Metallization of $\alpha$-boron by hydrogen doping

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Abstract. A theoretical assessment of doping $\alpha$-boron with hydrogen is presented aiming at high $T_c$ superconductor. Dissimilar to other impurities, hydrogen is unique because $T$ site is the most stable site. This position is well suited to the three-center bond. The bottom of conduction band has a large component at this center. Insertion of H atom increases the bonding character of this band through the three-center bond, which is otherwise a weak bond. Enhancement of bonding character of the three-center bond merges the bottom conduction and the top valence bands, yielding a relatively large density of states (DOS) at the Fermi level. This large DOS suggests that H doped $\alpha$-boron is a promising high $T_c$ material. When the gaseous state $H_2$ is used as the starting material, the formation energy is above 2 eV at the normal condition, so that heavy doping is not easy. High-pressure process can avoid this difficulty. It is predicted that hydrogen is incorporated easily at $p > 18$ GPa. A thermodynamic investigation has been made for high-pressure doping method when gases are used as the starting materials.

1. Introduction
This paper presents a theoretical assessment of doping $\alpha$-boron aiming at superconductivity. Boron is a promising high-$T_c$ superconductor because of strong electron-phonon coupling. As boron is however a semiconductor, it cannot exhibit superconductivity at normal conditions. Carrier doping to concentration as high as in metals is necessary, which is practically the most important and difficult problem. In a series of our studies, we have examined a variety of dopants [1, 2]. Among them, Li is the best candidate in terms of small formation energy $\Delta H_f$ and desirable band shift $^1$. The fact that Li is the most efficient dopant was found more than ten years ago by Gunji and Kamimura [3]. However the formation energy (0.5 eV) of Li is not small enough to achieve heavy doping.

In order to solve this difficulty, we found that high pressure synthesis is an efficient doping method [1, 4]. Indeed, high pressure process is useful in many other cases, such as B-doped diamond [5]. For heavily B-doped diamond, the reason to use high-pressure seems different [6], but actually we found that the same principle of decreasing $\Delta H_f$ under pressure is appropriate [7, 8]. The basic principle is simple:

Soft materials can be easily dissolved in stiffer materials under high pressure.

(P.1)

$^1$ In this paper, we take a convention that the positive formation energy means difficult doping.
This is a part of a well-known principle of thermodynamics, Le Chatelier’s principle. Actually, this principle was used to realize a heavily doped clathrate Ba₈Si₄₆ [9].

In the present paper, we have examined suitability of hydrogen to dope α-boron. In a previous study [2], we have seen that the formation energy $\Delta H_f$ of hydrogen is not small, 3.1 eV. But, this value was obtained assuming solid hydrogen as the reference state. Hydrogen is, of course, in the gas state at ambient conditions, and thus the $\Delta H_f$ in experiment could be largely different from this value. By considering the above principle, a good reason for using H is that the gas state of hydrogen is very soft, so that doping by hydrogen must be easier at high pressure.

Aside from ease of doping, there is another reason for examining H. Solid H itself has long been thought a candidate for high $T_c$ superconductor [10]. This idea has not been proven yet. However, sometimes hydrogen helps non-superconducting metals to exhibit superconductivity, such as PdHₓ [11]. In this case, the role of hydrogen is not as simple as doping. Recently, researchers came to think about more affirmative effect of hydrogen in hydrogenated molecular crystals. In fact, superconductivity has been found in molecular crystals such as SiHₓ [12]. In this case, silane crystal is considered as a high-density hydrogen solid. Similar effect may be expected for hydroboranes. Structural change in decaborane (B₁₀H₁₄) is reported under high pressure [13]. The research in this direction has been continuing.

With these reasons, studying H doping is far from a simple extension of previous doping studies. The formation energy is re-examined in a more systematic way. Various impurity configurations are investigated. More importantly, the doping efficiency at finite temperature and finite pressure has been estimated from thermodynamic considerations. Characterization of the electronic structure is a part of the present study from the above interests in a special role of hydrogen.

