

Crystal stability of  $\alpha$ - and  $\beta$ -boron

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The crystal stabilities of  $\alpha$ - and  $\beta$ -boron are studied theoretically by the density-functional calculations. The ground-state properties and thermodynamic properties are calculated by the pseudopotential method. These calculated thermodynamic properties include the effect of atomic disorder, observed experimentally, as well as the effect of phonons. The pressure dependence of the free energy is also studied. At zero temperature, it is found that  $\alpha$ -boron is more stable than  $\beta$ -boron. This does not change even if the zero-point energy and atomic disorders are considered. The contribution of these effects to the energy is small at  $T=0$  K. However, these effects eventually cause a phase transition to  $\beta$ -boron at high temperatures. By considering the phonon contribution as the chief source of the temperature dependence of the free energy, 970 K is obtained as the transition temperature, which is in qualitative agreement with the experimental value of 1400 K. The difference between these values could be attributed to anharmonic effects. The effect of thermal expansion on the transition temperature is insignificant. At finite pressures, the stability of various polymorphs can be determined mainly using the atom density. The basic feature underlying all the above properties is that  $\alpha$ -boron is dense, while  $\beta$ -boron is dilute. For  $\beta$ -boron, an energetic consideration shows that the disorder in the atom arrangement is inherent. The present calculations reveal a small change in bond length for specific intericosahedral bonds, which is caused by an atomic disorder.

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## I. INTRODUCTION

Solid boron has many crystallographic polymorphs.<sup>1</sup> Among them,  $\alpha$ - and  $\beta$ -boron are well-known polymorphs. The physical and chemical properties of boron have been, for a long time, studied from various viewpoints. A single international conference has been devoted to this matter since 1959.<sup>2</sup> Despite this, it is surprising to find an as yet unstudied property, i.e., the superconductivity at high pressures for  $\beta$ -boron.<sup>3</sup> A superconducting transition has occurred at a high pressure (160 GPa). The crystal structure after the superconducting transition is yet unknown, although many experiments<sup>4,5</sup> and theories<sup>6,7</sup> are continually carried out and tested, respectively. Recent theoretical studies suggest that a high-pressure phase is of the Ga-type structure.<sup>8,9</sup> However, before studying the superconducting phase of boron, we note that its stable structure even under the normal conditions has not yet been established.

The structural parameters of  $\alpha$ - and  $\beta$ -boron are compared in Table I, along with some of their physical properties that are relevant in this study. In the atom density  $\rho$ , the  $\alpha$  phase is denser than the  $\beta$  phase by 7%. The coordination number  $N_c$ , which is defined here as the number of bonds whose length is  $<2$  Å, characterizes how many boron atoms are associated with each other. The data of the Debye temperature  $\theta_D$ , bulk modulus  $B_0$ , and its pressure derivative  $B'$  are also listed. These data vary slightly, depending on the method by which the value is obtained. Nevertheless, it is seen that  $\alpha$ -boron is stiffer than  $\beta$ -boron, with respect to the bulk modulus and Debye temperature. This is consistent with the fact that  $\alpha$ -boron is denser than  $\beta$ -boron. Therefore, we can say that  $\alpha$ -boron is *mechanically* stable. This fact was not seriously considered before. However, this is an important property, as shown in the following.

The crystal structures of  $\alpha$ - and  $\beta$ -boron are illustrated in Fig. 1. Both have a rhombohedral Bravais lattice with the space group  $R\bar{3}m$  in its perfect form. The icosahedral unit  $B_{12}$  is a common building block. The structure of  $\beta$ -boron is complex. The unit cell is composed of 105 atoms, which can be classified into 15 nonequivalent atomic sites, on the assumption of  $R\bar{3}m$  symmetry.<sup>11</sup> The labeling scheme of these sites in the present study accords to that given in Ref. 11.

TABLE I. Structural parameters of  $\alpha$ - and  $\beta$ -boron in experiment. Lattice parameters  $a_0$  and  $\alpha$ , number of atoms  $N_{\text{atom}}$ , atom density  $\rho$ , coordination number  $N_c$ , Debye temperature  $\theta_D$ , and bulk modulus  $B_0$ . The bond length is presented as the minimum  $d_{\text{min}}$  and average  $d_{\text{avg}}$  for all the bonds.

	$\alpha$ -boron	$\beta$ -boron
$a_0$ (Å)	5.057 <sup>a</sup>	10.145 <sup>b</sup>
$\alpha$ (°)	58.06 <sup>a</sup>	65.17 <sup>b</sup>
$N_{\text{atom}}$	12 <sup>a</sup>	105 <sup>b</sup>
$\rho$ ( $\text{\AA}^{-3}$ )	0.1373 <sup>a</sup>	0.1278 <sup>b</sup>
$N_c$	5.50 <sup>a</sup>	6.40 <sup>b</sup>
$d_{\text{min}}$ (Å)	1.71 <sup>a</sup>	1.62 <sup>b</sup>
$d_{\text{avg}}$ (Å)	1.77 <sup>a</sup>	1.80 <sup>b</sup>
$\theta_D$ (K)	1430 <sup>c</sup>	1200–1300 <sup>d</sup>
$B_0$ (GPa)	213–224 <sup>c</sup>	185–210 <sup>f</sup>

<sup>a</sup>Reference 10.<sup>b</sup>Reference 11 and 12.<sup>c</sup>Reference 13.<sup>d</sup>Reference 13–15.<sup>e</sup>Reference 16.<sup>f</sup>Reference 4, 15, and 16.

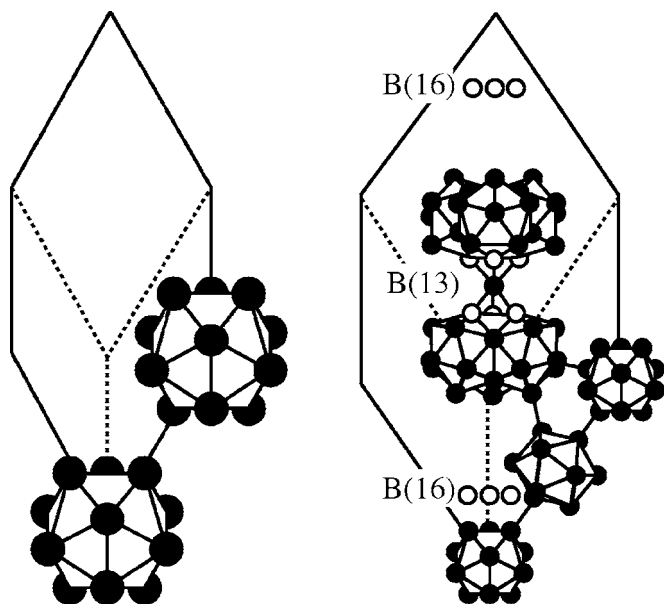


FIG. 1. Crystal structures of  $\alpha$ - (left) and  $\beta$ -boron (right) (Refs. 10–12).  $\alpha$ -boron has a rhombohedral structure (space group  $R\bar{3}m$ ) with 12 atoms in a cell.  $\beta$ -boron has the same space group, but it contains 105 atoms in a cell. The closed (open) circles represent atomic sites with full (partial) occupancy. Atomic sites with partial occupancy are indicated.

