Metallicity of boron carbides at high pressure

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Abstract. Electronic structure of semiconducting boron carbide at high pressure has been theoretically investigated, because of interests in the positive pressure dependence of resistivity, in the gap closure, and in the phase transition. The most simplest form B_{12}(CCC) is assumed. Under assumptions of hydrostatic pressure and neglecting finite-temperature effects, boron carbide is quite stable at high pressure. The crystal of boron carbide is stable at least until a pressure higher than previous experiments showed. The gap closure occurs only after \( p = 600 \) GPa on the assumption of the original crystal symmetry. In the low pressure regime, the pressure dependence of the energy gap almost diminishes, which is an exceptional case for semiconductors, which could be one of reasons for the positive pressure dependence of resistivity. A monotonous increase in the apex angle of rhombohedron suggests that the covalent bond continues to increase. The C chain inserted in the main diagonal of rhombohedral structure is the chief reason of this stability.

1. Introduction
Pure boron solids having icosahedron as the building block are classified as semiconductor and have many polymorphic modifications. These crystals do not exhibit superconductivity at normal conditions. In 2001, a superconducting transition was discovered at a very high pressure (160 GPa) when \( \beta \)-phase (symbolically written as B_{105}) of their polymorphic modifications was used as the starting material [1]. A lot of papers concerning the superconductivity of boron appeared since then: see a review paper [2]. However, even the structure at high pressure has been yet unknown, and thereby study on the mechanism of metallization is faced to difficulty. The authors and Japanese team have focused on the simplest polymorph, i.e., \( \alpha \)-phase (B_{12}), and very recently we have discovered superconductivity for \( \alpha \) phase at a high pressure (again around 160 GPa) [3]. In this case, it is proven that the superconductivity transition occurs without any phase transition [4]. Therefore, the metallization mechanism is a continuous gap closing [5]. This mechanism of continuous gap closing is indeed rare for semiconductors. Interplay of the strong covalent intericosahedral bonding and the relatively deformable icosahedron makes \( \alpha \)-phase a special case.

Now, we address ourselves to boron carbides, because it is predicted to have a transition temperature \( T_c \) about 35 K [6]. Boron carbide is symbolically written as B_{4C}, but the actual structure is rather complicated [7,8]. Boron carbide is also regarded as one of icosahedron-based boron crystals. The composition varies in some range, from B_{12}C_{3} to B_{13}C_{2} [9]. Standard band calculations predict that B_{12}C_{3} is a semiconductor, while B_{13}C_{2} is a metal. Experimentally, at normal conditions, boron carbides exhibit degenerate semiconductors over all the composition
range. In spite of extensive efforts to find superconductivity, there has been no success at the ambient pressure.

Even at ambient pressure, standard band calculations fail to describe the electronic properties of boron carbides [10, 11]. There are a couple of arguments concerning this problem [12–15]. Although consensus has not yet been established, it may be certain that the disorder which is commonly observed in this system is a cause of the insulating character [7, 8, 10, 11, 16–19].

At high pressure, an unusual property of boron carbides has been found that the electrical resistivity is increased with increasing pressure [20]. This property was once explained in terms of small bi-polaron mechanism [12]. However, this mechanism was subjected to criticism [15]. In this regard, the pressure dependence of the energy gap is important.

In this way, there are a lot of interesting questions about the high-pressure properties of boron carbides. Motivated by these issues, we have been studying theoretically the structural and electronic properties of boron carbides at high pressure by \textit{ab initio} calculations. The main concernings of this paper are the structural change and the band gap, especially, the gap-closing pressure, if present, by taking B$_{12}$C$_3$ as example.

2. Methods

In this paper, we assume a stoichiometric compound B$_{12}$(CCC), \textit{i.e.}, the $\alpha$-boron structure plus a CCC chain in the main diagonal of rhombohedron. Now, we know that the perfect crystal possessing this structure never happens in the real situation. Even in this composition, it is shown that a configuration (B$_{11}$C)(CBC) is energetically more favorable [10, 11]. Further complicated transpositions of atoms may occur [7, 8, 16–18]. In spite of this, we like to start with this simple structural model, because we wish to study the high-pressure properties. So far, there is no study stability of boron carbides at high pressures. In this case, it is important to examine the simplest structure and to understand what happens at high pressures.

Calculations were performed the first-principles pseudopotential method within local-density approximation (LDA). The used code is ‘Osaka2002’ [21] with a subroutine module ‘TSPACE’ [22]. We generated Troullier-Martins pseudopotentials [23] with aid of a full separable Kleinman-Bylander form [24] with the treating $p$-orbital as the local part. Plane waves up to a kinetic energy cutoff of 65 Ry have been included in the basis set. The Ceperley-Alder form [25] parameterized by Perdew and Zunger [26] was employed for the exchange-correlation functional. The Monkhorst-Pack mesh [27] of $2 \times 2 \times 2$ was used for k-point sampling. At this condition, we found the convergency of total energy is less than 1 mRy/atom. Symmetry constraints of $D_{3d}$ was imposed to atomic positions and the cell parameters in the structural optimization.