2. Method
In this study, first-principles pseudopotential method with local density approximation (LDA) based on density functional theory is used for the total-energy calculation. The used code is ‘Osaka2002’ [14]. Troullier-Martins’ pseudopotentials [15] are used, with aid of a fully separable Kleinman-Bylander form [16].

A Monkhorst-Pack $k$ mesh (2×2×2) is used in both 12-atom (a primitive cell of α-boron) and 36-atom (hexagonal cell) cells [17]. The cutoff energy for the plane-wave basis is 60 Ry. With this cutoff energy, the accuracy for the total energy is within 1 meV/atom.

For calculations of DOS and band structure, a program package 'TSPACE' developed by A. Yanase was used [18]. By virtue of TSPACE, all the symmetry properties of wavefunctions are clarified, and accordingly, accurate band dispersions and its connectivity at zone boundaries can be established. This is important for interpreting the bonding characters. An improved algorithm of calculating Fermi surface enables us to know accurate Fermi surface [19].

Structural parameters were optimized for both cell parameters and atomic positions. We achieved self-consistency with the residual stress less than 1 GPa. The residual forces were $5.0 \times 10^{-3}$ Ry/Bohr. With this condition, convergence of the formation energy was below 0.15 eV/cell.

In order to compare the formation energies between different concentrations, the formation energy $\Delta E_f$ is evaluated by a difference per impurity atom $X$, as

$$\Delta E_f = \frac{1}{n} \left[ E(X_nB_m) - (nE(X) + mE(B)) \right].$$  \(1\)

Readers may suspect that the doped α-boron crystals described in this paper are actually compounds with specific stoichiometry. This is true, but, we continue to treat these compounds as impurity systems, in connection to heavily doped semiconductors. Such treatment is common for doped fullerides (e.g. K₃C₆₀) and clathrates (e.g. Ba₈Si₄₆). In equation (1), the most
Figure 1. Crystal structure and impurity sites of α-boron. Important atom labels are indicated by numbers. The icosahedron B\textsubscript{12} has two Wyckoff positions at polar (p) and equatorial (e) sites. Impurity sites are indicated by blue sphere (O site) and red sphere (T site).

stable phase of X is assumed as the reference state. For hydrogen, a proposed model of an orthorhombic structure (space group, Pca\textsubscript{2}1) was used in our previous paper [2]. However, hydrogen is normally in a gas state H\textsubscript{2}. Hence, in the present paper, we use H\textsubscript{2} molecule as the reference state. In this case, we use an experimental value for the binding energy of 0.3483 Ry. Then the total energy of H\textsubscript{2} molecule becomes

\[ \frac{1}{2} [-2 \text{ (Ry)} - 0.3483 \text{ (Ry)}] = -15.975 \text{ (eV/atom)}. \]  (2)

The cohesive energy of H\textsubscript{2} to solid is estimated as 0.011 eV/atom from the facts that the enthalpy of fusion is 117 J/mol (at T=13.96 K and p=0.711 atm) and the enthalpy of vaporization is 904 J/mol (at T=20.39 K and p=1 atm) [20]. This value is very small in the present energy scale, and accordingly either state at low temperatures, the gas state or the solid state, can be used as the reference state within the present accuracy.

Under finite pressure p, enthalpy H plays a central role in an energetic consideration. The formation enthalpy \( \Delta H_f \) of the impurity X is obtained by adding pV to \( \Delta E_f \), where V is the crystal volume. The volume V is determined as a function of p by the structural optimization. At finite temperature, we will use the chemical potential, as described in Sec 3.4.

In our previous study on doping of various impurities [1, 2], it was found that in most cases, impurity atoms enter at the center of the rhombohedron, i.e., O site, which is the most spacious cite. An exception is hydrogen, for which we make further study here. The atomic configuration for H impurity is modeled by supercells of the primitive unit cell of α-boron (B\textsubscript{12}) and a conventional hexagonal unit cell (B\textsubscript{36}). The impurity sites to be investigated are O and
Table 1. Formation energy $\Delta E_f$, change in the lattice parameters, and bond length around H atom (NN and 2NN show the nearest neighbor and second neighbor, respectively) of several configurations of H impurity. Changes in the lattice parameter $\Delta a_0$, the rhombohedral angle $\Delta \alpha_{rh}$ and the cell volume $\Delta V$ are indicated by the relative change to those of non-doped $\alpha$-boron. Note that all listed bond lengths NN and 2NN are the bonds between H and B atom. In the columns of bond length, entry of $2.07 \times 6$ should be read as there are six equivalent bonds whose bond length is 2.07 Å.

