Superconductivity research on boron solids and an efficient doping method

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Abstract. Boron solids are, similar to diamond, strong electron-phonon coupling systems and therefore potentially have high-\(T_c\) superconductivity. For realizing high transition temperature \(T_c\), however, careful control of the valence electrons is necessary, which requires detailed understanding of the electronic structure. By critically reviewing recent development in this field, along with the situation in heavily doped diamond and clathrates, we show a promising route for high \(T_c\) in boron system. Although both \(\alpha\)- and \(\beta\)-boron become metallic and exhibit superconductivity at high pressure, the strong covalent character still remains, which significantly limits its \(T_c\) achieved by applying high pressure. Heavy doping of related compounds is desirable, as long as the basic electronic structure is retained, but it is extremely difficult at normal conditions. A promising method to achieve this is high pressure synthesis. Similar technique is useful for heavy doping of diamond. To design high-pressure experiment, the role of theory is important through predicting the phase diagram, which was not available for boron previously.

1. Introduction
It was believed that superconductivity of phonon mediated mechanisms could not exceed 30 K in its critical temperature \(T_c\); it was only possible in cuprates. Now this old belief must be completely discarded. Many high-\(T_c\) materials such as MgB\(_2\) and K\(_3\)C\(_60\) have been discovered, although their superconductivity is most likely described by the phonon-mediated mechanisms [1, 2]. In this respect, boron and diamond systems are particularly interesting, because they exhibit strong electron-phonon coupling. For boron case\(^1\), the superconductivity was once discussed more than twenty years ago in terms of small bi-polaron mechanism [3]. Unfortunately, the superconductivity of boron was not discovered in this way.

Big breakthroughs for superconductivity have occurred after 2000 in different context. The first and probably most influential one is discovery of MgB\(_2\) by the group of Akimitsu [4]. The superconductivity mechanism of MgB\(_2\) is now understood within the context of classical Bardeen-Cooper-Schrieffer (BCS) theory in terms of phonon-mediated mechanism. However, the case of MgB\(_2\) is in many respects beyond our expectations based on empirical rules which were useful for searching candidates before [5]. The second breakthrough was discovery of the superconductivity in \(\beta\)-rhombohedral boron at high pressure by Eremets et al [6]. Hereafter,

\(^1\) By using a word boron, the authors intend to include boron-rich solid such as boron carbides.
we abbreviate \( \beta \)-rhombohedral boron to \( \beta \)-boron, unless there is a risk to confuse. It is known that most semiconductors undergo phase transitions at high pressures and many of them exhibit superconductivity. Erements \textit{et al.} showed that boron is not an exception, although the transition pressure is extremely high \( \sim 160 \) GPa. The third breakthrough is discovery of superconductivity in heavily doped semiconductors. It was first found for B-doped diamond by Ekimov \textit{et al.} [7] and then for B-doped silicon [8] and B-doped SiC [9]. Further discoveries followed in doped InN [10] and AlN [11]. The significance of these findings is that superconductivity appears even at normal pressure, which is quite appealing for applications.

Regarding the structure of the superconducting phase of \( \beta \)-boron, there are many controversies; some experimentalists found a structural transition to amorphous phase [12], some found a transition to a tetragonal phase [13]. Theoretically, \( \alpha \)-Ga type was suggested [14, 15]. When the present authors started the structural study, it was surprising that there was no phase diagram available for boron; therefore, we decided to calculate it. According to our phase diagram, \( \alpha \)-boron is the stable phase at low temperatures and high pressures [16, 17].

Seeing the stability of \( \alpha \)-boron at high pressure, along with other reasons, the present authors and Japanese experimentalists started a collaboration on superconductivity of \( \alpha \)-boron. Very recently, the superconductivity has been found for \( \alpha \)-boron at high pressure [18]. Although the transition pressure and the critical temperature of \( \alpha \)-boron are almost the same as those of \( \beta \)-boron, this discovery is not just a duplication of the results for \( \beta \)-boron. The crystal structure including the icosahedral unit is proven to survive even after the superconducting transition; the rhombohedral structure is retained up to \( 200 \) GPa [19]. This stability is consistent with our prediction of the phase diagram. To our knowledge, it is the first time that a semiconductor exhibits superconductivity at high pressure without any structural transformation.

By analyzing the electronic structure, we convinced ourselves that the present \( T_c \) (below 10 K) is by no means the upper bound which boron can have. In fact, for boron and diamond systems, there are many predictions of high \( T_c \) around 40 K. If the electronic structure is carefully controlled, in particular the Fermi level, it is possible to obtain higher \( T_c \). A promising method of controlling the Fermi level is doping. Doping idea was proposed more than ten years ago [20, 21, 22]. However, doping \( \alpha \)-boron is difficult in experiment. In order to overcome this difficulty, the present authors have proposed an efficient doping method using high pressure [23, 24].

Looking at the case of heavily B-doped diamond, we notice that a similar technique of high pressure was used. Actually, superconductivity in B-doped diamond was demonstrated on samples produced by high-pressure and high-temperature (HPHT) method. Unfortunately, this technique is unavailable to many experimentalists. Once the superconductivity was found for films synthesized by chemical vapor deposition (CVD) [25], most researchers started using CVD method, and the \( T_c \) value was increased. However, the increase in the concentration of B and in \( T_c \) has almost saturated around several at.% of B and \( T_c \sim 10 \) K. Apparently, a breakthrough over this technical difficulty is needed. Recently, the present authors have demonstrated the effectiveness of high-pressure synthesis for B-doped diamond [26, 27].