However, site B(13) is only partially occupied with an occupancy of 73.4%.<sup>12</sup> The missing boron atoms appear at extra site B(16) with an occupancy of 26.6%.

The minimum bond length in  $\alpha$ -boron occurs at the intericosahedral (not intra-) bond. This is a distinct feature of solid boron; intericosahedral bonds are shorter than intra-icosahedral bonds.<sup>1</sup> This feature is also exhibited by  $\beta$ -boron, as will be discussed later.

The most easily available modification of boron that is found commercially or made within the laboratory is the  $\beta$  phase. Hence, this phase is considered to be the *thermodynamically* preferred one.<sup>1</sup> A more accurate meaning of thermodynamical stability will be clearer later. On the other hand, the  $\alpha$  phase can be synthesized at low temperatures.<sup>17</sup> Although there is such a distinction in the preparation conditions, the phase diagram is thus far unavailable. This is because there is no definite evidence for the phase transition between the  $\alpha$  and  $\beta$  phases. Although an attempt to observe the phase transition between these phases was made,<sup>18</sup> it was unsuccessful. It is difficult to complete a solid-state transformation between the  $\alpha$  and  $\beta$  phases because there is no simple and continuous displacement connecting these phases. The energy barrier between these phases may be so high that we could not observe the phase transition within a reasonable time of experiment.

Instead, experimentalists found a boundary in the preparation conditions, at which the obtained phase changes. The boundary temperature depends on the method of preparations: 1300 K in the hot filament,<sup>1</sup> from 1300 to 1500 K in the reduction of boron chalcogenides,<sup>17</sup> and  $\sim 1500$  K in the crystallization of amorphous boron.<sup>19</sup> This leads us to obtain a boundary temperature of  $\sim 1400$  K. This boundary tem-

perature provides a measure for the transition temperature between these phases,  $T_{\alpha\beta}$ ; hence, we shall refer to this temperature in place of  $T_{\alpha\beta}$  in the following. The questions now are why is the  $\alpha$  phase stable at low temperatures, why is the  $\beta$  phase stable at high temperatures, and what is important in determining  $T_{\alpha\beta}$ .

There is, thus far, no satisfactory answers to these questions. A study of the stability of these two phases by *ab initio* calculations was reported, indicating that the  $\alpha$  phase is more stable than the  $\beta$  phase.<sup>20</sup> This result is qualitatively consistent with the above-mentioned experimental facts. However, in the study, the  $\beta$  phase was modeled by a molecular cluster with a limited size. Band calculations must be carried out for the crystal.

In this study, we evaluate the stabilities of  $\alpha$ - and  $\beta$ -boron by *ab initio* calculations. For this purpose, a few theoretical works have been reported.<sup>6,20,21</sup> However, because of the complexity of  $\beta$ -boron, information about the  $\beta$  phase is very limited. Even though a Ga-type structure may be a promising candidate for a high-pressure phase, the present study can provide significant insight into our understanding of the physical properties of boron, because most of experimental data presently available are of the  $\beta$ -boron. In addition, these previous theoretical studies were performed only for zero-temperature properties.<sup>6,20</sup> On the other hand, the present study includes many thermodynamic considerations, such as those for the phonon calculation, pressure dependence, and the effects of disorder. This enables us to estimate the transition temperature  $T_{\alpha\beta}$ . Before proceeding to the discussion on the calculation, we begin with a brief summary of the theoretical achievements thus far obtained for the problem of the stability of boron crystals in Sec. II.

## II. THEORETICAL BACKGROUND

The theoretical study of the bonding nature of solid boron began with a study by Longuet-Higgins and Roberts, who investigated the molecular orbitals of the  $B_{12}$  unit,<sup>22</sup> with the concept of the so-called three-center bond in the chemistry language.<sup>23</sup> A  $B_{12}$  molecule has 13 intraicosahedral bonding orbitals, which are fully occupied. The remaining 10 electrons are distributed among 12 intericosahedral orbitals. Accordingly, two electrons are deficient for fulfilling the bonding requirement of the  $B_{12}$ . This is a key issue for understanding of the bonding nature of  $B_{12}$  unit: *although  $B_{12}$  is a favorable unit for satisfying the bonding requirement of boron atoms,  $B_{12}$  itself is not stable.*

To supply the two deficient electrons, boron atoms tend to gather each other by forming triangles or polyhedra. This is an economical way for a small number of electrons to be shared by many atoms. This qualitative account seems to give a reasonable explanation for the fact that there are many stable (or metastable) polymorphs that have complex structures, e.g.,  $\beta$ -rhombohedral, tetragonal-I ( $N_{\text{atom}}=50$ ,  $\rho=0.1291/\text{\AA}^3$ ), -II ( $N_{\text{atom}}\sim 78$ ,  $\rho=0.1306$ ), and -III ( $N_{\text{atom}}\sim 192$ ,  $\rho=0.1326$ ).<sup>1</sup>

After Longuet-Higgins' work, a number of more accurate calculations have been carried out for the electronic structure of  $\alpha$ -boron,<sup>24,25</sup> including modern density-functional

calculations.<sup>26,27</sup> The results of these calculations are essentially the same as the qualitative description by Longuet-Higgins. However, in density-functional calculations, the attribution of a definite number of electrons to the intra- and intericosahedral bonds described above loses its strict meaning because the charge density is distributed continuously everywhere.