| Config. | $\Delta E_f$ (eV/(H atom)) | $\Delta a_0$ (%) | $\Delta \alpha_{rh}$ (%) | NN (Å) | 2NN (Å) |
|---------|-----------------|-----------------|-----------------|-------|--------|
| HB$_{12}$ (O) | +3.40 | 0.10 | -0.15 | 2.07×6 | 2.57×12 |
| HB$_{12}$ (T) | +3.07 | 0.82 | -0.39 | 1.8 | 1.67×3 | 1.89×3 |
| H$_2$B$_{12}$ (T×2) | +2.39 | 1.53 | -1.57 | 2.1 | 1.70×3 | 1.84×3 |
| H$_3$B$_{12}$ (T×2 + O) | +2.77 | 2.76 | -2.4 | 4.4 | 1.76×3 | 1.83×3 |
| HB$_{36}$ (O) | +3.57 | 0.20 | -1.1 | -1.1 | 2.08×6 | 2.55×12 |
| HB$_{36}$ (T) | +3.43 | 0.69 | -0.84 | 0.72 | 1.77×3 | 1.84×3 |
| H$_2$B$_{36}$ (T×2) | +2.65 | 1.43 | -2.17 | 0.81 | 1.77×3 | 1.84×3 |
| H$_3$B$_{36}$ (T×2 + O) | +2.74 | 1.05 | -1.38 | 0.94 | 1.82×3 | 1.84×3 |

3. Results and discussion

3.1. Impurity site

The obtained hydrogen formation energies are listed in table 1. All energies are positive, so that heavy doping is impossible. However, when comparing $\Delta E_f$ between different supercells, we see a definite tendency. For the T or O site, $\Delta E_f$ decreases when the smaller supercell is used. This says that the higher the concentration, the smaller the formation energy. Only in the case of a triatomic chain, the formation energy is similar in the supercell and in the primitive cell. Furthermore, when comparing T and T×2, we see that association of two H atoms in the primitive unit cell is energetically favorable. The binding energy $E_b(H_2)$ defined by

$$E_b(H_2) = -2 [\Delta E_f(H_2B_{12}) - \Delta E_f(HB_{12})],$$

becomes +1.36 eV.

The smallest formation energy occurs for configuration H$_2$B$_{12}$ (T×2), for which the original crystal symmetry does not change. Henceforth, the main part of our discussion is focused on this configuration T×2. In this configuration, the hydrogen at T site has a six-fold coordination, unlike suggested by the name ”tetrahedral site”. The bond length of H-B$_{(e)}$ is 1.70 Å and that of H-B$_{(r)}$ is 1.84 Å. Here, the subscript indicates the Wyckoff positions of boron, as shown in figure 1. Both are substantially longer than typical lengths of hydroborate molecules, for example, in B$_2$H$_6$ molecule 1.192 for the terminal B-H and 1.329 Å for three-center B-H bond [21]. In this sense, the H seems not to form covalent bond to B atoms in $\alpha$-boron. Nevertheless, it participates in the host B-B bonds which has important contribution to metallization, as shown in the next section.

3.2. Charge density

The bonding nature of hydrogen can be understood by seeing the charge density distribution. The charge density of H$_2$B$_{12}$ configuration is plotted in figures 2 to 4.
Figure 2. Charge density of $\text{H}_2\text{B}_{12}$. The cut plane is one of mirror planes of the rhombohedral system, which is shown on the right side. The blue line indicates the boundary of the primitive unit cell. The charge density is plotted from 0 to 0.2 el/Bohr$^3$ with steps of 0.01 el/Bohr$^3$. A part of three center bond is indicated 3c and the intericosahedral bond is indicated by 2c. Important atom sites are indicated according to the scheme in figure 1. One H atom is located at 13, and another one at another symmetry-equivalent site.