The above development shows that no exotic mechanism is needed to obtain high \( T_c \), but instead, new ideas of compounds or new technologies such as high pressure and heavily doping are important. In this time of International Symposium on Boron, Borides and Related Materials, it was timely to organize a special session focusing on the superconductivity of boron solids. It is a good opportunity to share the establishments of this field in the last decade. However, retrospective reviewing is not the most important purpose of this session. Much effort should be focused on further development of material research. Questions of how to control these electronic structures and how synthesize such promising materials are of central importance. This view point is emphasized throughout this article. We apologize in advance for frequent referring to unpublished works or informal sources of discussion, because the research is ongoing.
The present study contains our proposed answers to the above question. In the first part of this paper, we review recent development of the structural study and the electronic structure of boron at high pressures. High-pressure research has provided many new insights into physics of boron in the last decade, since an interesting study on the pressure dependence of Raman spectra of $\alpha$-boron [28]. This part gives the background ideas upon which we have conceived the use of high-pressure process for heavy doping. Since many features are common in boron and in B-doped diamond, the basic strategy for high-$T_c$ semiconductors is described by treating both cases in parallel, in Sec. 3. The second part (Sec. 4) is the most important part of this paper, which describes our proposal for heavy doping of boron and diamond. By the nature of material research, the subjects treated here are encompassed from the basic properties of materials to synthesis, and hence summary is provided at the end of each section.

2. High-pressure structural study

2.1. Crystal structures

We now know that the superconducting behaviors of $\alpha$- and $\beta$-boron are almost the same with respect to $T_c$ and the transition pressure [6, 18]. The superconductivity of boron seems insensitive to the details of crystal structure. Does it mean that the role of structural study of boron is not important for the superconductivity research? The answer is definitely no. In the following, we will see that theories based on incorrect or hypothetical structures eventually lead to totally wrong understanding, even though there is a fortuitous agreement with experiment, when we focus on a specific property only. Structural study plays a central role in superconductivity research on boron solids, because boron has many complicated polymorphic modifications. However, many theoretical studies treated only simple structures such as fcc or bcc [29]. A simple reason for this is that computation is easy. Another reason might be a belief that materials favor close-packed structures, which is simple, at high $p$. Now, we must admit that the latter believe is wrong for boron at least up to 200 GPa. A recent experiment shows stability of $\alpha$-boron up to 200 GPa [19]. Although a phase transition of $\alpha$-boron to $\alpha$-Ga type structure was predicted [30], there is experimentally no indication of such a transition. Therefore, a prediction of $T_c$ based on this structure does not reflect the actual situation, although it is theoretically interesting.

For $\beta$-boron, the situation is more complicated. Since Eremets first demonstrated superconductivity [6], experiments were mainly carried out on this phase. Sanz et al found a structural transition to amorphous phase at $p > 100$ GPa at room temperature [12]. Irreversible transformation to amorphous phase was observed in clathrate compounds: $\text{Ba}_8\text{Si}_{16}$ (at 40 GPa) [31] and $\text{K}_8\text{Si}_{36}$ (32 GPa), etc. Sanz et al also reported that another rhombohedral structure appeared at $p > 20$ GPa under nonhydrostatic conditions. Ma et al found a transition to a tetragonal phase [13] at $p > 10$ GPa and $T > 1500$ K. There is no consensus about the structure when superconductivity takes place.

Step features were observed in the pressure dependence of the resistivity of $\beta$-boron [6] at 30 and 130 GPa. These steps were interpreted as a sign of phase transitions. Sanz et al suggested that the step at 30 GPa corresponds to the transition to another rhombohedral structure [12]. Hausermann et al suggested that the step at 130 GPa is due to the band closure of $\beta$-boron, while the step at 30 GPa is due to a transition to $\alpha$-boron [30]. Shimizu group found similar step structures in the resistivity of $\alpha$-boron [18]. On interpreting the step structure for $\alpha$-boron, the present authors attribute the step at 50 GPa to a subtle structural change, even though the crystal structure is maintained. This issue is described later.

When the authors started research on boron solids, they were surprised by absence of boron-related phase diagrams. Although $\alpha$-boron is obtained commonly at relatively low temperatures, it was widely believed that $\beta$-boron is the most stable phase over the whole temperature range [32]. After completing first-principles calculations on the total energy, along with other thermodynamic functions, we found that $\alpha$-boron is the ground state of boron, while $\beta$-boron
is stable only at high temperatures \([16]\). The transition temperature \(T_{\alpha\beta}\) is calculated as about 1000 K at \(p = 0\). The mechanism underlying this difference is simple - stiff materials are stable at low \(T\), while soft materials can be stable at high \(T\) because of contribution of entropy. The situation is very much like that of diamond-graphite system. It is a common observation that the dense and stiff phase (diamond) is stable at low \(T\) and at high \(p\), while the dilute and soft phase (graphite) is stable at high \(T\) and low \(p\).

![Phase diagram of boron](image)

**Figure 1.** Phase diagram of boron. The calculated phase diagram is taken from Ref. [17]. Experimental data are compared; 1: Sanz et al [12], 2: Runow [33], 3: Ma et al [13], 4: Wentorf [34], and 5: melting curve by Brazhkin et al [35].

