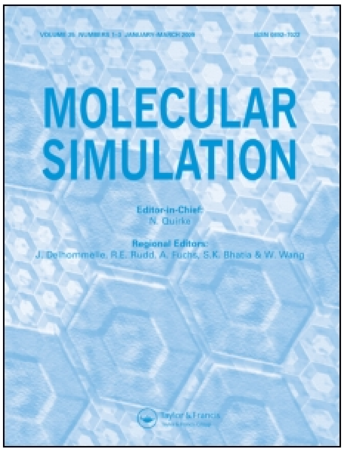

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The Pressure Dependence of Solid Boron

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We study the stability of icosahedron-based solid boron called α- and β-boron by first principles calculations. It is found that α-boron is the most stable phase at zero temperature. The actual structure of β-boron has disorders in the atomic arrangement. This affects slightly and decreases the total energy of β-boron, but does not change the above conclusion. The effect of this disorder, however, gives stability of β-boron at finite temperatures through the entropy term. On applying pressure, the stability of α-boron is increased. Under hydrostatic pressures, the deformation of icosahedra of β-boron exhibits differently from both of α-boron and boron carbide.

Keywords: β-rhombohedral boron; Deformation of icosahedra; First-principles calculations; Disorder modifications

PACS numbers: 62.50.+p; 63.20.−e; 63.20. Ry; 65.40.−b

INTRODUCTION

Since the discovery of superconductivity in solid boron under high pressures [1], there have been many theoretical [2–5] and experimental reports [6,7] for solid boron and its compounds. Solid boron has two major phases under room temperature and zero pressure, which are called α-boron [8] and β-boron [9,10]. It is believed that the most stable structure is α-boron and metastable one is β-boron, but the details of the stability are seldom understood. The study of solid boron has been, so far, limited to a more simple form, α-boron (12 atoms in a cell), because the crystal structure of β-boron is huge (105 atoms in a cell) and complicated. Furthermore, it includes atomic sites with partial occupancy. We studied the stability and its structure of β-boron under pressure by first-principles calculations, by taking into account the partial occupation of β-boron, and comparing the pressure dependence of the crystal structure of β-boron with those of α-boron [11] and boron carbide [12].

The crystal structure of solid boron is based on the icosahedral clusters which consist of twelve boron atoms. Figure 1 shows the crystal structure of β-boron. Near the center of a unit cell, there are three icosahedra sharing five boron atoms each other (triple B_{12}). There are sixteen equivalent atomic positions, which are characterized by symmetry operations, in the unit cell of β-boron. The site B(13) and B(16) are only partially occupied, whose atomic occupancies are 73.4% for B(13) and 26.6% for B(16) sites [9,10]. These sites are indicated by enclosing by boxes in the figure.

In α-boron, there exists an icosahedron at each vertex of the unit cell. Boron carbide has the same structure as α-boron except a C–B–C chain along the main diagonal of the unit cell. The (triple B_{12}) ≡ B ≡ (triple B_{12}) chain of β-boron can be regarded as a variant of the C–B–C chain of boron carbide. There are some reports on pressure dependence of the crystal structure for α-boron, β-boron and boron carbide. One of the authors (K.S.) [11,12] found that the unit cell of α-boron was more stiff in the *z*-direction than in the *xy*-plane, whereas the icosahedra were more compressed in the *z*-direction and were more elongated in the *xy*-plane under pressure.

Interestingly, the elastic deformation of boron carbide under pressure is completely opposite to these response of α-boron, even though the most stiff C–B–C chain is inserted along the *z*-direction. This difference is understood by the subtle difference in the geometry of the crystal structures.

In β-boron, Ma *et al.* [13] observed that the *a* direction on the hexagonal system was less compressible than in the *c* direction. From this observation, they conclude that the B_{10}–B–B_{10} chain was less rigid than the icosahedral clusters. Sanz *et al.* [14] observed a pressure-induced

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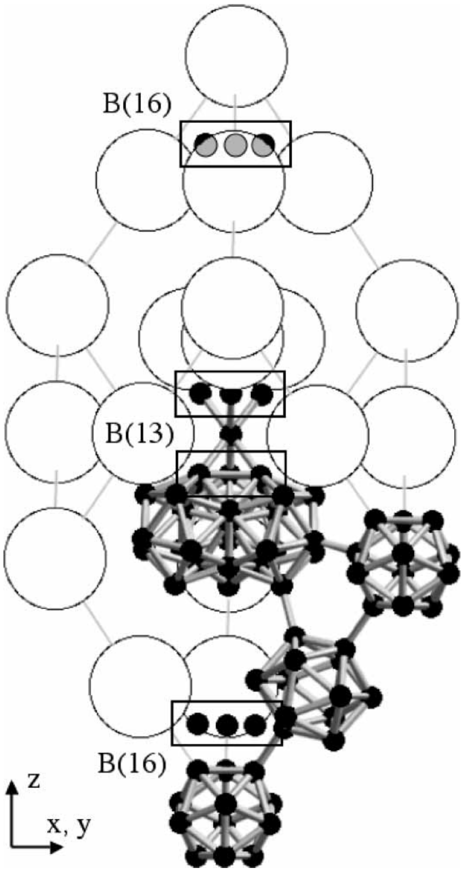

