS at the Fermi level and above in the pseudogap [see Supplemental Material22 and Fig. 1(S2) for more details.] The structural model, suggested in the present work, as well as two other diamond-based models15 fit the experimental proposal of a diamondlike framework.12 It is interesting that the structural differences between the three models of C5B result only in a subtle energetic difference; this opens the possibility of their coexistence at high-temperature conditions of synthesis.

CB4: This is the only stable compound in the observed phase diagram of C-B.25 We calculated the total energy of the stoichiometric CB4 phase employing the experimentally known structure prototype.26 After relaxation of the shape of the unit cell and atom positions, the values for the lattice parameters were a = 5.640 Å and c/a = 2.147, in good agreement with experiment (a = 5.60 Å and c/a = 2.164). At ambient pressure the formation enthalpy ΔH_form (with respect to equivalent amounts of freestanding elemental C and B) is negative [see Fig. 3(a)] unlike C3B and C5B. But with increasing pressure, ΔH_form of CB4 gradually increases and at pressure above ∼20 GPa it becomes unstable [Fig. 3(b)]. It would be expected to decompose or transform into a more stable phase. However, we did not find confirmation of this effect in the literature. Instead, the CB4 is stable to the highest applied pressure of 40 GPa.

Basic thermodynamic analysis. We discuss the stability of these structures in three levels of theory to clearly delineate the factors leading to stability.

(i) Level 1 description: T = 0 K stability of individual phases of ordered C3B and C5B. In the literature on C3B and C5B, stability was often argued on the basis of the sign of the formation enthalpy ΔH_form, i.e., relative to equivalent amounts of freestanding elemental constituents C and B at T = 0 K. However, to establish thermodynamic stability additional decomposition reactions need to be considered. These can be conveniently viewed by inspecting the ΔH vs X ground state line, i.e., the convex line connecting all lowest-energy phases at different compositions X [i.e., B–CB4–C], which is shown by the black line connecting red dots in Fig. 3. We observe that at T = 0 K both C3B and C5B are situated above the ground state line in the entire considered pressure range (Fig. 3). This implies the instability of both C3B and C5B with respect to decomposition into alternative phases. Thus, level 1 theory does not provide an explanation for the formation of these structures.

(ii) Level 2 description: finite T free energies of individual phases of disordered C3B and C5B. A possible explanation

FIG. 2. (Color online) (a) The formation enthalpy ΔH_form of the C5B with respect to the freestanding diamond plus α-boron (5C + B) as a function of pressure. The structural models show carbon as red and boron as green spheres; (b) the lowest-energy crystal structure, obtained with GSGO; (c) and (d), respectively, the Li (S1) and Li (S2) structures proposed in Ref. 15, which were considered as most stable in the previous studies.

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for the apparent disagreement between experiment and level 1 theory would be disorder effects, which may take place at high-temperature synthesis \cite{10,12} and change phase equilibrium in comparison to low temperatures. The configuration entropy serves an agent to stabilize disordered phases over ordered ones at high temperatures. To estimate the effects of disorder at about 2000 K we considered a structural model of random \( C_3B \) alloys with various proportions \( x \) between amounts of \( C \) and \( B \) in the alloy. The model is inspired by the fact that the atomic environments of \( C \) and \( B \) in the crystal lattice of our diamondlike \( C_3B \) are similar, so these sites can be interchanged [see Fig. 2(b)].