After that work, similar conclusion followed by others [36]. On the other hand, there are still debates on the stability of \(\alpha\)- and \(\beta\)-boron. Widom and Mihalkovič [37] showed that \(\beta\) phase becomes stable even at \(T = 0\) K, if all the defects which were reported by Slack et al [38] are taken into account. Further studied are in progress [39, 40]. In our study, even one kind of defect causes the stability of \(\beta\) phase, which significantly reduces the transition temperature \(T_{\alpha\beta}\) down to about 200 K [16]. The effect of defects is important to this extent. In this regard, examining defects in \(\alpha\)-boron is interesting, because \(\alpha\)-boron is so far considered as perfect occupancy system. The first study on this subject is made by us [41], with a tentative conclusion that defects do not occur in \(\alpha\)-boron at such concentrations that thermodynamical stability is significantly influenced.

Although still uncertain, the conclusion that \(\alpha\) phase is the ground state seems reasonable, considering the experimental facts. Crystals of \(\alpha\) phase are obtained in molten metal, where the eutectic temperature is as low as 830 \(^\circ\)C for B-Pt system [42] and similar for Pd-B system [43]. Molten metal synthesis is close to thermodynamic equilibrium. Kimura’s group showed that, by starting from amorphous boron, \(\alpha\) phase is obtained around 1200 \(^\circ\)C [44]. Below that temperature, no crystallization occurred. If \(\beta\) phase is stable, \(\beta\) phase should be grown in these conditions, because there is no special conditions which favor the \(\alpha\) phase.
Based on the ground-state energy calculations along with phonon calculations, a phase diagram of boron was calculated over full $p - T$ range [17]. Anharmonic effects are taken into account within quasiharmonic approximation. The calculated phase diagram is shown in figure 1. This is the first prediction of the phase diagram of boron. Only $\alpha$- and $\beta$-boron phases are considered. Although there are other polymorphs, the authors think that these two are representative of boron in many respects. For example, atomic density is the highest for the $\alpha$ and lowest for the $\beta$ phase, see Table I of Ref. [45]. The reader should understand this diagram as providing the limiting cases; other phases, if present, could appear in an intermediated region.

Let us check experimental situation on the phase diagram. So far, no systematic experiment has been performed. Only small pieces of data are available in scattered $p - T$ points. Runow observed a transition from $\alpha$ to $\beta$ phase at an estimated temperature of 1370°C [33]. Although the lattice spacing was perfect, there was a deficiency of 9 atoms for $\beta$-boron. Starting from a mixture of $\beta$ phase and amorphous phase, Wentorf was able to synthesize a new structure of pure boron [34]. The density (2.46-2.52 g/cm$^3$) was recorded as the highest among known boron polymorphs. Very recently, Dubrovinsky has rediscovered and characterized this phase [46].

The equations of states have been examined for various polymorphs; in a range 0-10 GPa [47], 0-100 GPa [12] and 0-30 GPa at elevated $T$ [13] for $\beta$-boron, 0-100 GPa [48, 49] for $\alpha$-boron, and 0-11 GPa [50] for boron carbide. Murnaghan’s equation-of-states [51]

$$\frac{V(p)}{V_0} = \left(1 + \frac{B_1}{B_0}p\right)^{-1/B_1}$$

fits well to all cases. The thus obtained bulk modulus $B_0$ at $p = 0$ and its pressure derivative $B_1$ are in good agreement with calculation. Here, we give typical values for later discussion; $B_0 = 210 - 240$ GPa and $B_1 = 4$.

Recently, a systematic examination of the transition between $\alpha$ and $\beta$ phases up to 50 GPa has been conducted by Mori et al [52]. A difficulty experienced by them is that, as usual in high-temperature experiments, reactions with unwanted parts of the apparatus sometimes take place, which appear as unknown peaks in X-ray diffraction study. Historically, such unknown peaks have been sometimes recognized since Decker and Kasper reported the first the crystal structure of $\alpha$-boron [53].

This prediction of phase diagram is also useful for obtaining good-quality crystals of $\alpha$-boron, which is very important for the superconductivity application. One way is to use high-temperature and high-pressure method. Starting with $p > 50$ GPa and $T > 2000$ K, crystal of $\alpha$-boron can be grown directly from the liquid phase. After calculating this phase diagram, the authors came to know an experiment on the melting of boron [35]. As shown in the figure, there is a large difference in the melting data. In Ref. [17], the melting curve was calculated from existing data on the free volume and the latent heat of fusion, on assumption that Eq. (1) is valid for both solid and liquid phases. After publishing paper [17], we came to know an experiment on the melting of boron [35], which is shown in this figure. There is a large discrepancy, in particular, for the initial gradient $dp/dT$. The data of the free volume and the latent heat of fusion in our calculation are largely different from data of [35].

In summarizing this section, we are able to delineate the phase diagram of boron. At low $T$ and high $p$, $\alpha$-boron is the most stable phase. Although there are still uncertainties in density functional theory (DFT) calculations, this conclusion seems reasonable. Indeed, it is otherwise difficult to interpret the crystal growth of $\alpha$-boron at low temperatures. For $\beta$-boron, phase transitions certainly occurs at high pressures, because $\beta$-boron is thermodynamically unstable there. However, what structure appears around the superconducting transition is still an open question. A good news for superconductivity research is that $\alpha$-boron exhibits superconductivity, and that the original structure is retained even after the superconducting transition, as indicated by the calculated phase diagram.
2.2. Electronic properties

Numerous theoretical studies were published immediately after the discovery of superconductivity of \(\alpha\)-boron, even though there had already been many published papers on the electronic structures of boron solids [54, 55, 56, 57, 29, 58]. At early stage, calculations were performed only on simple structures, such as \(\alpha\)-boron [59, 60] or even simpler hypothetical structures [61, 15, 30, 62, 63]. Later, calculations on \(\beta\)-boron appeared [64, 16, 37]. All calculations after 1990 are modern DFT calculations. Here, we focus mainly on the pressure dependence of the electronic structure. Studies on the superconductivity are described in the next section. Discussion on hypothetical structure of \(\alpha\)-Ga type is omitted here, for the reason described earlier.