Figure 2 shows the charge distribution on a mirror plane of the rhombohedral lattice. The peak of charge density at H site is 0.21 el/Bohr$^3$, which is almost the same as that of the intericosahedral B-B bond. In this sense, H seems isolated from other B atoms. However, one can see that the H atom has weak bonding to an adjacent icosahedron (13−1−7) in the $ab$ plane. On the other hand, there is no bonding to the neighboring icosahedron along the $c$ axis (atom 4), which would be expected for the truly tetrahedral coordination.

In order to see this in-plane character more closely, we show the charge distribution in an ab plane, as shown in figure 3. Note that the cut plane is a plane formed by three equatorial B atoms, and that the H atom is slightly off the plane. For this reason, the maximum charge density in this figure is not the maximum of three-center bond. At the center of a triangle formed by three equatorial B atoms, a peak of charge density is located, which is the characteristic of three-center bond. Hence, the insertion of H atoms in this way enhances the three-center bond.

Around a hydrogen atom, six bonds are formed. This is shown by the charge distribution around the H atom in figure 4. One can see that around the H atom, there are three vertical
Figure 3. Charge density of H$_2$B$_{12}$. The cut plane is shown on the right side, which is an $ab$ plane containing the equatorial sites of icosahedra. The green line indicates the boundary of the hexagonal system. The blue line indicates the boundary of the primitive unit cell. The charge density is plotted from 0 to 0.2 el/Bohr$^3$ with steps of 0.01 el/Bohr$^3$. Hydrogen atom is located at the center of a blue triangle, but is slightly off the plane.

Figure 4. Contour map of the charge density around a hydrogen atom in H$_2$B$_{12}$. Shown is the contour map on the sphere surface around the H(13) atom with a radius 0.8 Å. The spherical coordinates ($0 < \theta < 2\pi$, $-\pi/2 < \phi < \pi/2$) are mapped on a circle. Charge density is plotted from 0.026 to 0.073 el/Bohr$^3$. The upper hemisphere faces three equatorial B atoms, while the lower one faces three polar B atoms.
lines of maximum charge density. These lines are formed by a connection from an equatorial atom 7 to a polar atom 1. In addition, in the upper hemisphere, the charge density is higher than in the lower part. This is a consequence of the fact that the bond length of H to the equatorial B atom H-B\(_{(e)}\) is shorter than that of H-B\(_{(r)}\).

### 3.3. Electronic structure

Density of states of H\(_2\)B\(_{12}\) is calculated and compared with undoped system, as shown in figure 5. In the figure, we see that the whole gap is filled by electrons upon H doping, leading to metallic character. The part of the valence band is not significantly changed. The density of states at Fermi level \(N(E_F) = 0.10 \text{ state/(eV·atom)}\). This value is comparable to that of hypothetic metallic fcc phase of boron (see table 1 of Ref. [8]), which is expected to have a moderate value of \(T_c\) [22].

Band diagram helps us to understand which band contributes to the metallization. Figure 6 shows a band diagram of doped and undoped \(\alpha\)-boron. For labeling of the \(k\)-points and symmetry lines, we refer to Ref. [23]. As shown in the figure, lowering of the conduction bottom band is significant toward \(F\) point, where the point group of wavevector \(k\) is \(C_{2h}\). On the other hand, the change in the valence band is not substantial, as in DOS.

![Band diagram](image)

**Figure 5.** Density of states of H\(_2\)B\(_{12}\) (red line) and pure \(\alpha\)-B (B\(_{12}\)) (black line). Occupied states are indicated by a filled region for H\(_2\)B\(_{12}\).

The symmetry properties of wavefunctions are very important for interpreting the bonding characters and are given in another paper [24]. Here, only a qualitative description is summarized in table 2.