FIGURE 1 The crystal structure of β-boron. The black spheres and big circles denote boron atom and B_{12} icosahedron, respectively. The sites enclosed with a box denote the partial occupancy sites, whose atomic occupancies are 73.4% for B(13) and 26.6% for B(16).

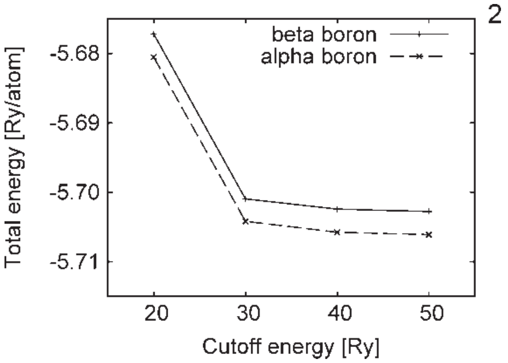

FIGURE 2 Cutoff energy dependence of total energy for α- and β-boron without relaxation of cell and atoms. In the reciprocal lattice space, One or twice division for β- or α-boron is used, respectively.

amorphization at about 100 GPa, and found that β-boron is stable up to 100 GPa.

STABILITY UNDER NORMAL CONDITIONS

The calculations were performed by a code of the *ab-initio* pseudopotential method with the local density approximation along with an iterative energy-minimization scheme utilizing Hellman–Feynman forces [15]. The used code is our "OSAKA2002-nano". Stresses are calculated by a method of Refs. [16,17]. To optimize the crystal structure, the atomic positions and the cell parameters are fully relaxed by using Hellman–Feyman forces and stresses. Here, Troullier–Martins type pseudopotentials [18] are used. The electronic wave functions are expanded by a plane–wave basis set. Monkhorst–Pack's method [19] is used for *k*-point sampling.

Because a crystal parameter *a* for β-boron is twice of that of α-boron, one division in the reciprocal lattice space of β-boron amounts to twice division of α-boron. In the following, we compare the total energy by keeping this equivalent sampling in mind. In the case of $E_{\mathrm{cut}} = 40$ Ry, we obtain $E_{\mathrm{tot}}(\beta) - E_{\mathrm{tot}}(\alpha) = 0.00333$ when the number of divisions is $(\beta, \alpha) = (1, 2)$ and $E_{\mathrm{tot}}(\beta) - E_{\mathrm{tot}}(\alpha) = 0.00400$ when the number of divisions is $(\beta, \alpha) = (2, 4)$. And so, the energy difference in relation to *k*-sampling points is 105.7 K in temperature conversion.

To evaluate convergence for the Cutoff energy for the plane–wave expansion, we calculated the total energy by changing E_{cut} from 20 up to 50 Ry. Figure 2 shows the Cutoff energy dependence of the total energy per atom. The energy difference is almost constant within the entire region. The Cutoff energy of 40 Ry is required, if we need the accuracy of the order of meV. From the figure, it is clear that α-boron is more stable than β-boron by 26.7 mRy/atom. When we optimized a unit cell for both structures at $E_{\mathrm{cut}} = 40$ Ry, the calculation results of lattice parameters were −1.5% of the experimental value, which is a typical LDA error. Therefore, we used 40 Ry as the Cutoff energy in this study.

In order to understand why α-boron is more stable than β-boron, we decompose the total energy E_{tot} into the electronic part E_{el} and the ionic part E_{ion}, which are listed in Table I. In the electronic part, E_{el} of α-boron is lower than that of β-boron. Because β-boron has a larger coordination number than α-boron, many coordinations make solid boron stable. But, in the ionic part, E_{ion} of β-boron is lower than that of α-boron. Because ionic electrostatic potential increases when the coordination number increases. The energy gain in E_{el} and the energy loss

TABLE I Comparison of the total and its components of α and β-boron. The energy difference Δ*E*is evaluated by the energy of α-boron as the origin. The energy unit is Ry/atom

	E_{el}	E_{ion}	E_{tot}
α-boron	0.57656	−6.28304	−5.70649
β-boron	−0.02643	−5.66184	−5.70382
Δ*E*	−0.60299	0.60566	0.00267

in E_{ion} between α- and β-boron were almost cancelled out, but only small imbalance leads to the stability of α-relative β-boron.