Satisfying the bonding requirement can also be achieved using doping impurities, such as the compounds  $B_{12}P_2$ ,  $B_{12}As_2$ , and maybe  $B_{12}C_3$ . The impurity atoms commonly form a linear chain along the main diagonal of the rhombohedral unit cell. In  $B_{12}C_3$ , the effect of introducing C atoms seems to be slightly different from those in the other compounds. The results of phonon spectrum analysis indicate that the presence of the C chain enhances the chain bond itself, while it tends to destroy the intraicosahedral bonds.<sup>28</sup>

In regard to the mechanical stability, one of the present authors had previously discussed the difference between the  $\alpha$  and  $\beta$  phases using the constraint theory.<sup>29</sup> In the  $\alpha$  phase,  $B_{12}$  units are connected to each other by a *point contact*, that is, a single bond, whereas in the  $\beta$  phase,  $B_{84}$  units are connected to each other by a *face contact*, that is, multiple bonds. Consequently, the structure of the  $\alpha$  phase is unstable for shear strains. One shortcoming of this argument is, however, overlooking the role of angle forces; the angle forces were assumed to be very small. After that paper, there was an interesting paper on the phonon spectrum of  $\alpha$ -boron by Vast *et al.*<sup>30</sup> Their result for the librational mode at  $527\text{ cm}^{-1}$  suggests that the angle forces are large. These large angle forces lead to the mechanical stability of the structure of  $\alpha$ -boron. In fact, the bulk modulus of  $\alpha$ -boron is larger than that of  $\beta$ -boron, as shown in Table I.

In this regard, it is worth noting that the angle forces of  $\alpha$ -boron are actually not quite large. Their magnitude is similar to that of the angles forces found for typical semiconductors; typical angle force constants are a few percent of those of bond stretching. The true reason for the significant influence of the angle forces is that there are a large number of angles that determine to the phonon properties, which is a consequence of having a nontypical structure of icosahedra.<sup>31</sup> Because of this large number of angle forces, the  $\alpha$  phase is mechanically stable. Other unsolved problems and controversial issues regarding the properties of boron still exist.<sup>32</sup> Discussion on some issues, in particular, those of the elastic properties, is given with criticism in Ref. 33.

Up to this point, we may qualitatively describe the stability of boron; that is,  $\alpha$ -boron is *mechanically* stable, while  $\beta$ -boron is *thermodynamically* stable. Now, we want to obtain a quantitative description for such stability by *ab initio* calculations in Secs. III–V.

### III. CALCULATION METHOD

The calculation method used is the *ab initio* pseudopotential method with local-density approximation (LDA), along with an iterative energy-minimization scheme.<sup>34</sup> The code used is the code OSAKA2002, which we developed. Troullier-Martins's pseudopotentials<sup>35</sup> are used, with the aid of a full separable Kleinman-Bylander form.<sup>36</sup> The plane-wave basis

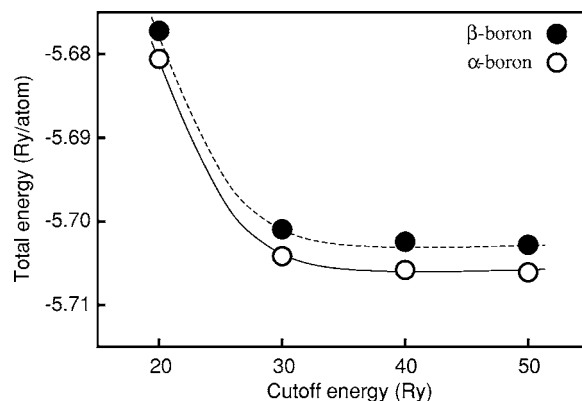


FIG. 2. Energy convergence against cutoff energy  $E_{\text{cut}}$  of plane-wave expansion. As the  $k$  sampling, a single ( $\Gamma$ ) point is used for  $\beta$ -boron, while a  $2 \times 2 \times 2$  mesh is used for  $\alpha$ -boron.

is used for expanding the wave function. The Ceperly-Alder form<sup>37</sup> parametrized by Perdew and Zunger<sup>38</sup> is employed for the exchange-correlation functional.

The Monkhorst-Pack scheme is used for  $k$ -point sampling.<sup>39</sup> A way of the  $k$ -point sampling is important when comparing different structures. The structure of  $\beta$ -boron can be regarded as a  $2 \times 2 \times 2$  superlattice of  $\alpha$ -boron. Accordingly, the equivalent  $k$ -point sampling is 1:2 for  $\beta$ - and  $\alpha$ -boron. When the energy is compared between these phases, this sampling method was used.

The energy convergence is examined against the cutoff energy  $E_{\text{cut}}$  in the plane-wave expansion, as shown in Fig. 2. The absolute total energy  $E_{\text{tot}}$  is converged within 1.5 mRy when  $E_{\text{cut}}=40$  Ry. However, the convergence for the energy difference of these phases already reaches 0.1 mRy at this cutoff energy.

When the  $k$  sampling points are doubled,  $2^3 \rightarrow 4^3$  for  $\alpha$ -boron and  $1^3 \rightarrow 2^3$  for  $\beta$ -boron, the change in  $E_{\text{tot}}$  is  $<1$  mRy. For  $\alpha$ -boron, a further increase in the number of  $k$  sampling points from  $4^3$  to  $6^3$  makes virtually no difference, i.e.,  $\Delta E_{\text{tot}} \approx 10^{-3}$  mRy. Therefore, in the following, the conditions  $E_{\text{cut}}=40$  Ry and  $\Gamma$ -point sampling are commonly used for  $\beta$ -boron ( $k$  sampling of  $2^3$  for  $\alpha$ -boron), unless otherwise stated.

To find the optimum structure at hydrostatic pressures, an iterative energy-minimization method is employed by utilizing Hellman-Feynman forces<sup>40</sup> and stresses.<sup>41</sup> In the atom relaxation, the iteration is continued until the residual force reaches a value of  $<10^{-5}$  Ry/Bohr per atom. In the cell relaxation, it is continued until the residual stress reaches a value of  $<10^{-6}$  Ry/Bohr<sup>2</sup>.

The symmetry constraint for the atom positions (or the cell shape) is employed in the structural optimization if an appropriate symmetry is expected. The frozen-phonon calculation is performed to obtain zone-center phonons.

### IV. ZERO-TEMPERATURE PROPERTIES

First, let us compare the stabilities of  $\alpha$ - and  $\beta$ -borons at zero temperature. Here, we assume the perfect symmetry  $R\bar{3}m$  for  $\beta$ -boron, for simplicity.

TABLE II. Lattice parameters  $a_0$  and  $\alpha$ , bulk modulus  $B_0$  at zero pressure and its pressure derivative  $B'$  of  $\alpha$ - and  $\beta$ -boron. The numbers in parentheses indicate the error relative to the experiment in percent. The references for the experiments are cited in Table I.