The energy cost of such exchange of the \( C \) and \( B \) atoms in this lattice, which is in fact realized in the models of the Li et al. \cite{15} [Figs. 2(c)-2(d)], is relatively small [see Fig. 2(a)]. Consequently, the \( C_3B \) can carry configurationally entropy associated with such cross substitutions. In contrast, the local environments of \( C \) and \( B \) atoms in the ordered layered hexagonal \( C_3B \) structure are markedly different [Fig. 2(b)]. So cross substitution and its associated entropy is unlikely. Thus, we consider only diamondlike random alloys \( C_3B \) as an alternative to the ordered \( C_3B \) and \( C_5B \) phases. We simulated such disordered diamondlike \( C_3B \) alloys for several concentrations, using the special quasirandom structure (SQS) model \cite{22} for the distribution of \( C \) and \( B \) atoms on the fully relaxed diamond-based 196-atom supercells (see more details in the Supplemental Material\textsuperscript{,} 22 Sec. S.I). The configuration entropy was estimated within a mean-field approach: \( S_{\text{conf}} = -k_B T \left[ x \ln(x) + (1-x) \ln(1-x) \right] \). The calculated \( \Delta H_{\text{conf}} \) of the disordered alloys at 0 K were very high at all considered pressures, but increasing the temperature increases the configuration entropy for the disordered phases. At 2000 K \( \Delta H_{\text{form}} \sim T \Delta S_{\text{conf}} \) of the disordered alloys (see blue line in Fig. 3) are lower than the \( \Delta H_{\text{form}} \) of the ordered \( C_3B \) and \( C_5B \) compounds, but they are still very positive. Thus, configuration entropy for single phases is not enough to stabilize disordered \( C_3B \) and \( C_5B \).

(iii) Level 3 description: Configuration disorder effect for the compound generating reaction. The experiments that produced the diamondlike \( C_3B \) \cite{11} and \( C_5B \) \cite{15} at high-pressure and high-temperature conditions used the graphitelike phase as a precursor starting material. For the ordered \( C_3B \) such a process can be described by the reaction

\[
\text{[ordered graphitic } C_3B \text{]} + 2C \text{ (graphite)} \rightarrow \text{[ordered diamondlike } C_3B \text{]}. 
\]

The sum of energies of the proportionally taken freestanding initial components of the reaction is shown in Fig. 3 (green line).

Such a reaction was examined in Ref. 14 by means of the GGA calculation at \( T = 0 \) K. It was shown that at ambient pressure the enthalpy of that reaction at \( T = 0 \) K is positive [see Fig. 1 (S3)], and, hence, the stabilization of \( C_3B \) is not possible. But with compression the reaction enthalpy becomes negative and in favor of the stabilization of \( C_3B \). However, Ref. 14 considered very high-energy structures for the \( C_3B \) and \( C_5B \) and used the GGA functional for graphite, which severely overestimated the energy of this phase. We have recalculated the reaction enthalpy at \( T = 0 \) K, using our ordered GSGO structural models and avoiding the large GGA error for graphite by using instead the diamond phase of \( C \). We found a small positive reaction enthalpy in the entire considered pressure range up to 40 GPa [Fig. 1 (S3)], i.e., the ordered \( C_3B \) phase is not stabilized by the reaction.

However, if we calculate the reaction free energy \( \Delta F_{\text{react}} \) by considering the effect of configuration entropy on the disordered \( C_3B \) and \( C_5B \), we find (see Fig. 4 that shows the free energy of the reaction \( \Delta F_{\text{react}} \) as a function of temperature at various pressures) that (i) at 0 K \( \Delta F_{\text{react}} \) of both reactions are positive at all considered pressures, indicating that the reactions do not go forward. (ii) But as soon as temperature approaches 2000 K \( \Delta F_{\text{react}} \) of both reactions becomes negative, and, consequently, the reactions could go forward, stabilizing the disordered diamondlike \( C_3B \) and \( C_5B \) phases. Thus, the disagreement between experiment and level 1 theory regarding synthesis of the diamondlike \( C_3B \) and \( C_5B \) phases at high pressure and temperature can be explained by the metastable precursor reaction (level 3 theory) between metastable graphitelike \( C_3B \) and diamond and assisting by the effects of disorder. Besides, our prediction that the synthesized diamondlike \( C_3B \) and \( C_5B \) represent disordered alloys between \( C \) and \( B \) may also explain the experimental difficulties in determining unique positions for \( C \) and \( B \) atoms.

