Valence control of α-rhombohedral boron by electronic doping

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Abstract

It was previously predicted that doping Li into semiconducting boron (α-rhombohedral) brought metallic character to the matrix and possibility a high-T_c superconductor. However, experiments show that Li doping of α-rhombohedral boron is difficult. In this paper, the potential for Li doping of boron is re-examined using the *ab initio* pseudopotential method. Based on the calculated formation enthalpy, an efficient method for doping is proposed. The method utilizes high pressure, such as 10 GPa. Slight changes in the structural parameters for Li insertion are also resolved, which may be useful for the experimental detection of Li in boron. The stability of α-rhombohedral boron at high pressures is also compared to that of Ga-type structure, which has been put forth as a candidate for the high-pressure phase. The present study gives further confirmation of the stability of α-rhombohedral boron at least up to 70 GPa.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Solid boron is a semiconductor under normal conditions. There are several polymorphic modifications, even at zero pressure. Among them, α- and β-rhombohedral boron are well known phases. Recently, a superconducting transition has been found at a pressure of about 160 GPa for the β phase [1], which is accordingly stimulating researchers' interest in this material. Effort to dope this β phase has been continuing, in the hope that the transition pressure can be decreased by doping with appropriate impurities [2].

Although it is worth working further on β boron, there is yet another choice, namely the examination of α boron. Although superconductivity has so far not been found for α boron, this choice has a benefit in that the crystal structure is relatively simple, so that the analysis is much simpler than that of β phase. This simplicity is an important feature, because in many cases the electronic band-gap structure is very sensitive to native defects. In β boron, it is known experimentally that the crystal structure possesses intrinsically some kinds of defect,

which render doping of β boron difficult. The intrinsic defect for β boron has recently been demonstrated through a theoretical study [3]. Therefore, it seems better to examine the control of valence for boron in the α phase.

The idea of doping α boron is not new, but has already been proposed by Gunji and Kamimura [4] years ago and subsequently by Hayami *et al* [5, 6]. Even though the prediction of the superconducting transition is still difficult for boron [7], there is hope of obtaining a high superconducting transition temperature for the light element boron. In the papers [4–6], various dopant atoms were examined. Among those dopant atoms examined, Li is the best-studied impurity. The previous studies [4, 5] gave a commonly positive formation energy for Li doping, which suggests that Li doping is easy. However, experimentally, Li doping has been unsuccessful up to now [8]. There must be something difficult other than the formation energy. In real situations, it is often the case that the reactions are controlled by the activation energy rather than by the formation energy. The reaction is too big a problem to be covered in this study; another study is required from a different field. In this paper, we concentrate on investigating Li doping from the standpoint of the formation energy. More importantly, this approach can lead us to find a better way of doping. The proposed method utilizes high pressure. Use of high pressure is also an interesting method for the synthesis of α boron itself with a high quality [9].

When high pressure is utilized, the stability of the structure is one of the major concerns. In a previous paper, the relative stability of α boron compared to β boron was shown [3]. This stability is enhanced at high pressures. Hence, it seems no problem to expose α boron to high pressure, as far as comparison is made with β boron. Recently, α-Ga-type structure has been proposed as a candidate for the high-pressure phase [7, 10]. These authors show that α-Ga structure becomes more stable than the α-rhombohedral phase above 74 GPa. Therefore, we examine this structure in order to check whether the stability of the α-Ga-type structure replaces α-rhombohedral boron at high pressures and, accordingly, whether it spoils our doping effort. Hereafter, α-rhombohedral boron is called simply α boron (or α-rh in order to avoid ambiguity), while α-Ga-type boron is called simply Ga-type boron.

2. Calculation method

Density-functional theory calculations were performed on the total energy. The code that was used is 'Osaka2002', which was developed by the present authors [11]. Troullier-Martins' pseudopotentials [12] are used, with the aid of a full separable Kleinman–Bylander form [13]. The plane-wave basis is used for expanding the wavefunction. In most of the calculations, use is made of the local-density approximation (LDA) with a Ceperly–Alder form parameterized by Perdew and Zunger [14]. For the Ga-type structure, the generalized gradient approximation (GGA) is also examined, in which the formulae of PBE96 is used [15].