	$a_0$ (Å)	(%)	$\alpha$ (°)	(%)	$B_0$ (GPa)	$B'$
$\alpha$ -boron						
Calc.	4.967	(-1.78)	58.65	(1.02)	218.4	4.8
Expr.	5.057		58.06		213-224	4.0
$\beta$ -boron						
Calc.	9.996	(-1.47)	65.22	(0.08)	203.5	4.5
Expr.	10.145		65.17		185-210	2.2-4.2

Table II shows a summary of the structural parameters and static properties obtained in the calculations. The calculated lattice parameters are in good agreement with the experimental ones. The calculated  $a_0$  is smaller than the experimental one by about 1%. This is a typical LDA error. The apex angle  $\alpha$  is smaller than  $60^\circ$  for  $\alpha$ -boron, while it is larger than  $60^\circ$  for  $\beta$ -boron. The deviation of this angle from  $60^\circ$  has a consequence on the elastic properties of boron, as discussed in Ref. 29; this determines the direction in which the crystal is relaxed by the application of stress. On the basis of this argument, we may expect the anisotropy in the elastic constants of  $\beta$ -boron as  $C_{33} < C_{11}$ . This is observed in the pressure dependence of the angle  $\alpha$  of  $\beta$ -boron in a recent experiment.<sup>5</sup>

Let us look at more closely the structure of  $\beta$ -boron. There are three different types of icosahedra, which are labeled A, B, and C, as shown in Fig. 3. The corresponding intraicosahedral bonds are labeled 7, 8, and 9. Between these icosahedra, there are many intericosahedral bonds. We define six types of intericosahedral bond, which are shown in the figure. In Table III, we list the calculated bond lengths and compare them to the experimental ones.

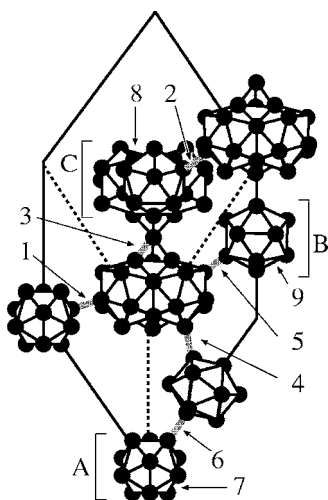


FIG. 3. Typical bonds in crystal structure of  $\beta$ -boron. A, B, and C are labels of nonequivalent icosahedra, whereas numerical indices 1-6 (7-9) are labels of intericosahedral (intraicosahedral) bonds.

It is observed that all the intericosahedral bonds are shorter than the intraicosahedral bonds. This is the common property of boron-rich solids described earlier, and the present study also confirms this property for  $\beta$ -boron. A good agreement between the calculated and experimental bond lengths is obtained. Most of the calculated bond lengths are slightly smaller than the experimental ones. This is a typical trend for LDA; in LDA, the binding energy tends to be overestimated. We note that an opposite trend is found only for bonds 3 and 6. These bonds involve the partial-occupancy sites B(13) and B(16). This issue will be discussed later.

Let us investigate the elastic properties. In Table II, the calculated bulk modulus  $B_0$  at zero pressure and its pressure derivative  $B'$  are compared to the experimental ones. A good agreement between the calculated and experimental values is obtained. It is observed that  $\alpha$ -boron is stiffer than  $\beta$ -boron by 7% in  $B_0$ . This is consistent with the fact that  $\alpha$ -boron is denser than  $\beta$ -boron by 7%.

The pressure derivative of the bulk modulus  $B'$  is a measure of anharmonicity. It seems that  $B'$  of  $\alpha$ -boron is slightly larger than that of  $\beta$ -boron (again by 7%). Using the simplest model of the cubic Bravais lattice with the nearest-neighbor interactions only,  $B'$  is given by

$$\frac{\partial B}{\partial p} = 1 + \frac{1}{3} \gamma_b. \quad (1)$$

Here,  $\gamma_b$  is the ratio of the cubic anharmonicity  $g$  to the harmonic force constant  $f$ ,  $\gamma_b = ga/f$ , where  $a$  is an appropriate length of the cell (or bond). The Grüneisen constant  $\gamma_G$  is defined as the relative change in the phonon frequency  $\omega$  with respect to the relative change in the volume  $V$ ,  $\gamma_G \equiv -\partial \ln \omega / \partial \ln V$ . In this simplest case,  $\gamma_G = \gamma_b/6$ . From this, we estimate  $\gamma_G$  of  $\beta$ -boron to be 1.75. This value is comparable to those obtained from phonon frequencies.<sup>31</sup>

Now that the structural and elastic properties are well reproduced in the calculation, we can investigate the stabilities of  $\alpha$ - and  $\beta$ -borons. As observed in Fig. 2, the energy difference is well converged. The converged value gives the energy difference of the ground state,

$$\Delta E_G = +36.3 \text{ meV/atom}. \quad (2)$$

Throughout this paper, we employ a convention that the energy difference is measured by considering  $\alpha$ -boron as the

TABLE III. Comparison of experimental and calculated bond lengths of  $\beta$ -boron. The experimental bond lengths are given in ( $\text{\AA}$ ), and the calculated ones are shown by the error relative to the experimental values. The labels of bonds are seen in Fig. 3.

Index	Bond	Expr. <sup>a</sup> ( $\text{\AA}$ )	Calc. (%)	
			$R\bar{3}m$	Disorder
1	A-C	1.62	-0.94	
2	C-C	1.68	-1.06	
3	B(15)-B(13)	1.69	1.33	-1.68
4	B-C	1.69	-0.84	
5	B-C	1.72	-2.54	
6	A-B	1.73	3.19	-1.28
7	intra A	1.76	-1.68	
8	intra C	1.81	-1.17	
9	intra B	1.84	-2.23	

<sup>a</sup>Reference. 11.

reference state. Hence, a positive value indicates the stability of the  $\alpha$  phase over the  $\beta$  phase.

As described in Sec. I, Takeda *et al.* obtained a positive-energy difference in the present sign convention.<sup>20</sup> The energy  $\Delta E_{\text{tot}} = +680$  meV/atom, which they obtained, is very large. This is probably because the structure is modeled using a finite-size cluster. Nevertheless, it is of value at a point that a positive-energy difference is demonstrated for the first time. Seki *et al.* also obtained a positive  $\Delta E_{\text{tot}}$  by the full-potential linear combination of atomic orbital method.<sup>42</sup> The value  $\Delta E_{\text{tot}} = +0.05$  eV/atom, which they obtained, is similar to the present value in Eq. (2). Now, it is almost certain that  $\alpha$ -boron is more stable than  $\beta$ -boron at zero temperature.