The conduction bottom band has a component of the inter-icosahedral three-center bond. Therefore, on doping, the three-center bond is enhanced, which results in contraction of the bond length of three-center bond. This makes the rhombohedral lattice more elongated along the \(c\) axis. This change is clearly seen in the apex angle of the rhombohedral lattice \(\Delta\alpha_{rh}\) listed in table 1. In a previous paper [2], we showed that decrease in \(\alpha_{rh}\) on doping is a common property when inserting various elements apart from carbon. The basic reason of the decrease in \(\alpha_{rh}\) is this character of the conduction-bottom band: three-center bonding character.
**Figure 6.** Energy band structures of $\text{H}_2\text{B}_{12}$ (red line) and $\text{B}_{12}$ (black line) near the Fermi energy. The symmetry of wavefunctions are indicated for the valence top (V.T.) and the conduction bottom (C.B.) bands of undoped $\alpha$-boron.

**Table 2.** Bonding characters of the valence top (V.T.) and conduction bottom (C.B.) bands: (B) bonding, (AB) antibonding, (N) non-bonding. The *intraicosahedral* bonding is further decomposed to three types of bonds:

| component symmetry of $\mathbf{k}$ | V.T. | C.B. |
|-----------------------------------|------|------|
| intra- $p - p$                    |      |      |
| intra- $p - e$                    | AB   | B    |
| intra- $e - e$                    | B    | AB   |
| three-center                     | N    | B    |
Another effect of filling the conduction-bottom band is elongation of icosahedron along the c axis. This is because the conduction bottom band has anti-bonding character as to the intraicosahedral $p - e$ bond, as shown in table 2. This change will be described in more details in our forthcoming paper [4].

3.4. High pressure doping

We have shown that $\Delta E_f$ of hydrogen is not small, when the gas state of H$_2$ at low temperature is used as a starting material. Now, most experiments are performed at room temperature. At finite temperature, $E(H)$ in equation (1) should be replaced by the chemical potential $\mu$; actually a half of $\mu(H_2)$. Other parts of equation (1) have no significant pressure dependence, so that we keep them constant. Then, we are required to evaluate the chemical potential to the normal state $T = 300$ K and $p = 1$ atm. As to the reference state of hydrogen, whether the state is at $T = 0$ or 20.39 K, or at $p = 0$ or 1 atm makes no difference in our energy scale.

![Figure 7. The chemical potential of H$_2$ as a function of T at the normal pressure.](image)

Liquid hydrogen vaporizes at $T_b = 20.39$ K. Above $T_b$, we describe the gas state of H$_2$ by Van der Waals (VdW) equation of state as

$$p = \frac{RT}{v - b} - \frac{a}{v^2}. \quad (4)$$

Validity of the VdW equation is not so wide to cover the present range of pressures [25]. But, at any rate, this form of equation of state is the most available form in the literature. In order to calculate the chemical potential $\mu$, we are required to calculate the internal energy $u$ of gas. A simple form of $u$ compatible with VdW is as follows [26],

$$u = cRT - \frac{a}{v}, \quad (5)$$

where $c=5/2$ for diatomic molecule. Then, the chemical potential $\mu$ is obtained by,

$$\mu = u + pv - RT \ln \left( (v - b) \left( u + \frac{a}{v} \right)^\frac{c}{v} \right), \quad (6)$$

with a constant term.

For numeric estimation, $a = 0.0248$ Pa/m$^6$ and $b = 26.6 \times 10^{-6}$ m$^3$ are used for H$_2$ [26]. As seen before, the cohesive energy of hydrogen solid compared with a free H$_2$ molecule is small.
enough. Thus we can take the energy given by equation (2) as the energy of a free \( \text{H}_2 \) molecule at \( T = 20.39 \) K and \( p = 1 \) atm. Then, variation of \( \mu \) of \( \text{H}_2 \) gas is calculated as a function of \( T \) at \( p = 1 \) atm. The result is shown in figure 7. The chemical potential decreases as \( T \) increases because of the entropy term. The difference in \( \mu \) between \( T = 20 \) and 300 K is \(-0.037 \) eV. Therefore, at the normal condition, the formation enthalpy of hydrogen is

\[
\Delta H_f = \Delta E_f - \frac{1}{2} \Delta \mu(\text{H}_2) = 2.39 + 0.037/2 = 2.41 \text{ eV}, \tag{7}
\]

where \( \Delta E_f \) is the formation energy listed in table 1 and \( \Delta \mu(\text{H}_2) \) is change in the chemical potential of \( \text{H}_2 \) gas from the melting point to room temperature. This says that when the \( \text{H}_2 \) gas state at the standard condition is referred to, \( \Delta H_f \) is slightly increased, because the gas state is the most stable state at the standard condition. Doping hydrogen from \( \text{H}_2 \) gas is again difficult.