For \(\alpha\)-boron, the change of the electronic structure at high pressure has been studied by Zhao and Lu [59] using the generalized gradient approximation (GGA) as the electron-correlation part. Evidently, the intention of this article is to explain the metallization of boron which was experimentally shown for \(\beta\)-boron [6]. However, the main results they show are those on \(\alpha\)-boron, because of computational costs. They show that \(\alpha\)-boron is stable up to 270 GPa and that the band gap continuously decreases to zero around 160 GPa. Owing to the similarities of \(\alpha\)- and \(\beta\)-boron, it is inferred that the band-gap closure occurs also for \(\beta\)-boron at similar pressure. We now know that \(\alpha\)-boron indeed retains its rhombohedral structure up to 200 GPa [19]. Then, the work of Zhao and Lu [59] is really a good reference for \(\alpha\)-boron. Even though the gap value is somewhat ambiguous due to a problem inherent to DFT, overall behavior is consistent with the experiment. In \(\alpha\)-boron, at zero pressure, an icosahedral unit is bonded to six nearest neighboring icosahedral units; these strong bonds of the length 1.71 Å bring covalent character to this crystal. In the second-nearest neighbors, six icosahedra are connected in the \(ab\) plane. These bonds are the so-called three-center bonds; they are very weak with the bond length of 2.03 Å. These three-center bonds are significantly enhanced at high pressures and eventually form a high coordination number around an icosahedron. High coordination numbers are a typical feature of metals.

We have also confirmed this band closure and the structural change by our own calculations. The three-center bond has its chief component in the conduction bands, and when this bond is shortened, the bottom of the conduction band eventually merges with the top of the valence band. It should be noted that even though the electronic structure turns to be metallic, there is yet a remnant of semiconducting origin at a very small density-of-state (DOS) at the Fermi level, which qualitatively separates the parts of valence and conduction bands. The metallic phase of \(\alpha\)-boron (probably \(\beta\)-boron too) has both characters of metal and semiconductor. Metals possessing such a mixed character are known, for example, in WC [65, 66] and in \(\alpha\)-Ga [67].

Although we are satisfied with this explanation, our calculations resolve further interesting features. Actually, the way of deforming the lattice frame and the icosahedral units are contrasted between \(\alpha\)-boron and \(\beta\)-boron [19]. This fact itself was found in model calculation on the elastic response of boron solids [68]; see a review [45]. Among \(\alpha\)-, \(\beta\)-boron and boron carbides, the apex angle \(\alpha_{\text{rh}}\) of the rhombohedral lattice is slightly deviated from 60°; just 60° transforms the rhombohedral Bravais lattice to fcc. The deviation \(\Delta\alpha_{\text{rh}}\) from 60° is negative for \(\alpha\)-boron, while it is positive for \(\beta\)-boron and boron carbides. In all these cases, the pressure dependence of \(\Delta\alpha_{\text{rh}}\) is such that the deviation increases with increasing pressure. Increase in \(\Delta\alpha_{\text{rh}}\) means crystal anisotropy, which implies more covalent character for boron solids. In this sense, the covalent character of boron solids is initially increased on applying pressure. But, there must be some point at which this change ceases. After this point, metallic character is expected to increase. For \(\alpha\)-boron, this turning point is about 50 GPa, which was found in a collaboration of theory and experiment [19]. This pressure is well correlated to a small change in the Raman spectrum. The librational mode of \(\alpha\)-boron has many exceptional features. One of them is almost no pressure dependence of the vibration frequency [28]. However, for \(p > 50\)
GPa, slight lowering of frequency with increasing pressure is observed [19, 48]. The frequency of the librational mode $\omega_l$ is governed by angle forces, which arise from strongly oriented character of the covalent bonds [69]. Forming high coordination number reduces the covalent character, and hence angle force and $\omega_l$ decrease.

![Figure 2. Energy gap of $\beta$-boron with and without defects.](image)

In the electrical resistivity of $\alpha$-boron, Kaneshige et al [18] found step structures in the pressure dependence, in a way similar to $\beta$-boron. A step appears around 50 GPa. As discussed above, this feature is not due to phase transition but it should be ascribed to some change within the rhombohedral structure of $\alpha$-boron. Accurate band calculations show that turning from the covalent to metallic character, although still semiconductor, makes a change in the pressure dependence of the energy gap. The change in the energy gap alters the pressure dependence of resistivity, which is observed in experiment. The details will be given in a forthcoming paper [70].

For $\beta$-boron, effect of defects is problematic. One time of band calculation is manageable in the present status of computational technology, partly shown in [59]. However, we now know that $\beta$-boron has a variety of defects. The presence of defects significantly alters the stability of crystal [16, 37]. There is a report demonstrating softening of phonons at high T [36]. Of course, it modifies the gap states too. Here, in figure 2, we show our preliminary results of DOS structure of $\beta$-boron, which indicate how strongly the defects influence the gap state. Because there are so many configurations of defects, no conclusive results have been drawn concerning $\beta$-boron with defects.