To determine how we can interpret the present result from the traditional chemistry's viewpoint, as described in Sec. II, let us analyze the total energy. In the pseudopotential formalism,<sup>40</sup> the total energy  $E_{\text{tot}}$  is expressed as

$$E_{\text{tot}} = T + U_{\text{ion}}^{\text{ps}} + E_{\text{H}} + E_{\text{ex}} + E_{\text{ewald}}. \quad (3)$$

The first four terms on the right-hand side of the equation are the kinetic, ion-electron interaction, Hartree, and exchange-correlation energies. The electronic contribution ( $E_{\text{el}}$ ) to the total energy comprises these terms. The last term of Eq. (3) is the electrostatic ion-ion interaction energy ( $E_{\text{ion}}$ ). This way of decomposing  $E_{\text{tot}}$  into the electronic and ionic parts is not quite unambiguous. In a deep level, the ionic part and the pseudopotential part are associated with each other.<sup>40,43,44</sup>

However, in the following we assume their independence for a practical reason.

The components of the total energy are shown in Table IV. In the electronic part  $E_{\text{el}}$ , the energy of  $\beta$ -boron significantly decreases. This is what we expect from the chemistry's viewpoint, as described in Sec. II. The association of more boron atoms in  $\beta$ -boron, which is observed in the increase in the coordination number  $N_c$  from 5.5 to 6.4, implies stronger chemical bonds. However, this energy gain is canceled by the ionic part  $E_{\text{ion}}$ . The Coulomb repulsion increases as  $N_c$  increases because of the increase in  $N_c$ . Hence, regarding the stability of  $\beta$ -boron, the chemistry's viewpoint would still be correct if only the electronic part  $E_{\text{el}}$  is considered. However, another contribution of  $E_{\text{ion}}$  overcomes the electronic contribution, resulting in the relative stability of  $\alpha$ -boron.

## V. FINITE-TEMPERATURE PROPERTIES

Up to this point, we have seen that  $\alpha$ -boron is more stable than  $\beta$ -boron at zero temperature. Now, we proceed to the thermodynamic consideration at finite temperatures. Once temperature is involved, many complex effects arise. In the following, we consider a few of these effects, which may affect the determination of the transition temperature  $T_{\alpha\beta}$ . The effects are atom disorder, phonons, and thermal expansion.

TABLE IV. The electronic  $E_{\text{el}}$  and ionic  $E_{\text{ion}}$  parts of the total energy  $E_{\text{tot}}$ . The energy difference  $\Delta E$  is obtained by considering the energy of  $\alpha$ -boron as the reference. Energy is given in rydbergs per atom.

	$E_{\text{el}}$	$E_{\text{ion}}$	$E_{\text{tot}}$
$\alpha$ -boron	0.57656	-6.28304	-5.70649
$\beta$ -boron	-0.02643	-5.67739	-5.70382
$\Delta E$	-0.60299	0.60566	0.00267

TABLE V. Comparison of total energies of four disordered configurations of  $\beta$ -boron, of those of high-symmetry  $\beta$ -boron and  $\alpha$ -boron. For a disordered system, the multiplicity  $w_i$  of the  $i$ th type disorder is given.

Crystal	Configuration	$w_i$	$E_{\text{tot}}$ (Ry/atom)
$\alpha$ -boron			-5.70649
$\beta$ -boron	$R\bar{3}m$		-5.70382
	First disorder	1	-5.70416
	Second disorder	2	-5.70414
	Third disorder	2	-5.70416
	Fourth disorder	1	-5.70412

### A. Effect of atom disorder

When the crystal structure of  $\beta$ -boron was first characterized, a disorder in the atomic arrangement was already observed.<sup>11</sup> As described in Sec. I, the atom occupancies of B(13) and B(16) are 73.4 and 26.6%, respectively. Another complex situation regarding the occupancy was observed (see Ref. 45). Crystals of perfect occupancies have never been reported thus far. Many researchers believe that the disorder is an inherent property of the crystal structure of  $\beta$ -boron. The effect of this disorder was recently studied by Seki *et al.* by the full-potential linear combination of the atomic orbital method.<sup>42</sup> They found that the disordered phase is more energetically favorable than the high-symmetry phase.

We also examine the effect of this disorder, focusing on the transition temperature  $T_{\alpha\beta}$ . To simulate this disorder, we construct a disordered model, by moving one atom from site B(13) to site B(16). This model corresponds to the atom occupancy of site B(16) of 16.7%. There are six choices for the atom position of site B(16) for a fixed vacancy position of B(13). Because of the mirror symmetry, which remains even after the disorder is introduced, these six configurations are classified into four nonequivalent ones.

The result is shown in Table V. Here,  $w_i$  is the multiplicity of the  $i$ th atom configuration. In all the disordered configurations, the energy decrease by  $\sim 4$  meV/atom, compared to the high-symmetry one. This result demonstrates that the disorder in the atomic arrangement is intrinsic for the crystal structure of  $\beta$ -boron. However, even by considering the effect of disorder, the order of energy between the  $\alpha$  and  $\beta$  phases is not altered at  $T=0$ . The ground-state energy difference becomes

$$\Delta E_{G,d} = +32.2 \text{ meV/atom}, \quad (4)$$

when the disorder is considered.

It is interesting to examine the effect of disorder on the change in bond length. The result is shown in the last column of Table III. The listed bond lengths of the disordered system are the averages for the six configurations. We observe that the calculated lengths of bonds 3 and 6, which were found in Sec. IV to be slightly long, are smaller. All the deviation from the experimental ones fall within a reasonable range. Accordingly, the change in the length of bonds 3 and 6 is a sign of occurring of the disorder.

Then, we examine how the disorder of  $\beta$ -boron affects the transition temperature  $T_{\alpha\beta}$ . At a finite temperature  $T$ , the disorder contribute to the stability though entropy. This effect is observed by evaluating the Helmholtz free energy

$$\Delta F_d = -kT \ln \left( \sum_{i=1}^4 w_i e^{\Delta E_i/kT} \right), \quad (5)$$

where  $k$  is the Boltzmann constant. Again, the energy of  $\alpha$ -boron is used as a reference. The result is shown in Fig. 4. As  $T$  approaches zero,  $\Delta F_d$  becomes the energy difference  $\Delta E_{G,d}$  given by Eq. (4). As previously observed, the effect of the disorder is only a fraction of the total difference  $\Delta E_G$  at  $T=0$ . However, as  $T$  increases, the effect becomes significant through the increase in entropy. The transition occurs at 200 K.