In order to overcome the positive \( \Delta H_f \), we try to apply high pressure. The basic idea of applying pressure is increase in the energy of soft impurity as stated in the principle (P.1). However, quantitative description becomes complicated for gaseous states. The calculation of the pressure dependence of \( \Delta \mu \) has no difficulty. Now that we are treating a gas state, remember that the work is not a thermodynamic property. The result highly depends on the process in which the high pressure is achieved. In the following, we will describe two cases of compression separately, fixing temperature at \( T = 300 \) K.

**Figure 8.** Formation enthalpy of hydrogen in \( \alpha \)-boron as a function of \( p \) at a fixed \( T = 300 \) K. \( \text{H}_2\text{B}_{12} \) is used as the structural model for H-doped \( \alpha \)-boron. For isothermal compression, ideal gas (dashed and blue line) and VdW gas (red line) models are compared. For adiabatic compression, a calculation of ideal gas is shown by the blue line.

**Isothermal compression**   First, let us consider an ideal gas. In isothermal compression, enthalpy \( u + pv \) does not change for ideal gases. Even though a work was done to compress a gas, the work dissipates to the surroundings leaving no effect on the gas. Only the entropy term \(-TS\) has pressure dependence. As shown by the dashed blue line in figure 8, the entropy term \(-TS\) has a slight decrease in the formation enthalpy, because on applying pressure, the gas state becomes more dense, which decreases the entropy \( S \).

Next, consider a non-ideal gas. When \( \text{H}_2 \) gas is described by the VdW model, the formation enthalpy is changed to the red line in figure 8. The situation is almost the same as the ideal
gas case until \( p = 10^4 \) atm (1 GPa). Significant change appears at \( p > 10^4 \) atm. The primary contribution comes from the first term of equation (4). At \( p > 10^4 \) atm, the specific volume \( v \) becomes comparable to the limiting volume \( b \). The sign of the formation enthalpy is changed at \( p = 18 \) GPa. Quantitatively, this value is not so accurate, because the validity of VdW description is limited in a wide range of pressure [25]. However, qualitative conclusion seems reasonable by considering the experimental observations. In fact, inclusion of gaseous atoms, such as He, are commonly observed in the specimen at high pressures, when the gas is used as a pressure-transmitted medium.

**Adiabatic compression**  The fact that compressing a gas does not decrease \( \Delta H_f \) until very high pressure \( p > 10^4 \) atm, could be changed using adiabatic compression. In this case, the work \( W \) which is done by applying pressure is completely transformed to the internal energy of gas, leaving the entropy term unchanged. For ideal gases, the work \( W \) can be calculated analytically as

\[
W = c \left( p_2 v_2 - p_1 v_1 \right),
\]

where the subscripts 1 and 2 indicate the initial and final states, respectively. As shown in figure 8, the effect of using adiabatic compression is not significant. At relatively low pressure, isothermal compression is even slightly better than adiabatic compression because of the entropy term.

In either case, the effect of compression appears only when the pressure exceeds 10 GPa, where the density almost equals that of liquid. Although this is very high pressure, development of high-pressure techniques enables us to reach it easier than before. We see a successful example in doped clathrates. Yamanaka *et al* demonstrated the effectiveness of using high-pressure process for synthesis of \( \text{Ba}_8\text{Si}_{46} \) [9].

**4. Summary**

The potential of hydrogen doping into \( \alpha \)-boron for metallization has been theoretically examined. The role of H is dissimilar to Li case, for which the effect of doping is just filling a lowest part of the conduction band. The case of hydrogen is special. It enters \( \alpha \)-boron at \( T \) site, where the H has six-fold coordination, and enhances the bonding character of the conduction bottom band through the weak three-center bond. This closes the energy gap yielding the metallic character.