The Monkhorst–Pack scheme was employed for k-point sampling: a $2 \times 2 \times 2$ mesh for α-rh boron and a $4 \times 4 \times 4$ mesh for bulk Li. The energy convergence was examined versus the cutoff energy E_{cut} in the plane-wave expansion. The absolute total energy E_{tot} was converged within 0.01 Ryd/atom when $E_{\text{cut}} = 30$ Ryd. The convergence for the energy difference between doped and non-doped boron already reaches 1 mRyd/atom at this cutoff energy. We used this cutoff energy for the investigation of Li doping of α-rh boron. For bulk Li, the occupancy of the Kohn–Sham levels was treated as being free in the self-consistent field (SCF) calculation. In this scheme, the total energy of bulk Li was converged at $E_{\text{cut}} = 40$ Ryd.

When comparison is made for the stability between α-rh and Ga-type boron, E_{cut} was increased to a sufficiently high energy, i.e. 65 Ryd. As shown in figure 1, the convergence of E_{tot} for both phases reaches 0.1 mRyd at this cutoff energy, and the energy difference between
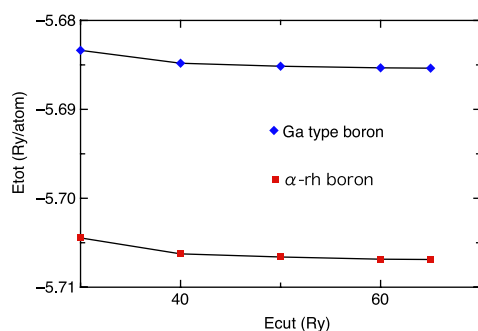
Figure 1. Energy convergence for E_{tot} of α-rh and Ga-type boron against E_{cut}.

the two phases was less than 0.01 mRyd. This accuracy may be enough for comparison at $p = 0$ GPa. At high pressures, because the demand for E_{cut} becomes more severe, we keep this high E_{cut}. Actually, the cutoff value was adjusted slightly around this value in order to keep the same basis set.

When comparing different structures, care should be taken with the k sampling method. For Ga-type boron, the number of atoms per cell is only one third of that for α boron, so a finer mesh should be used. The influence of the k mesh for Ga-type was investigated. Since the energy difference between $4 \times 4 \times 4$ and $12 \times 12 \times 12$ meshes was insignificant, i.e. 2 mRyd/atom, we still use $4 \times 4 \times 4$ mesh for Ga-type boron. However, we shall keep this accuracy in mind in the following discussion.

The atom positions and cell parameters are fully optimized by Helmann–Feynman forces and stresses [16]. All these parameters are treated as being free, although crystal symmetry is kept throughout the optimization process. For calculations of the density of state and the band structure, the program package 'TSPACE', which was developed by A Yanase, is used.

3. Results and discussion

3.1. Li doping of α-rhombohedral boron

The crystal structure of α-rh boron is the simplest among the various crystallographic modifications of boron. An icosahedron B_{12} is located at the vertex of the rhombohedral unit cell. The icosahedral units are stacked in the cubic-like close-packed sequence, connected by two-centre (covalent) bonds between adjacent layers. Within a plane, icosahedral units are connected by three-centre bonds. Li is inserted at the O-site, i.e. the centre of the main diagonal of the rhombohedral unit. The original symmetry of pure α-boron does not change on this insertion.

The structural parameters of non-doped α-boron after optimization are listed in table 1, while those of Li-doped α-boron are listed in table 2, along with other calculations and experiments, if available. The calculation method of [4] is a pseudopotential Gaussian basis calculation with LDA, and the method of [6] is the same as ours with GGA.

As to the lattice parameters, we see good agreement between different calculations and experiments. In experiment, of course, only those for pure α boron are available. It is seen that the cell length a_0 is slightly increased on the insertion of Li, by 2% in our calculation. This magnitude is enough to resolve in the x-ray diffraction method. Conventional chemical analysis methods, such as EPMA, have a common difficulty in distinguishing light elements.