The calculated transition temperature  $T_{\alpha\beta}$  is much lower than the experimental one. In evaluating  $T_{\alpha\beta}$  in this manner, we assume only a perfect form for  $\alpha$ -boron, while various disorders are assumed for  $\beta$ -boron. To our knowledge, any disorder has not been reported for  $\alpha$ -boron. Nevertheless, it is questionable that there is no disorder for  $\alpha$ -boron. The experimental difficulty in the preparation of a sufficiently large specimen of good quality for  $\alpha$ -boron itself implies imperfections and intrinsic defects. It may be inappropriate to estimate the free-energy difference currently, unless the

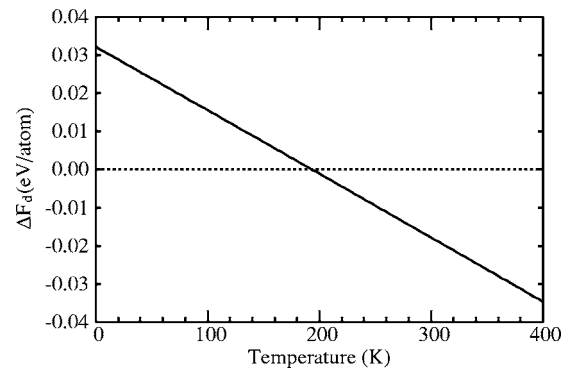


FIG. 4. Difference in Helmholtz free energy  $\Delta F_d$  between  $\alpha$ - and  $\beta$ -boron due to atom disorder. At  $T=0$  K,  $\alpha$ -boron is the stable phase. When temperature exceeds  $\sim 200$  K,  $\beta$ -boron becomes stable.

disordered configurations of both phases are considered on an equal footing.

Accordingly, at present, we defer assessing the transition temperature from the viewpoint of the atom disorder. In Secs. V B and V C, we consider only a perfect high-symmetry structure for  $\beta$ -boron.

### B. Effect of phonons

Usually, most of the finite temperature properties are determined by phonons. The phonon contribution to the free energy is given, using the harmonic approximation, by

$$F_h = \frac{1}{2} \sum_{\ell}^{N_f} \hbar \omega_{\ell} + kT \sum_{\ell}^{N_f} \ln[1 - e^{-\hbar \omega_{\ell}/kT}], \quad (6)$$

where  $\omega_{\ell}$  is the frequency of the  $\ell$ th mode and  $N_f$  is the number of modes. The first term on the right-hand side is the zero-point energy. The remaining term determines the temperature dependence. In this simplest form, the temperature dependence results from the Bose factor only. Anharmonicity brings a lot of complex effects. There are several ways of expressing anharmonic effects, depending on the degree of approximation.<sup>46–48</sup> We utilize the convention of Leibfried and Ludwig.<sup>48</sup> In a perturbative treatment, the phonon contribution is a sum of the harmonic and anharmonic parts; that is,  $F_{ph} = F_h + F_{anh}$ . The first term of this free energy is, of course, given by the harmonic expression, Eq. (6). However, even in  $F_h$ , anharmonicity can have a consequence through the change in  $\omega_{\ell}$  by the volume change. This is the so-called quasi-harmonic approximation. In this case, the first term of the phonon contribution  $F_h$  is replaced with the quasi-harmonic contribution  $F_{qh}$ . It is widely accepted that for mechanical properties, this quasi-harmonic approximation is adequate, while is not for caloric properties, such as the specific heat.<sup>48</sup> In this section, we consider the harmonic contribution only.

Our method of obtaining phonons is a standard frozen-phonon method; hence, the obtained modes are zone-center modes only. In this case, it would be desirable to use the equivalent cell size between  $\alpha$ - and  $\beta$ -boron. However, for a practical reason of computations, we still use the primitive unit cells for both phases. For  $\alpha$ -boron, there is no difficulty in the frozen-phonon calculation. A good agreement between the calculated and experimental phonon spectra has already been obtained.<sup>30,31</sup> In contrast, for  $\beta$ -boron, large-scale calculations severely restrict the accuracy of calculation.

The error in the force  $\Delta f$  is converged only by the order of the square root of the energy error,  $\Delta f \sim \sqrt{\Delta E}$ . For maintaining the same accuracy of  $f$  for both phases, we should maintain the accuracy of  $\Delta E$  of the same order of magnitude for both phases. Fulfilling this requirement for  $\beta$  boron is very difficult. Even worse for  $\beta$ -boron is that more low-frequency modes are involved; thus, a requirement of convergence for  $\Delta E$  becomes more severe. By the residual force in self-consistent calculations, the frequency resolution is estimated to be around  $100 \text{ cm}^{-1}$ . Low-frequency modes less than this should be ignored. In fact, for  $\beta$ -boron, we have four imaginary-frequency modes, besides three acoustic

TABLE VI. Phonon properties: number of nonzero-frequency modes  $N_f$  and the zero-point energy  $U_{ph}^0$ .

Modification	$N_f$	$U_{ph}^0$ (meV/atom)
$\alpha$ -boron	33	128.7
$\beta$ -boron	312	124.1
$\Delta U_{ph}^0 = U_{ph}^0(\beta) - U_{ph}^0(\alpha)$	=	-4.6

modes. In the following, we simply ignore these imaginary-frequency modes, and consider the average of the remaining 308 modes in determining thermodynamic properties.

Aside from this difficulty, a good thing for borons is that even  $\alpha$ -boron is already a large cell, so that even  $\Gamma$ -point calculations can give a description of the phonon properties at some levels. In the phonon dispersion of  $\alpha$ -boron,<sup>31</sup> we observe that the dispersion is weak.

The numbers of phonon modes are listed in Table VI. Once the phonon spectra are obtained, we can easily evaluate the free energy as a function of  $T$ , and other properties, such as the specific heat, using the harmonic approximation. By analyzing the specific heat, we can determine the validity of this approximation. Figure 5 shows a comparison between the calculated and experimental specific heats. The experimental ones are for amorphous boron.<sup>49</sup> In many respects, the physical properties of amorphous boron are considered to be similar to those of  $\beta$ -boron.<sup>17</sup> Therefore, we may regard the specific heat of amorphous boron as similar to that of  $\beta$ -boron.