A significant modification of the conduction bottom yields a favorable consequence on the superconductivity. The density of states at Fermi level is relatively large, suggesting a promising candidate for high \( T_c \).

When the gas state \( \text{H}_2 \) is used as the starting material, the formation energy is above 2 eV at the normal condition, so that heavy doping is difficult. High-pressure process is useful for efficient doping. However, application of the Le Chatelier’s principle (P.1) should not be literally taken for high-pressure doping method. Even though gas states are very compressible, isothermal compression has no effect for ideal gases. In either adiabatic compression for any gas or isothermal compression for non-ideal gases, the effect is very small at low pressure. Only at very high pressure \( p > 18 \) GPa, where the density of gas is comparable to that of liquid, the effect is appreciable. The cutting-edge techniques of high pressure research enable us to utilize high pressure experiment for material processing purpose.

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References
[1] Dekura H, Shirai K and Katayama-Yoshida H 2007 J. Phys.: Condens. Matter 19 365241
[2] Dekura H, Shirai K and Katayama-Yoshida H 2007 Physica B 401-402 702
[3] Gunji S and Kamimura H 1995 Phys. Rev. B 54 13665
[4] Dekura H, Shirai K and Katayama-Yoshida H Metallization of $\alpha$-boron by efficient impurity doping in preparation
[5] Ekimov E A, Sidorov V A, Bauer E D, Mel’nik N, Curro N J, Thompson J D and Stishov S M 2004 Nature 428 542
[6] Dubrovinskaia N, Dubrovinsky L, Miyajima N, Langenhorst F, Crichton W A and Braun H F 2006 Z. Naturforsch 61b 1561
[7] Shirai K, Dekura H and Yanase A 2009 Phys. Status Solidi B 246 673
[8] Shirai K, Dekura H and Masago A 2008 16th Int. Symp. Boron, Borides and Related Materials (Matsue, Japan) in this volume
[9] Yamanaka S, Enishi E, Fukuoka H and Yasukawa M 2000 Inorg. Chem. 39 56
[10] Ashcroft N W 1968 Phys. Rev. Lett. 21 1748
[11] Skoskiewics T 1972 Phys. Status Solidi A 11 k123
[12] Eremets M I, Trojan I A, Medvedev S A, Tse J S and Yao Y 2008 Science 319 1506
[13] Nakano S, Hemley R J, Gregoryanz E A, Goncharov A F and Mao H K 2002 J. Phys.: Condens. Matter 14 10453
[14] http://www.cmp.sanken.osaka-u.ac.jp/~koun/osaka.html
[15] Troullier N and Martins L 1991 Phys. Rev. B 43 1993
[16] Kleinman L and Bylander M 1982 Phys. Rev. Lett. 48 1425
[17] Monkhorst H J and Pack J D 1976 Phys. Rev. B 13 5188
[18] http://www.cmp.sanken.osaka-u.ac.jp/~yanase/
[19] Dekura H, Shirai K and Yanase A J. Comput. Theor. Nanosci. In press
[20] of Japan C S (ed) 2004 Handbook of Chemistry, 5th ed. (Tokyo: Maruzen) in Japanese
[21] Greenwood N N 1973 Comprehensive Inorganic Chemistry ed Bailar J C, Emeléus H J, Nyholm S R and Trotman-Dickenson A F (Oxford: Pergamon) chap 11
[22] Papaconstantopoulos D A and Mehl M J 2002 Phys. Rev. B 65 172510
[23] Yanase A 1995 Fortran Program for Space Group (TSPACE) (Tokyo: Shokabo) in Japanese
[24] Shirai K, Dekura H and Yanase A Electronic structure and electrical resistivity of $\alpha$-boron under high pressure submitted to J. Phys. Soc. Jpn.
[25] Cengel Y A and Boles M A 2002 Thermodynamics - an engineering approach, 4th ed. (New York: McGraw Hill)
[26] Callen H B 1985 Thermodynamics and an Introduction to Thermostatistics 2nd ed (New York: John Wiley and Sons)