We summarize the metallization process of $\alpha$-boron at high pressure. If we judge the metallization by closure of the band gap, the transition is obviously abrupt around 150 GPa. However, the change in the electronic structure is continuous as indicated by band calculations, and hence it is difficult (and maybe meaningless) to say when metallization begins. In spite
Table 1. Prediction of $T_c$ and the related parameters, $N(E_F)$, $\langle\omega\rangle$, $\lambda$, and $\mu^*$. Crystals are conveniently grouped into three. The first and second groups are boron crystals including boron carbide; the first group gathers hypothetical structures, while the second real systems of icosahedron-based polymorphs. The last group gathers other related materials. Pressure $p$ is given in GPa.

| structure          | structure (ref.) | $N(E_F)$ | $\langle\omega\rangle$ | $\lambda$ | $\mu^*$ | $T_c$ | notes |
|--------------------|------------------|----------|------------------------|-----------|---------|-------|-------|
| boron              | (Papaconstantopoulos and Mehl [61]) | fcc 0.15 | 107 0.39-0.53 0.09-0.13 | 5-15 | $p = 307$ |
|                    | (Häussermann et al [30]) | $\alpha$-Ga 0.02 | | | | | |
|                    | (Ma et al [62]) | $\beta$-Ga 0.22 | 124 0.38 0.12 | 6 | $p = 160$ |
|                    | (Bose et al [63]) | fcc 136 | 0.84 | 0.17 | $> 50$ | high $p$ |
| boron carbide      | (Calandra et al [72]) | B$_{12}$ (CBC) 0.24 | 65.8 0.81 | 0.1 | 36.7 | |
| $\beta$-boron      | (present work)  | B$_{12}$ 0.03 | | | | | $p = 200$ |
|                    | (Xiang et al [73]) | diamond | | | | | |
|                    | (Calandra et al [74]) | $\beta$C$_5$ | 0.03 105 | 0.39 | 0.10 | 4.4 | B: 2.8 % |
| MgB$_2$ (An and Pickett [75] and Kortus et al [76]) | diamond ? | 0.12 | 67.4 | 0.89 | 0.1 | 45 | B: 16.7 % |
|                    | hex 0.19 62 | 1.0 | 0.1-0.15 | 32-46 | $N(E_F)$ per B |
| Li$_x$BC (Rosner et al [71]) | hex 0.23 | 58 | 1.5 | 0.09 | $> 40$ | $x = 0.5$ |

of this, we may regard 50 GPa as an estimate for the beginning of metallization. The signs of transition are: (i) the change in pressure dependence of the apex angle $\Delta\alpha_{rh}$, which indicates a transition from anisotropic to isotropic deformations; (ii) slight softening in the librational mode, which suggests weakening of covalent character; (iii) the step structure in the resistivity, which is a consequence of the change in the energy gap.

3. Idea for high $T_c$ materials
After the discovery of superconductivity of $\beta$-boron, many theoretical studies on $T_c$ have been published on boron and related solids [61, 71, 72, 62, 63]. Indeed, the predicted $T_c$ is scattered from 5 [61] to more than 50 K [63]. Obviously, listing of such a widely spread numbers alone does not make sense for prediction.

Combination of DFT calculation and Eliashberg theory makes theoretical prediction of $T_c$ more reliable for simple metals and semiconductors; this is particularly true for the electron-phonon coupling parameter $\lambda$. A difficult problem is evaluation of the pseudopotential parameter $\mu^*$, which presents the retarded Coulomb repulsion. A common practice is fitting to the experimental $T_c$. This practice is particularly effective when the pressure dependence of $T_c$ is known [77, 78]. In this sense, this approach is not regarded as first-principles. Recently, there was an attempt to calculate $T_c$ without explicitly using these parameters $\lambda$ and $\mu^*$. Gross et al
have succeeded to formulate the ground state of superconductivity within the framework of DFT by introducing an additional variable; the order parameter is taken as a fundamental variable; see a review [79]. The agreement with experiment is profound, $34.1 \text{K}$ for MgB$_2$ [80]. However, the accuracy depends on the electron correlation functional, which is formally present but its concrete form is not known.

![Diagram](image)

**Figure 3.** Two ways of valence control of semiconductors. Starting from the normal state of a semiconductor (left figure), applying pressure causes band closure (middle upper). For B-doped diamond, heavy doping yields Fermi surface at the top of the valence band (middle lower). Further doping increases $N(E_F)$ (right).

In this way, accurate prediction of $T_c$ is still difficult. Nevertheless, the authors believe that if we take enough care for the structure, we can find a coherent understanding from those scattered predictions on $T_c$. In Table 1, we compare those scattered $T_c$ for various boron crystals and related materials. The data are grouped according to the structures. Some rows are added for comparison, even though they supply the density of state $N(E_F)$ only. Readers should be aware that only a selected set of data is picked out from the original reference, and that calculation approaches are different from author to author. For example, Ma *et al* deduced $\mu^*$ in order to match $T_c$ [62], so by construction, the $T_c$ agrees with the experiment. Since the present authors are not specialists in $T_c$ calculation, assessment of these results is not our intention. The list is of course incomplete; there are references missing in this table, for example, the superconductivity of dodecaboride such as ZrB$_{12}$ [81]. Our aim here is an insight into design of high-$T_c$ materials among boron-rich solids. By classifying the predicted $T_c$ according to the structures, we see some trends in $T_c$.

First, we note that the conditions of the prediction by Bose *et al* [63] are unrealistic, although challenging. Their calculations assume simple structures. The listed values in Table 1 are those for the atom volume $\Omega_{\text{atom}} = 20 \text{Bohr}^3$. Although they do not show the corresponding pressure, we can estimate it using Murnaghan’s equation of state (1): $p = 730 \text{GPa}$ for bct and $660 \text{GPa}$
for fcc structure. Here, we used data of Ref. [29] for $B_0$ and $V_0$, while $B_1=4$ is assumed. Both pressures are out of our currently accessible region.