3. Lattice parameters at high pressure

For boron carbides, DFT calculations have given sufficient accuracy of structural parameters compared with experiment [10, 11, 16]. A review as to what properties DFT calculations clarify about boron carbides are found in Vast’s paper [28]. Here, we compare only the lattice parameters and bulk modulus of boron carbides in theory and experiment in Table 1. There is good agreement with previous theoretical and experimental works [10, 16]. The actual structure (B$_{11}$C)(CBC) has a lattice parameter $a_0$ slightly smaller than that of (B$_{12}$)(CCC). Bulk modulus is not sensitive to the details of the structure of boron carbides.

Pressure dependence of the lattice parameters is plotted in Fig. 1. Notice that the apex angle $\alpha_{th}$ increases monotonously. This is apparent contrast to the $\alpha$-boron case. As discussed in a previous paper [5], the deviation of the apex angle $\alpha_{th}$ from 60$^\circ$ has significant meaning on the stability of icosahedron-based boron solids. For the $\alpha$-boron case, the $\alpha_{th}$ is slightly smaller than 60$^\circ$. The $\alpha_{th}$ initially decreases with increasing pressure, and at approximately 50 GPa turns to increase. In contrast, for boron carbide, $\alpha_{th}$ increases only over all the pressure range.
Table 1. Comparison of the lattice parameters of B\(_{12}\)(CCC) in the rhombohedral system. Only for different configurations, the configurations are remarked. Also listed are the bulk modulus \(B_0\) at \(p = 0\) and its pressure derivative \(B'\).

|               | \(a_0\) (Å) | \(\alpha_{rh}\) (°) | \(B_0\) (GPa) | \(B'\) | notes     |
|---------------|-------------|----------------------|---------------|-------|-----------|
| Calculation   |             |                      |               |       |           |
| present       | 5.11        | 66.0                 | 246.1         | 3.7   |           |
| [10]          | 5.182       | 65.61                |               |       |           |
| [10,29]       | 5.141       | 65.76                | 216.9         |       | (B\(_{11}\)C)(CBC) |
| [16]          | 5.12        | 65.9                 | 248           | 3.5   |           |
| Experiment    |             |                      |               |       |           |
| [7]           | 5.155       | 65.67                |               |       | \(B_{12}\)C\(_3\) |
| [7]           | 5.191       | 65.63                |               |       | \(B_{13}\)C\(_2\) |
| [30]          |              |                      | 234.9         | 4.26  |           |

Figure 1. Lattice constants of \(B_{12}\)(CCC) as a function of pressure.

Actually the increase continues up to 700 GPa! From the experience of study on \(\alpha\)-boron, this suggests that intericosahedral and chain bond enhances its covalent character.

4. Energy gap at high pressure
The band structure and the electronic density of states of \(B_{12}\)(CCC) at ambient pressure are shown in Fig. 2. DOS was obtained by using a mesh of \(N_k=18^3\) \(k\) points. The symmetry and its label of special points or lines in the Brillouin zone are given in Ref. [5].

The energy gap, associated with the semiconducting character, is a big problem about boron carbides. Even determining of the energy gap in experiment is a difficult task. By an optical measurement, an indirect gap was once identified as 0.48 eV [31]. Since then, the presence of high-density of gap states and strong excitons have been recognized [32, 33], and the gap structure becomes more complicated. According to recent experiments [33, 34], the true band gap may be 2.09 eV. On the other hand, all band calculations so far published show a large band gap more than 3 eV [10,11,17–19,35,36].

Essentially, this situation is not changed even by modern DFT calculations. DFT band structures of boron carbides are seen in a series of paper by Kleinman’s group; Ref. [10] for \(B_{11}\)C(CBC) and Ref. [11] for \(B_{12}\)(CBC). LDA band calculations have shown large energy gaps for boron carbides; 2.78 eV (indirect \(F^-L\) in the present notations) for \(B_{11}\)C(CBC) [10] and 2.92 eV for \(B_{12}\)(CBC) [11]. Note that \(B_{12}\)(CBC) appears as metal in the standard band calculation,
but it still exhibit clearly the valence and conduction bands. In our calculation, the gap is 2.68 eV for B_{12}(CBC). The fact that the calculated gaps are large itself is unusual in that LDA gap has a tendency to underestimate energy gap. In this respect, it is interesting to find that the LDA gap of B_{12}(CCC) is rather close to the experimental gap. This is why we dare to show the band structure of B_{12}(CCC). We think that this agreement is fortuitous, but it may provide a clue to the gap problem of boron carbides.