In the previous discussion, it is concluded that α-boron is more stable than β-boron in the perfectly ordered phase. But, there are experimental orders in β-boron which have partial atomic occupancies, this might make the energy of β-boron lower than that of α-boron.

Sekitatsu *et al.* [20] investigated this possibility at first by the full potential linear combination of atomic orbital method. There exist six B(16)'s if the vacancy site B(13) is fixed, and so they are classified into four kinds of atomic sites by the crystal symmetry. They calculated total energy of one type of this disorder among four kinds of atomic sites. Here, the number of 105 atoms per cell does not change. In this theoretical case, atomic occupancies are 83.3% for B(13) and 16.7% for B(16), thus the space group of this structure becomes P1. We call the structure with the space group P1 ($R\bar{3}m$) a disorder (high symmetry) modification. They reported a disorder modification was more stable than the high symmetry one.

We calculated the total energy in terms of four kinds of modifications. As shown in Table II, it is seen that all the disorder modifications are more stable than the high symmetry β-boron by about 0.34 mRy/atom But α-boron is still more stable than the disorder β-boron by about 2.33 mRy/atom. Therefore, the stable phase does not change from α-boron to another phase at the zero temperature.

However, the effect of disorder is not limited to the total energy, but it could effect the free energy at finite temperature. To discuss the stability under finite temperature, we introduce Helmholtz free energy. The difference between α- and β-boron is given by

$$\Delta F(T) = -k_B T \log\left(\sum_{i=1}^{4} w_i e^{\Delta E_i/k_B T}\right), \qquad (1)$$

$$\Delta E_i = E_i - E_\alpha,$$

where k_B and T are Boltzmann constant and temperature, respectively. ΔE_i is total energy difference of the i-th disorder phase with respect to that of α-boron E_α. Figure 3 shows the free energy variation as a function of T. The positive free energy means α-boron is more stable than β-boron, and vice versa. It is of course that α-boron is stable one at the zero temperature. With increasing temperature, the free energy decreases by the contribution of entropy. At 200 K, β-boron is more stable than α-boron. Experimentally the transformation temperature 1400 K [21], and hence, the present estimation the calculation 200 K is too low. Taking phonon Effects into account, we may obtain the calculated transformation temperature in good agreement with experiment.

TABLE II Total energy per atom of high symmetry and four kinds of disorder modifications. w_i is the number of the modifications equivalent sites to the i-th disorder modification

Modifications	w_i	E_{tot} *(Ry/atom)*
α-boron		−5.70649
β-boron		−5.70382
The 1st disorder	1	−5.70416
The 2nd disorder	2	−5.70414
The 3rd disorder	2	−5.70416
The 4th disorder	1	−5.70412

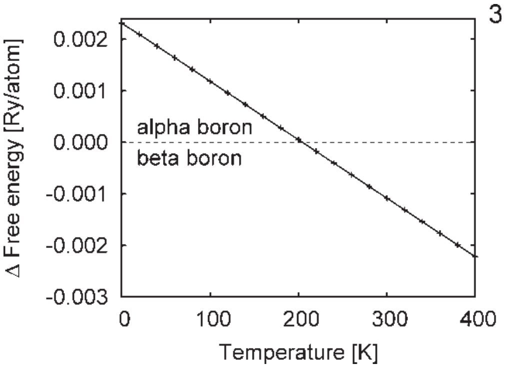

FIGURE 3 The difference of Helmholtz free energy which is obtained by taking the free energy of α-boron as the reference. The positive free energy means α-boron is more stable than β-boron, and vice versa.

UNDER PRESSURES

In the previous section, it is found that α-boron is more stable than β-boron under low temperatures and the zero pressure. In this section, we consider the elastic properties of boron.

Stable Structure Under Pressures

To see which of α- and β-boron was more stable under pressure, we examined the pressure dependence of the crystal structure of α- and β-boron. By calculating variations of the total energy as a function of pressure, we can obtain the bulk modulus B and enthalpy $H(p)$. We obtained in this way that $B = 236.3$ GPa for α-boron and $B = 204.6$ GPa for β-boron, where experimental values were 213 GPa [22] for α-boron and 210 GPa [23] (201 GPa [13]) for β-boron. We can see from the bulk modulus that α-boron is more stiff than β-boron. It is consistent with the fact that α-boron is more stable than β-boron under normal conditions.