Next, we see that for simple metal structures $N(E_F)$ is large, more than $0.1 \text{ /eV}	ext{-atom}$, in all cases investigated. On the other hand, for semiconductors, which include $\alpha$-boron and diamond, $N(E_F)$ is smaller by one order of magnitude, even though these crystals become metallic by applying pressure or doping. The case of $\alpha$-Ga type boron is intermediate between metal and semiconductor. As stated before, $\alpha$-boron becomes metallic above 150 GPa, but it still has the semiconducting character. This character is reflected in the smallness of $N(E_F)$.

Boron carbide case is different. Viewing boron carbide as C-doped boron may be wrong, as the phonon spectrum suggested [82]. Rather, strong C bonds seem to exhibit their own bonding environment. Based on the standard band calculation, it is concluded that boron carbide $B_{13}C_2$ is a metal from the beginning, for an obvious reason of the odd number of valence electrons. Hence, large $N(E_F)$ is obtained as expected. In spite of this, experiment shows the semiconducting character. There are arguments concerning this problem [83, 84, 85, 86]. Probably the disorder which is commonly observed in this system is a cause of the insulating character [87, 88, 89, 90]. A related reason may be Mott-Hubbard insulator caused by electron correlation [91, 92]. So far, no consensus has been established for the electronic nature of boron carbides.

Anyway, the semiconducting property of boron carbide is an experimental fact. Hence, it is no surprise to see that superconductivity has not been discovered for boron carbide at normal pressure, although numerous efforts were dedicated to search superconductivity in this material [93]. High-pressure technology may provide useful insights into boron carbides too. An unusual positive pressure dependence of the resistivity was found up to 2.5 GPa [85]. Further examination of high-pressure properties of boron carbides is interesting, which is now in progress by Japanese collaborators.

From the above consideration, we can summarize what happens around boron crystals at high pressure and in heavily doped diamond. Figure 3 illustrates the situations of both semiconductors. For $\alpha$-boron case, by applying pressure, the band gap is closed. But, its strong covalent character still remains in the shape of DOS. Overall separation of the valence and conduction bands is still present, and thereby the Fermi level is located close to the minimum point in DOS. Accordingly, $T_c$ does not increase as expected. For obtaining higher $T_c$, moving the Fermi level $E_F$ deeply inside the conduction or valence band is required. This can be done by doping.

The situation is similar for heavily B-doped diamond. Upon heavy doping, the Fermi level is shifted to the top of the valence band [94]. Even though now $T_c$ reaches 10 K [95], the Fermi level $E_F$ is still just under the top of valence band [94]. Hence, if we push down $E_F$ deeply into the valence band, we could obtain high $T_c$. In actual situation of diamond experiment, of course, not all the B atoms can enter at the substitutional site. Some part of B atoms form dimers or may go to interstitial site, which are electrically inactive [96, 97]. On the other hand, there are arguments that in some cases the disorder enhances $T_c$ [98, 99]. We will not be concerned too much with this problem here. Our standpoint is that disorder is not good for superconductivity. Very recently, Calandra and Mauri have shown an interesting calculation that cubic $BC_5$ (actually slightly distorted) has a deep $E_F$ in the valence band [74]. The predicted $T_c$ is above 40 K. This shows a good solution to avoid the effect of disorder in impurity systems.

Lastly, we mention a technical issue in calculating $E_F$, which is important to predict $T_c$. In many cases, doping level significantly modifies $E_F$, so that accurate determination of $E_F$ is crucial. In calculating Fermi surface, fine mesh of Brillouin zone and interpolation method are used. However, interpolation sometimes causes spurious components, in particular for those materials possessing nesting Fermi surface. Sophisticated algorithms utilizing symmetry are needed. A utility program TSPACE developed by Yanase is such a powerful tool for doing this.
The present authors and Yanase have developed an improved scheme of band interpolation specialized to obtaining Fermi surfaces [101]. An improved algorithm shows a beautiful Fermi surface for Li-doped $\alpha$-boron [101].

We have seen that, for both boron and diamond, the basic strategy for obtaining high $T_c$ is doping as heavily as possible. It is recommended to use stoichiometric compounds like BC$_3$, as long as such a compound retains the basic electronic structure of the parent crystal. Then, any problem caused by disorder would be avoided. Li-doped $\alpha$-boron (LiB$_{12}$), which we propose here, actually belongs to this category, even though we often refer this as impurity system. Similar usage of terminology is made in doped fullerides [102], in which the highest $T_c$ is now recorded as 38 K for Cs$_3$C$_{60}$ [103]. Clathrate compounds such as Ba$_8$Si$_{46}$ are called doped-clathrates, and they exhibit superconductivity [104]. It is unclear whether or not boron carbide belongs to this category. Examination of superconductivity at high pressure is very important.

4. High pressure doping method
Doping idea itself is very common, and anyone can conceive this. A practical problem is how to achieve heavy doping of a material under consideration. In usual semiconductor processes, the doping level is far less than 1 at.%. Contrary to this situation, in superconductor research, heavy doping above 1 at.% is required. Efficient doping method is indispensable.

In boron case, this problem is crucial. Doping of various metallic elements to $\beta$-boron has been investigated over the years [105]. However, doping of impurities yields gap states, which hinder effective doping. In this respect, $\alpha$-boron is a good candidate for doping, as stated earlier. Although it was predicted that Li doping to $\alpha$-boron is easy from energetics consideration [21, 22, 106], this doping has not been succeeded experimentally [44]. Something must be wrong with these predictions.