Apparently, a distinct feature of the band of B_{12}(CCC) from those of B_{11}C(CBC) and B_{12}(CBC) is the presence of ‘mid gap’ state, whose symmetry at Γ point is $E_u$. This ‘mid gap’ wavefunction is plotted in Fig. 2(b), which shows that the predominant component is $p$ orbital of the central C atom in the chain. Non-bonding character of this band is clear from this figure, and thus it is reasonable to appear in the gap. Because of this ‘gap’ state, the energy gap becomes almost half of that of B_{11}C(CBC) or B_{12}(CBC). The energy gap is 1.56 eV of the direct-transition type, which occurs at $L$ point.

The energy gap is plotted as a function of pressure as shown in Fig. 3. As discussed in a previous study on α-boron [5], the pressure dependence of the energy gap $A_g \equiv dE_g/dp$ is a measure of the ‘rigidity’ of the electronic structure and is related to the deformation potential $a_g$. For typical semiconductors, $A_g$ falls in a range of several tens of meV/GPa with minus sign.

However, for boron carbide, $A_g$ is one order of magnitude smaller than those of other semiconductors, that is, -2 meV/GPa by averaging over all the pressure range. This is particularly surprising, by considering that the value is much smaller than even that of α-boron, -17 meV/GPa, although the structure is different only in the presence of the C chain otherwise the same. This small value is comparable to that of γ-boron (-1 meV/GPa), which is a recently discovered high-pressure phase of boron [37]. When we look at a low pressure region ($< 10$ GPa), the slope $|A_g|$ is less than 1 meV/GPa, and it seems even positive for the initial slope. Samara et al found a positive pressure dependence of the resistivity [20]. If we adapt our previous analysis [5],

$$\frac{d \ln \rho}{dp} = \frac{A_g}{kT},$$

(1)

to their data $d \ln \rho/dp = 0.375$ GPa$^{-1}$ for $T= 300$ K, then we obtain $A_g = +9.7$ meV/GPa. This
order of magnitude is in a range in the present calculation. If our result of positive slope is more than numeric errors, the experimental result of $p$ dependence of resistivity could be accounted for within the standard band theory. To ensure this, more careful calculations are required.

Our calculations show that if the crystal symmetry is constrained in the original $R\bar{3}m$, a crystal $B_{12}(\text{CCC})$ survives as semiconductor until about $p = 600$ GPa. Of course, this pressure is by far higher than the presently accessible range. The present conclusion does not exclude the possibility of occurrence of phase transition before the gap closure.

In experiment, so far, all results show that boron carbides undergo a transition to amorphous phase far lower than the above pressure. Gogotsi’s group reports a phase transition of boron carbide to disordered or undefined phases by static indentation technique, and the estimated pressure is about 44-49 GPa [38, 39]. Also, they cite in their paper a transition pressure about 20 GPa measured by Manghnani. Pressure-induced amorphization is reported [40]. In addition, dynamic indentation has been applied to see amorphization [41]. A computer simulation shows that the amorphization occurs at 6 GPa by shock conditions [42].

However, we should note that these experiments were performed under non-hydrostatic conditions. Recently, Mori’s group performed high-pressure experiment for boron carbide under hydrostatic conditions [43]. They reported that boron carbide retains the original crystal structure more than 100 GPa. Based on their experimental results and our calculation, it is supposed that boron carbide is stable, in the static condition, up to a pressure far higher than before believed. The next question is whether phase transition occurs before the gap closure. Most of semiconductors undergo phase transition before gap closure [44]. An exception is $\alpha$-boron [5], besides the obvious exception of diamond.

5. Conclusions
In this paper, we have theoretically studied high pressure structure of idealized $B_{12}(\text{CCC})$. The electronic structure of $B_{12}(\text{CCC})$ is quite rigid against pressures. The energy gap is closed only after applying $p = 600$ GPa, under assumptions that the crystal symmetry $R\bar{3}m$ and the finite-temperature effects are ignored. In particular, in a range $p < 10$ GPa, the pressure dependence of the gap almost diminishes. Therefore, in this range, this rigidity of the gap could be one of reasons for the positive pressure dependence of resistivity which was found in experiment.

The strongest chain bond must be responsible to this rigidity. This reflects the fact that the rhombohedral angle $\alpha_{\text{rh}}$ continues to deviate from 60° until the gap closure occurs.

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**Figure 3.** Pressure dependence of the energy gap $E_g$. The right figure is an expansion of the left around $p = 0$ GPa.
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