Enthalpy is given by

$$H(p) = E_{\text{tot}}(p) + pV(p), \qquad (2)$$

where p is a given pressure. The total energy $E(p)$ is what we obtain for calculating the total energy in the electronic structure calculation, but in this time

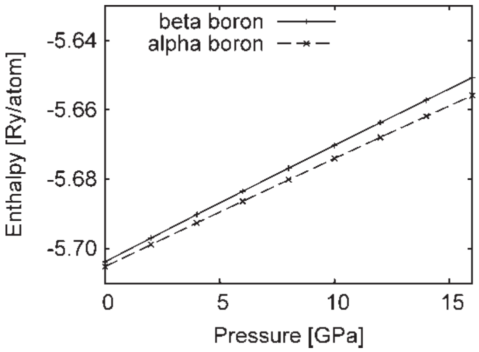

FIGURE 4 Enthalpy of α-boron and β-boron up to 16 GPa. This is calculated under the condition which is symmetry constraints.

should be evaluated by the optimized structure under p. The enthalpy is shown in Fig. 4. The upper and lower lines are β- and α-boron. They increase almost linearly with increasing temperature in a range examined. If temperature rises, the gain in the enthalpy of α-boron relative to β-boron is further increased. Therefore, it is concluded that α-boron is more stabilized at high pressures.

Pressure Dependence of the Lattice Structure

In this section, we consider pressure dependence of details of the structure of β-boron, and it is compared with α-boron and boron carbide. Pressure dependence of crystal structures of α-boron and boron carbide is reported in Refs. [11,12]. Change of the unit cell is described in the "Introduction" section. Further complications occur around icosahedra in the unit cell. Figure 5(a) shows a pair of adjacent icosahedra in those materials under normal conditions. We characterize the shape of icosahedra by the "length", i.e. the size along the z-axis and by the "width", i.e. the size in the xy-plane. In this way, we mimic the deformation of icosahedra by ellipsoids approximately. Figure 5(b) shows the case of α-boron, it is found that two spheres are deformed to two flat ellipsoids. Figure 5(c) is the case of boron carbide, it is found that two spheres are deformed to two ellipsoids elongating along the z-axis. This deformation about icosahedra is related to the variation of the unit cell through a subtle way. This thorough argument is described in Ref. [11].

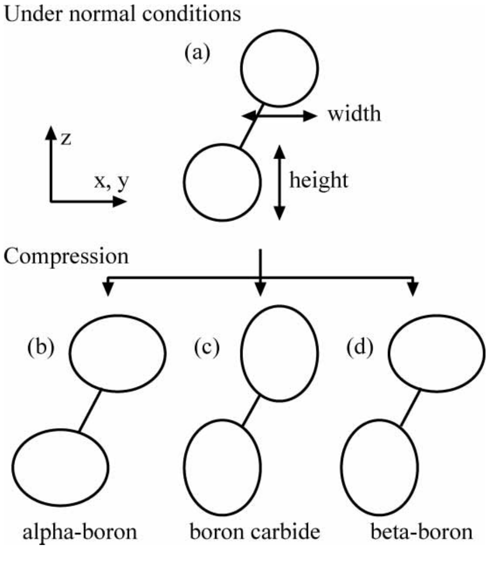

FIGURE 5 Schematic view of the relaxation process for the compression of α-boron (b), boron carbide (c) and β-boron (d). The circle denotes the icosahedra under normal conditions (a).

We investigate the variation of icosahedra of β-boron. There are two kinds of icosahedra in β-boron, the first icosahedron is on the vertex of the rhombohedral unit cell representing to the bottom circle in Fig. 5, and the other is on the middle point between two vertices represented by another sphere. From the calculated results, it is found that the height and width of the second type is shorten by 0.087 and 0.120% per GPa, respectively, and those the first type is shorten by 0.175 and 0.141% per GPa, respectively. Figure 5(d) shows this deformation of icosahedra. From this figure, we can see that the deformation of β-boron is a mixture of those of α-boron and boron carbide.

SUMMARY

In this study, we discussed the stability of α- and β- boron by employing first-principles calculations based on the pseudopotential method. In the electronic part of total energy, β-boron was more stable than α-boron. It is concluded that α-boron is more stable than β-boron by 26.5 mRy/atom at zero temperature. This conclusion is not changed, even if we take disorder phases into account.

To estimate the transformation temperature between α- and β-boron, we calculate the Helmholtz free energy contribution from the atomic disorder. The transformation temperature of 200 K is obtained by this estimation, This is too low in comparison with the experimental value 1400 K. Further Effects of finite temperature, such as phonons must be taken into account, which study is now in progress.

Pressure dependence of the structure of β-boron is studied. It is found that the deformation of β-boron is a mixture of those types of α-boron and boron carbide.

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