We have revisited this issue of Li doping to $\alpha$-boron in a more systematic way, and have found that it is difficult to dope Li at normal conditions [23, 24], contrary to previous studies. Further investigation led us to find an effective method of doping Li. The method is utilizing high pressure [23, 24, 107]. By analyzing our result, we have established the principal mechanism of high-pressure method for doping [26].

Before proceeding to discussion on the efficient doping method, we would like to appreciate a pioneering work of Gunji and Kamimura more than a decade ago [20, 21] to find Li as a good dopant among various impurities. We have confirmed the suitability of Li doping which they found, except for the problem of formation energy. Among various impurities, Li is ideal in that the change in the electronic structure is best described by rigid-band shift with a quite high $N(E_F) = 0.28$ /eV-atom [24]. The rigid-band shift due to doping is sometimes referred to, but actually is scarce in real materials. Few cases are K$_3$C$_{60}$ [108] and Li-doped carbon clathrates [109].

4.1. Theory of solubility limit
The solubility $c$ of impurity can be controlled through the formation enthalpy $h_f$ as

$$c = \exp \left( -\frac{h_f}{kT} \right),$$

where $k$ is Boltzmann’s constant [110]. The formation enthalpy $h_f$ is a material constant if the host crystal $A$ and impurity atom $B$ are fixed. Nonetheless, $h_f$ can be controlled by changing external conditions. The formation enthalpy $h_f$ is defined by the difference in energy $E$ between the reactants and the product as

$$h_f = E_{AB} - (mE_B + E_A),$$

where $m$ is the stoichiometric factor.
where \( m = 1/c \). In writing this equation, it is understood that the starting materials are of their most stable phases in the ambient conditions. At finite \( T \) and \( p \), all the energies appearing in Eq. (3) should be replaced by the corresponding chemical potentials \( \mu \). Chemical potentials depend on concentration as well as on \( T \) and \( p \). In semiconductor processes, their dependence on the charge state is also important for controlling the impurity concentration. By changing the starting states of reactants, we can control \( h_f \) and thereby the concentration of the impurity.

The solubility \( c \) is determined by the chemical equilibrium condition

\[
\mu^2_A = \mu^1_A, \tag{4}
\]

where the superscripts 1 and 2 indicate the reactant and the product systems, respectively. The impurity system 2 has an entropy contribution due to random distribution, \( kT \ln c \).

We will show in the following the usefulness of the high-pressure process for Li doping to \( \alpha \)-boron, based on the foregoing theory. The theory is quite general. Recently, we have analyzed an interesting method of Ekimov’s experiment on heavily B-doped diamond and succeeded to describe the experimental conditions [26, 27], based on the same theory. An application to B-doped diamond is also given below.

4.2. Li doping to \( \alpha \)-boron

Let us first describe the situation of the Li doping to \( \alpha \)-boron [23]. This example corresponds to a situation at \( T = 0 \) K, so that the analysis is easier. The involved reaction is expressed as

\[
B_{12} + Li \rightarrow Li@B_{12}. \tag{5}
\]

and accordingly the formation enthalpy \( h_{f, Li} \) of Li in \( \alpha \)-boron can be calculated by Eq. (3). Full calculation by the first-principles pseudopotential method was done [23]. At \( p = 0 \), \( h_{f, Li}^0 \) was obtained as +0.55 eV. This positive formation energy is very common in semiconductors, so that Li doping is realized only with very small concentrations, well below at.%. Our previous paper [23] illustrates that this situation can be changed by applying high pressure. The pressure dependence of \( h_f(p) \) is shown in figure 4. The sign of \( h_{f, Li}(p) \) is changed at \( p = 8 \) GPa, so that above 8 GPa heavy doping appears possible.

The main cause of this pressure dependence comes from the starting state of Li, \( i.e., \) metallic Li. Metallic Li is a soft material compared with boron, so that the most part of the pressure dependence is carried by the bulk modulus of the starting state of Li. From this observation, we can deduce a simple rule that softer materials can be easily doped in stiffer materials under high pressure.

This rule is simple but has wide applicability. The rule is founded by a well-known principle of thermodynamics, Le Chatelier’s principle: a perturbation induces a process that attenuates the initial perturbation. In the present case, the perturbation is volume change. In fact, it is a common observation by high-pressure experimentalists the inclusion of gaseous atoms such as He in the specimen at high pressures. An affirmative example is seen in doped clathrates. Yamanaka \textit{et al} use high-pressure process for synthesizing Ba$_8$Si$_{46}$ [104]. The reaction they used is

\[
8\text{BaSi}_2 + 30\text{Si} \rightarrow \text{Ba}_8\text{Si}_{46}. \tag{6}
\]

They point out that the free volume of Ba$_8$Si$_{46}$ is smaller by 15 \% than that of the reactant mixture, from which they found it efficient to use high-pressure synthesis.

4.3. B-doped diamond

Ekimov \textit{et al.} synthesized heavily doped diamond with boron concentrations above 2 at.\% in the boron carbide-graphite system under high pressure and high temperature, at \( p = 8 - 9 \) GPa.
and $T = 2600 - 2800$ K [111]. In this case, the analysis is more involved, because of finite temperature and multi-component systems. The details should be referred to Ref. [26], and here we describe the main results only.