Table 1. Structural parameters of non-doped α-rh boron. Lattice parameters a_0, α, bulk modulus B_0, and atom density ρ are listed. The residual force Δf and the residual stress $\Delta \sigma$ are also listed in order to check the accuracy.

	a_0 (Å)	α (deg)	B_0 (GPa)	Δf (Ryd/Bohr)	$\Delta \sigma$ (Ryd/Bohr^3)	ρ (atom/Bohr^3)
Present	4.959	58.64	225.5	6.6×10^{-4}	2.2×10^{-6}	2.128×10^{-2}
Other works						
Expt. [17, 18]	5.057	58.06	200			2.035×10^{-2}
Calc. [4]	5.063		233	10^{-3}–10^{-1}		
Calc. [6]	5.04	58.10				2.053×10^{-2}

Table 2. Structural parameters of Li-doped (O-site) α-rh boron. The same captions in table 1 are applied here too.

	a_0 (Å)	α (deg)	B_0 (GPa)	Δf (Ryd/Bohr)	$\Delta \sigma$ (Ryd/Bohr^3)	ρ (atom/Bohr^3)
Present	5.060	57.66	221.25	3.2×10^{-3}	2.4×10^{-6}	2.222×10^{-2}
Other works						
Calc. [4]	5.077		417	10^{-3}–10^{-1}		
Calc. [6]	5.20	57.7				2.045×10^{-2}

Therefore, the change in the lattice parameter could provide a good means for the detection of Li in boron, assuming that Li is inserted at the O site.

It is noted that a_0 is slightly elongated, while the apex angle α becomes smaller, on the insertion of Li. The rhombohedral cell is accordingly stretched in the diagonal direction. This is in contrast to the situation for boron carbide $B_{12}C_3$, in which case the cell shrinks on insertion of the C chain. The roles of doping by Li and C seem to be different. Actually, for $B_{12}C_3$, the C atom attracts more electrons rather than giving electrons to the B_{12} unit [19].

The atom density in our calculation is increased by 4%, while that of [6] is decreased by -0.4%. In this case, the difference would come from the different exchange–correlation functionals. In any case, the difference is small. A big discrepancy is found in the bulk modulus when Li is doped, 221 GPa in our calculation and 417 GPa in [4], even though the change in atom density is only slight. By considering the large discrepancy in the bulk modulus, we have checked the internal consistency of calculation for the total energy and stress. The total energy E_{tot} and stress σ_{ij} for Li-doped α-boron are calculated as functions of the applied pressure p. In Osaka2002, for a given pressure, crystals can be optimized with respect to all the atom coordinates and all the cell parameters. The total energy and stress are plotted as functions of the volume V in figure 2. The volume derivative of total energy, $\partial E_{\text{tot}}/\partial V$, should give the diagonal average of the stress tensor, $\sum_i \sigma_{ii}/3$, under hydrostatic pressure. As shown in the figure, this relationship holds well. Accordingly, the bulk modulus deduced in this calculation is reliable.

The formation enthalpy ΔH_{f} of Li is calculated from

$$\Delta H_{\text{f}} = (H(\alpha\text{-B}) + H(\text{Li})) - H(\alpha\text{-B:Li}). \tag{1}$$

The sign convention is employed in order to keep consistency with other works [4, 6]. A positive sign for ΔH_{f} means that Li doping is energetically favoured. At finite pressure p, the enthalpy H is obtained by adding pV to the total energy E_{tot}, where E_{tot} and V are those values for the optimized structure.