In summary, we discovered via DFT evolutionary GSGO calculations ordered structures for graphitelike \( C_3B \) and diamondlike \( C_3B \) phases, which have lower energies than the

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### Table: Formation enthalpies of the C-B phases

<table>
<thead>
<tr>
<th>Pressure (GPa)</th>
<th>( \Delta H_{\text{form}} ) (meV/atom)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>10</td>
<td>80</td>
</tr>
<tr>
<td>20</td>
<td>160</td>
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<tr>
<td>30</td>
<td>240</td>
</tr>
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**Figure 3.** (Color online) Black line shows the formation enthalpy \( \Delta H_{\text{form}} \) of the binary phases in B-C system at \( T = 0 \) K and various pressures. The ground state line is shown as black solid line, connecting lowest-energy phases of the reaction. Black circles correspond to \( C_3B \) and \( C_5B \), obtained in this work by the GSGO method. Notably, black circles are above the ground state line. Blue line is the energy of random alloy phases at \( T = 2000 \) K. The green line is a sum of energies of the proportionally taken freestanding initial components of the reaction \( \text{[graphitelike } C_3B \text{]} + n C \rightarrow \text{[diamondlike } C_3B \text{]}(x \text{ is a proportion between } C \text{ and } B \text{ in the alloy}; n \text{ is amount of } C) \).
and diamond-C.

ordered graphitelike C3B phase. In the lower panel (b) the energy
various pressures. In the upper panel (a) the energy reference is the
10P. V . Zinin, L. C. Ming, H. A. Ishii, R. Jia, T. Acosta, and
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previously proposed structural models. Both C3B and C5B
have positive formation enthalpies and structures with unusual
layer-stacking sequences. (i) We examined $T = 0$ K stability
of individual phases of ordered C3B and C5B relatively to
the other stable phases at different concentration (convex hull,
consisting of B - CB4–C) and found that C3B and C5B have
very high energy and would decompose. (ii) We calculated
finite-$T$ free energies of individual phases of disordered C3B
and C5B. It turns out that while at high temperature the
disordered structures have lower energy than that of ordered
ones, but the formation enthalpy of the disordered phases
are still very positive. (iii) Since the starting material in the
experiment is graphitelike carbo-boride, we considered the
finite temperature formation reactions: [graphitelike C3B] + 2C ⃗
[diamondlike C5B] and [graphitelike C3B] ⃗
[diamondlike C3B]. We showed that the reactions go forward
only at high temperature stabilizing the disordered C3B and
C5B. The disordering between C and B atoms in diamondlike
C5B and C3 may explain experimental difficulty to resolve the
crystal structure of these phases.

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23Information of crystal structure of the GSGO C3B: Space Group: No. 160, R3m, C3v-5, Hexagonal lattice: a = 2.608 Å, c = 37.402 Å; atomic positions: C 3a (0, 0, 0.304), C 3a (0, 0, -0.459), C 3a (0, 0, -0.307), C 3a (0, 0, -0.418), C 3a (0, 0, -0.181), C 3a (0, 0, 0.263), C 3a (0, 0, -0.140), C 3a (0, 0, 0.089), C 3a (0, 0, -0.348), B 3a (0, 0, 0.423), B 3a (0, 0, 0.041), B 3a (0, 0, 0.138); alternatively the structure can be represented as follows, rhombohedral lattice: a = 2.608 Å, c = 12.558 Å, α = 90°, β = 84.04°, γ = 120°; atomic positions: C (0.391, 0.696, 0.913), C (0.918, 0.459, 0.623), C (0.615, 0.307, 0.078), C (0.836, 0.418, 0.746), C (0.361, 0.181, 0.458), C (0.475, 0.737, 0.788), C (0.280, 0.140, 0.580), C (0.821, 0.911, 0.268), C (0.696, 0.348, 0.956), B (0.155, 0.577, 0.268), B (0.918, 0.959, 0.122), B (0.724, 0.862, 0.414).

24Information of crystal structure of the GSGO C5B: Space Group: No. 156, P3m1, C3v-1; hexagonal lattice: a = 2.52(2) Å, c = 13.03(6) Å; atom positions: C 1a (0.0, 0.0, 0.353), C 1a (0.0, 0.0, 0.672), C 1c (2/3, 1/3, 0.154), C 1a (0.0, 0.790), C 1c (2/3, 1/3, 0.511), C 1b (1/3, 2/3, 0.194), C 1c (2/3, 1/3, 0.632), C 1b (1/3, 2/3, 0.313), C 1b (1/3, 2/3, 0.830), C 1a (0.0, 0.471), B 1c (2/3, 1/3, 0.0321), B 1b (1/3, 2/3, 0.952).