The reaction of Ekimov’s method is symbolically written as

$$\text{B}_4\text{C} + \text{G} \rightarrow \text{B@D}. \quad (7)$$

Here, G and D denote graphite and diamond, respectively. Actually, this reaction is composed of the following three reactions,

$$\begin{align*}
4\text{B} + \text{C} &\rightarrow \text{B}_4\text{C} + g_{f,\text{B}_4\text{C}}, \quad (8a) \\
\text{D} &\rightarrow \text{G} + g_{f,\text{DG}}, \quad (8b) \\
\text{B} + m\text{D} + g_{f,\text{B@D}} &\rightarrow \text{B@D}_m. \quad (8c)
\end{align*}$$

The impurity concentration at arbitrary $p$ and $T$ can be obtained by calculating

$$\mu_B^2 - \mu_B^1 = \frac{1}{4} g_{f,\text{B}_4\text{C}} + mg_{f,\text{DG}} + g_{f,\text{B@D}} + kT \ln c_B = 0. \quad (9)$$

Calculations of the $T$ and $p$ dependence of the free energies were performed by using various available data. Appreciable dependence appears only for the free energy difference between graphite and diamond $g_{f,\text{DG}}$. The $T$ dependence has been calculated by taking only the phonon contribution within the harmonic approximation. A problem for determining the solubility limit is the formation energy of boron in diamond $g_{f,\text{B}}$. In particular, the concentration-dependent formation energy is required for such a high concentration regime. For diamond, there is no reliable data on the formation energy $g_{f,\text{B@D}}$. Hence, in a previous paper, we calculated $g_{f,\text{B@D}}$ by \textit{ab initio} pseudopotential method [27]. Even though there are still some difficulties to determine $g_{f,\text{B@D}}$, we have estimated $g_{f,\text{B@D}} = 1.0$ eV, if the situation of a supercell BC$_63$ is regarded as the representative of B doping.
Figure 5. Calculated solubility of boron in diamond synthesized by Ekimov’s method. A contour map for \( c_B \) is plotted with an interval 2 at.%. This figure is taken from Ref. [27].

In this way, we are able to calculate the B concentration in diamond at arbitrary \( p \) and \( T \), based on the reaction (7). A contour map of the B concentration in the \( p-T \) plane is shown in figure 5. In the figure, the experimental line for the phase boundary between graphite and diamond [112] is indicated by a dashed line. By considering that many thermodynamic quantities are involved in this calculation, the agreement seems good. The experimental conditions, where Ekimov et al [7] reached boron concentration of 2.8 at.\%, are indicated by a red region. As clearly shown in this map, as increasing pressure, we can obtain higher boron concentrations in diamond.

A problem of the phase diagrams obtained by such calculations is that these are obtained by thermodynamic consideration alone. Any idea how fast or how slow phase transformations are completed is missing in the phase diagram. In many cases, occurrence of phase transformations depends on the process in which the experiment has been performed. This complicates direct comparison of the prediction and experiment. Practical problems regarding this phase diagram are discussed in Ref. [27].

In spite of the complications of the real situation, the authors think that heavily B-doped diamond (above 10 at.\%) could be obtained by HPHT method, if the experimental conditions are chosen wisely. In particular, the starting materials including the crucible material are important. Recently, a diamond-structure compound \( \text{BC}_5 \) was synthesized by Solozhenko [113]. This compound is predicted to have \( T_c \) above 40 K [74]. This compound should not be stable, based on our preliminary calculation. However, Solozhenko’s result shows that even such an unstable compound could be synthesized at high pressure and high temperature with using appropriate starting materials.

5. Conclusion
We have reviewed a recent development of superconductivity research on boron solids. Throughout this paper, the authors tried to discuss the situation of boron in connection with
other related materials, such as B-doped diamond and clathrates, in order to make discussion
general as possible.

Crystal of $\alpha$-boron is ideal for superconductivity research in many respects: structural
simplicity, stability over a wide range of pressure, relatively defect-free structure and
controllability of the valence electrons. Hence, the discovery of superconductivity in $\alpha$-boron is
significant.

Although superconducting transition has been discovered with relatively low $T_c$ in both $\alpha$-
and $\beta$-boron, our investigation shows that its potential for high-$T_c$ has not been fully disclosed
yet. There is still potential to raise $T_c$, if we control appropriately the valence electrons. Heavy
doping or use of compound as the alternation could improve $T_c$ significantly. Although the
doping idea itself can be easily found in the literature, the present idea is based on our deep
understanding of the electronic structure of boron. The basic feature of solid boron is that
the covalent character is so strong that it survives even after metallic transition, which makes
$N(E_F)$ rather small around the superconducting transition pressure.

A practical problem for doping is how to synthesize such heavily doped boron or another
compound. A promising method is high-pressure synthesis, which has been proven to be useful
for doped clathrates. By using this method, we have showed in calculation that heavy doping of
Li to $\alpha$-boron can be achieved. For B-doped diamond case, further application of high pressure
could increase the B concentration, which results in higher $T_c$.

In both cases of boron and diamond, accurate construction of phase diagrams is very
important, which was partly achieved in our study. This is also true for a new compound
$\text{BC}_5$, because this compound can be obtained only when special starting materials are chosen.

Added note After submitting this paper, another interesting paper was published concerning a
high-pressure phase of boron. Solozhenko’s group found a new phase of boron at high pressure
[114]. It seems to us that this ”new” phase is the same as the orthorhombic phase which has
recently re-discovered by Dubrovinsky’s group [46]. This phase was originally discovered by
Wentorf in 1965 [34]. However, at that time, he showed only the diffraction pattern and the
structure was left as undetermined.

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