At zero pressure, ΔH_{f} is -0.549 eV. Our result shows a slight negative value, which suggests that Li-doped α-boron is unstable. Previous studies have shown positive values
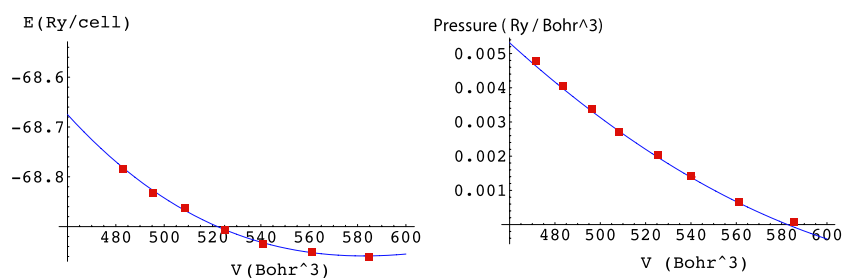
Figure 2. Volume dependence of the total energy E_{tot} (left) and stress σ (right) of Li-doped α boron. Actually, the stress in the right figure is the average of the diagonal components σ_{ii}. In the right, the obtained stress indicated by dots is compared to the volume derivative of the total energy $-dE_{tot}(V)/dV$ indicated by a solid curve.
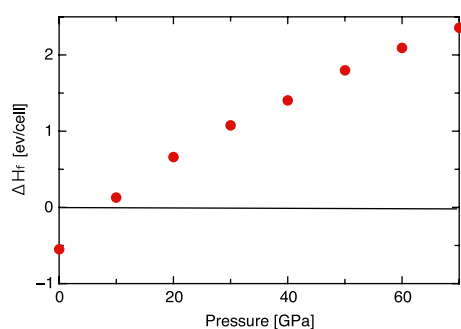

Figure 3. Formation energy of Li in α boron ΔH_f as a function of pressure.

(2.38 [4] and 0.17 eV [6]). The reason for the discrepancy is not clear. However, we can mention that, in our calculation, internal consistency between the total energy and stress was well established, and that the structural optimization was performed with greater accuracy than others, which are illustrated in tables 1 and 2. In any case, whether ΔH_f is positive or negative seems marginal for boron in LDA or GGA calculations. Instead of persisting with difference in this magnitude, we shall concentrate on seeking a condition for unambiguously increasing ΔH_f by some means.

We examined the pressure dependence of ΔH_f. The enthalpy ΔH_f is evaluated at each pressure, where all structures are fully optimized. The result is shown in figure 3. As seen in the figure, ΔH_f changes in sign above 10 GPa. Even though the curve might be shifted to some extent by calculation parameters as described above, ΔH_f becomes definitely positive at high pressures. This change is primarily brought about by the smallness of the bulk modulus of Li (14.8 GPa in our calculation and 11.6 GPa in experiment [20]); the change in Li contribution is dominant in the change in E_{tot} with respect to p. Based on this result, we propose a promising method for Li doping, namely utilizing a high pressure of more than 10 GPa. This value is no longer difficult regarding the present status of high-pressure techniques.

3.2. Ga-type boron

The hypothetical α-Ga-type structure has been proposed as a candidate for the high-pressure phase of boron. Experimental evidence for this structure has not yet be obtained. The α-Ga-
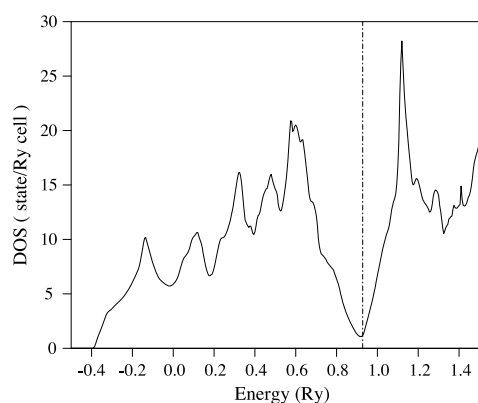
Figure 4. The density of state of Ga-type boron under zero pressure. The Fermi energy lies at 0.928 Ryd.

Table 3. The structural parameters of Ga-type boron at zero pressure; a, b, and c are lattice constants, x, y and z are the position of the B atom in relative coordinates. x is always zero. ρ is the atom density and B_0 is the bulk modulus.

	a (Å)	b (Å)	c (Å)	y	z	ρ (atom/Bohr^3)	B_0 (GPa)
Present	2.9079	5.2754	3.2247	0.1558	0.0888	2.396×10^{-2}	235
Other [7]	2.9131	5.2792	3.2356	0.1562	0.0898	2.382×10^{-2}	265

type structure has an orthorombic lattice, which contains four boron atoms. The space group is D_{2h}^{18}. This phase does not have icosahedral units as other polymorphs of boron do.