It should be noted that the experimental specific heat is obtained at a constant pressure  $C_p$ , while the calculated specific heat is obtained at a constant volume  $C_v$ . These two specific heats are thermodynamically related,<sup>50</sup> as shown by

$$C_v = C_p - \alpha_v^2 V_0 B_T T, \quad (7)$$

where  $\alpha_v$  is the volume-thermal expansion coefficient,  $V_0$  is the volume per atom, and  $B_T$  is the bulk modulus obtained by the isothermal process. Using the experimental  $\alpha_v$ ,<sup>51</sup> we can

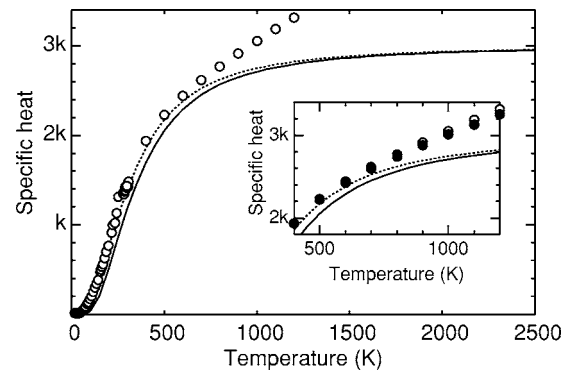


FIG. 5. Comparison of calculated and experimental specific heats. Solid and dashed lines indicate the calculated specific heats of  $\alpha$ - and  $\beta$ -boron, respectively. Open circles indicate experimental specific heats  $C_p$  (amorphous boron).<sup>49</sup> Closed circles in the inset indicate experimental  $C_v$  values evaluated using Eq. (7).

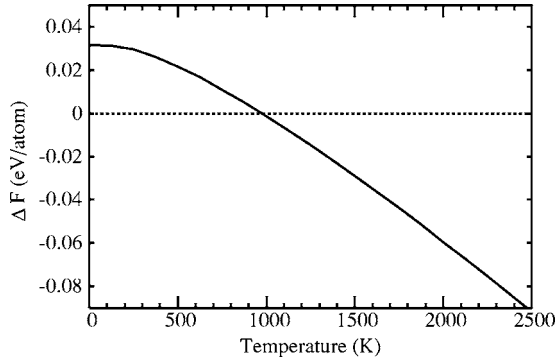


FIG. 6. Energy difference  $\Delta F$  of total free energy  $F=E_G+F_h$  between  $\alpha$ - and  $\beta$ -boron.  $F_h$  denotes the harmonic part of the phonon contribution. At  $T=0$  K,  $\alpha$ -boron is the stable phase. When temperature exceeds 970 K,  $\beta$ -boron becomes stable.

obtain  $C_v$  from  $C_p$ . The results are indicated by closed circles in the inset of this figure. For  $\beta$ -boron, a good agreement between the calculated and experimental results is obtained in the range  $T < 600$  K. The harmonic approximation is considered adequate for this temperature range. For  $T > 600$  K, the experimental  $C_v$  begins to deviate from the calculated one and even exceeds the classical limit of the Dulong and Petit law. This indicates that the anharmonic contribution  $F_{\text{anh}}$  becomes significant in this high-temperature range. For the evaluation of  $F_{\text{anh}}$ , not only the contribution of the cubic terms to the free energy  $F_3$  but also that of the quartic terms  $F_4$  should be considered on equal footing.<sup>47,48</sup> We do not discuss this topic any further.

Let us compare the zero-point energies  $U_{\text{ph}}^0$  listed in Table VI. The phonon energy of  $\alpha$ -boron is higher than that of  $\beta$ -boron by 3.6%. This is reasonable because we have already known that  $\alpha$ -boron is stiffer than  $\beta$ -boron with respect to the bulk modulus. Thermodynamically, however, stiffness means instability because of the decrease in entropy via the increase in vibration frequency. The ground-state energy is a sum of the total energy and zero-point energy  $U_{\text{ph}}^0$ . The difference in ground-state energy between the  $\beta$  and  $\alpha$  phases is

$$\Delta U^0 = \Delta E_G + \Delta U_{\text{ph}}^0 = +31.7 \text{ meV/atom.} \quad (8)$$

Accordingly,  $\alpha$ -boron is still stable at  $T=0$  K.

Comparing Eq. (8) to Eq. (2), the energy correction by phonons is small at  $T=0$  K. However, the phonon contribution becomes significant at high temperatures with the increase in entropy. The difference in the total free energy  $F=E_G+F_h$  between the  $\alpha$  and  $\beta$  phases is plotted as a function of  $T$  in Fig. 6. At  $T=970$  K, the stable phase is changed from the  $\alpha$  phase to the  $\beta$  phase. This transition temperature  $T_{\alpha\beta}$  is reasonable, compared to the experimental value,  $\sim 1400$  K.

As shown in Fig. 5, in the range  $T > 600$  K, in which the transition temperature is found, the harmonic approximation is inadequate; hence, the free energy is expected to deviate from that calculated using Eq. (6). Although an accurate description of the anharmonic effect on the free energy is currently not possible, we can infer qualitatively the effect of cubic anharmonicity. As seen in Sec. IV, the cubic terms of

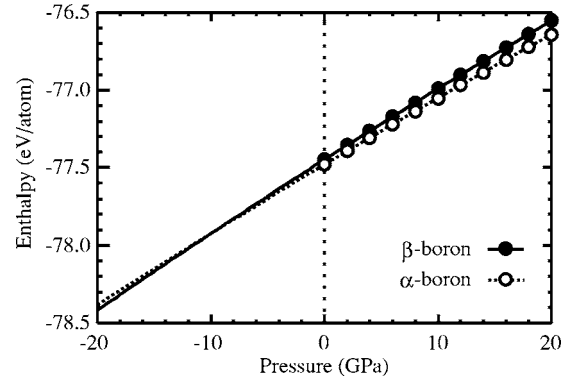


FIG. 7. Pressure dependence of enthalpies of  $\alpha$ - and  $\beta$ -boron. These curves are nearly linear. The two lines intersect each other at  $p=-9.93$  GPa.

anharmonicity  $\Phi^{(3)}$  are larger in the  $\alpha$  phase than in the  $\beta$  phase. The cubic terms  $\Phi^{(3)}$  contribute to the free energy as  $F_3 \sim -(\Phi^{(3)})^2$ , i.e., a negative contribution.<sup>47,48</sup> This makes the free energy of the  $\alpha$  phase lower than that of the  $\beta$  phase. As a consequence, the transition temperature increases. Therefore, we expect that the discrepancy in transition temperature will be reduced to some extent. However, to quantitatively estimate the effect of anharmonicity, we should evaluate the quartic terms as well, as previously described.