The structural parameters optimized by LDA at zero pressure are compared with another work [7] (GGA) in table 3. In our calculation, after optimization, the residual force and stress were at levels of about 10^{-4} (Ryd/Bohr^3) and 10^{-5} (Ryd/Bohr^3), respectively. As seen in table 3, the agreement between these two calculations is good, in spite of the use of different electron correlation functionals.

A comparison of the total energy between α-rh boron and Ga-type boron shows that the former is stable by 0.292 eV/atom at zero pressure. It is noted that our calculation of the atom density is greater than that for α-rh boron by 12.5% (see table 1). This suggests that Ga-type is stable at high pressures, in a similar manner between α- and β-boron [3, 9].

The density of states (DOS) and band structure of Ga-type boron are shown in figures 4 and 5, respectively. In these figures, we see that Ga-type boron seems metallic even at zero pressure[3]. By considering that the atom density of Ga-type boron is higher than that of α-rh boron, it is reasonable that Ga-type boron becomes metallic. However, the electronic density of state at the Fermi energy is very small, i.e. 0.018 states/eV atom, which agrees with that of reference [10]. This situation is commonly termed an insulator with a pseudogap.

Our LDA calculations show that the stability of α-rh boron versus Ga type is changed around 75 GPa, which agrees with the transition pressure estimated by GGA calculation [10].

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[3] This point that Ga-type boron is metallic has been checked by another code (STATE), with the same conclusion. In this respect, we are indebted to Dr S Yanagisawa for his calculation using STATE.
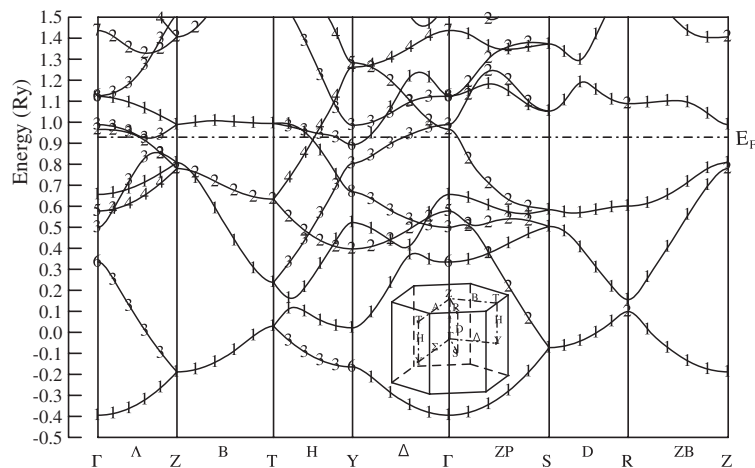
Figure 5. The band structure of Ga type boron under zero pressure. The labels of irreducible representations are those of TSPACE. The correspondence to Mulliken notation is given for the Γ point: 1, A_g; 2, A_u; 3, B_{3g}; 4, B_{3u}; 5, B_{2g}; 6, B_{2u}; 7, B_{1g}; 8, B_{1u}.

4. Summary

We have examined the potential for Li doping of α-rhombohedral boron, aiming for a high-T_c superconductor. The formation energy of Li that was obtained is marginal at the normal condition as to whether the sign is positive or negative. When pressure is applied, the formation energy immediately becomes positive, so Li doping must be easier. Based on this observation, a method for the application of high pressures of more than 10 GPa is proposed. The structural parameters are determined when Li is doped; a 2% increase in the lattice parameter for an Li concentration of 8%. This may be useful for the experimental detection of Li in α-rh boron.

This method is not invalidated, at least up to 70 GPa, even by considering Ga-type structure, which is proposed as a candidate for the high-pressure phase.

Acknowledgments

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