In summarizing the arguments up to this point, we can again characterize, but with conviction this time, that  $\alpha$ -boron is mechanically stable, while  $\beta$ -boron is thermodynamically stable. In the present context, the mechanical stability is referred to when the elastic part  $E_G$  is dominant. In contrast, the thermodynamical stability is referred to when  $TS$  is dominant, whether this has its phonon or disorder origin. In this sense, it would be better to refer to “entropically stable.” This feature is by no means specific to boron, but may be a ubiquitous feature among various crystals. We can find, in normal metals, this property that the low-temperature phase is mechanically stable, while the high-temperature phase is thermodynamically stable.<sup>52</sup> Recent studies of BN show that a dense (cubic) phase is stable at low temperatures, whereas a dilute (hexagonal) phase is stable at high temperatures.<sup>53</sup>

### C. Effect of volume change

In thermal expansion, the volume  $V$  changes due to anharmonicity. Since  $V$  is a macroscopic parameter that directly specifies thermodynamic states, the change in  $V$  results in changes in microscopic anharmonic parameters.<sup>54</sup> A standard description of thermodynamic states when  $V$  is varied is given by the enthalpy  $H=U+pV$ . Here, the internal energy  $U$  in the thermodynamics contains the elastic energy  $\Phi_{\text{el}}$  and phonon energy  $U_{\text{ph}}$ , as  $U=\Phi_{\text{el}}+U_{\text{ph}}$ . The elastic energy  $\Phi_{\text{el}}$  is what we obtain by calculating the total energy  $E_{\text{tot}}$ ; in this case, it can be evaluated using the optimized structure at a fixed pressure  $p$ .

The enthalpy variation as a function of  $p$  at zero temperature is shown in Fig. 7. The structural optimization is carried out by imposing the symmetry constraint  $R\bar{3}m$ . We observe



that the change in enthalpy is nearly linear in  $p$ ; thus, the pressure dependence of  $H$  is dominated by the  $pV$  term.

The difference in the enthalpy  $\Delta H_{\alpha\beta}$  between  $\alpha$ - and  $\beta$ -boron at zero pressure is equal to  $\Delta U_0$  given by Eq. (8). The difference increases with increasing pressure. This indicates that  $\alpha$ -boron becomes more stable at high pressures. This is reasonable because  $\alpha$ -boron is denser than  $\beta$ -boron. On the other hand, if the volume is expanded,  $\beta$ -boron would be stabilized. Dilute systems are energetically favorable for low (or negative) pressures. This is consistent with the fact that all of the tetragonal phases, which are synthesized only at high temperatures, are more dilute than the  $\alpha$  phase, as described in Sec. II. At this point, we can qualitatively describe that the stability at low (or negative) pressures is akin to the stability at high temperatures.

Finally, the effect of volume change on the estimation of the transition temperature is discussed. When the pressure is varied, the effect on  $H$  is straightforward, that is, of the first order, because of  $H=E+pV$ . On the other hand, when the temperature is varied, the effect on  $F$  is only of the second order, if the stress free condition is imposed.<sup>48</sup> This may be expressed as

$$F(T) = F_0 + F_0^{\text{ph}}(T) - \frac{1}{2} \frac{F_v(T)^2}{B_0 V_0}, \quad (9)$$

where the second term on the right-hand side represents the phonon contribution to  $F$  at a constant volume, whereas the third term represents the contribution of volume change. Here,  $F_v$  is the partial derivative of  $F_0^{\text{ph}}$  with respect to  $v = \ln V$ . This is related to the temperature-dependent coefficient of the thermal expansion  $\alpha_v(T)$  as  $\alpha_v(T) = -(1/B_0 V_0) \partial F_v(T) / \partial T = -\bar{\gamma} C_v(T) / B_0 V_0$ , where  $\bar{\gamma}$  is the averaged mode-dependent Grüneisen constant.

Using  $\gamma_G$  obtained in Sec. IV, we obtained  $\alpha_v(T)$ . The  $\alpha_v$  value obtained is  $3.1 \times 10^{-5}/\text{K}$  at room temperature, which is three times as large as the experimental one.<sup>51</sup> By integrating  $\alpha_v$  from  $T=0$ , we obtained  $F_v(T)$  and thereby  $F(T)$ . In this manner, we evaluated  $\Delta F(T)$  between the  $\alpha$  and  $\beta$  phases as a function of  $T$ . A numerical estimation shows that the effect of the third term of Eq. (9) on the transition temperature  $T_{\alpha\beta}$ ,  $< 10$  K, is insignificant. Therefore, the estimated  $T_{\alpha\beta}$  shown in Sec. V B, ignoring the thermal expansion, is sufficient.

## VI. CONCLUSIONS

We have studied various properties of  $\beta$ -boron by the *ab initio* pseudopotential method. By comparing to those of the well-studied  $\alpha$  phase, the features of  $\beta$ -boron can be clarified.

In short, the basic difference of the two phases can simply (maybe best) be described using the atom density; the  $\alpha$

phase is dense, while the  $\beta$  phase is dilute. Accordingly, the  $\alpha$  phase is stiff, while the  $\beta$  phase is soft. This is shown by the bulk modulus and phonon frequencies. From this, it is reasonable to consider that the  $\alpha$  phase is more stable than the  $\beta$  phase at  $T=0$  K. The energy difference is 36.3 meV/atom. The traditional interpretation based on the chemistry's viewpoint, i.e., more association of boron atoms is energetically favorable, is correct in terms of the electronic part of the total energy. However, another contribution of the Coulomb repulsion between ions completely spoils this energy gain, which makes the  $\alpha$  phase more favorable at  $T=0$  K.

The atomic disorder observed at site B(13) is inherent to the  $\beta$  phase. The energy gain due to this disorder is only a few million electron volts at  $T=0$  K, but becomes significant at high temperatures because of the increase in entropy. However, we defer to determine the effect of this disorder on the transition temperature because of lack of information about such disorders in  $\alpha$ -boron. Around this site, the experimental bond lengths slightly deviate from the theoretically predicted ones, assuming the perfect symmetry. The deviation of these bond lengths itself is regarded as signature of occurring of disorder.

The contribution of phonons to the free energy is also significant. At high temperatures, the  $\beta$  phase becomes stable. This stability is due to the softness of  $\beta$ -boron; the phonon frequencies of  $\beta$ -boron are relatively low, which results in an increase in entropy at high temperatures.

Using the harmonic approximation, we have estimated the transition temperature  $T_{\alpha\beta}$ , to be 970 K. This value is reasonable by considering various uncertainties. By comparing the calculated specific heat to the experimental one, we found that anharmonic effects appear above 600 K. This may affect the estimation of the transition temperature.

The stability of the  $\alpha$  phase at low temperatures increases with pressure. On the other hand, the  $\beta$  phase is a dilute system and, accordingly, it becomes stable when the volume is expanded. Tetragonal phases are intermediate between them. The effect of volume expansion on the transition temperature is insignificant; that is, it is only of the second order.

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