High-pressure properties of icosahedron-based solid borons

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High-pressure experiments have led to significant contributions to understanding of physical properties of icosahedron-based solid boron. In this paper, we critically review recent results on properties of boron polytypes. The topics discussed are stability of α- and β-boron, elastic properties, phonon properties. In interpreting high-pressure experiments, special care is needed. In many cases, confusion is emerged from difference between the macroscopic applied deformation and the resulting microscopic displacement of atoms.

1   Introduction

Boron crystals have many fascinating properties. First, there are many variety of polymorphic modifications, such as α-, β-boron, most of which are classified as semiconductor [1, 2]. Selected properties of these polymorphs are listed in Table 1. Boron is distinct from usual semiconductors at a point that the crystal structures are composed of icosahedra B_{12}. On the other hand, it is also different from molecular crystals, such as fullerenes, at a point that the *inter*molecular (*inter*icosahedral) bond is stronger than the *intra*molecular (*intra*icosahedral) bond. The *inter*icosahedral bond is characterized as strong covalent bond. This special situation leads some researchers to refer to it as *inverted*-molecular crystal [3].

Recent discovery of superconductivity of boron at high pressures [4] attracts much attention to this material. At present, the high-pressure phase is yet unknown, even though many researchers attack to this problem [5–7]. But, before studying high-pressure phase, we must recognize that even at normal conditions relative stability among various polymorphic modifications is a controversial issue.

In addition, there are seemingly contradictions among experimental and theoretical studies concerned with the above traditional understanding. We have witnessed that suspicion to this understanding sometimes arose by showing new experimental data. Many of these are related to high-pressure experiments.

We have systematically studied the physical properties of α-, β-boron, and boron carbide, by model and *ab initio* calculations [8–11]. Those properties studied include the atomic structure and its pressure dependence, phonon spectra, elastic properties, thermodynamic properties. Now, we can answer for the above questions. In this paper, we critically review recent results of studies on the properties of boron concerned with the above issues.

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Table 1 Comparison of various polymorphs of boron [1]. The preparation temperature T_{prep} are given for illustration purpose only. The number of atoms per cell N_{atom} and atomic volume Ω_{atom} are given.

polymorph	T_{prep} (°C)	N_{atom}	Ω_{atom} (Å^3)
α-rhomb.	~1000	12	7.2823
β-rhomb.	>1100	105	7.8533
α-tetra. (I)	1150 ~ 1300	50	7.7481
tetra. (III)	1280 ~ 1500	~192	7.5424
tetra. (II)		~78	7.6552

2 Crystal structures

Among variety of polymorphs of boron, α- and β-rhombohedral boron are the most commonly obtained phases. These structures are illustrated in Fig. 1. In β-boron, there are 105 atoms in a unit cell. Icosahedra are placed at each corner of the rhombohedron and the center of each side. In addition, a $B_{10} - B - B_{10}$ chain is placed along the main diagonal of the cell. Ideally, the crystal has $R\bar{3}m$ symmetry. In real crystals, some sites have a partial occupancy [2]. This is not due to careless preparation, but specific types of disorder have a role to stabilize the crystal structure of β-boron [11].

3 Stability of α- and β-phases

Experimentally, it is known that at high temperatures β-boron is synthesized, while α-boron is synthesized only at low temperatures. The boundary temperature $T_{\alpha\beta}$, although depends on the preparation method, can be estimated about 1500 K [1]. Until recently, there was no theoretical understanding to this transition temperature. Now, we have succeeded to give a proper account for the stability of α- and β-phases and its transition temperature [11]. According to this study, the basic properties of α- and β-phases are summarized as follows.

(i) Zero-temperature properties; At $T = 0$ K, α-boron is more stable than β-boron. The energy difference is 18.7 meV/atom, including the effect of the zero-point vibrations. The bulk modulus of α-boron is larger than that of β-boron. This is consistent with the fact that α-boron is denser than β-boron.
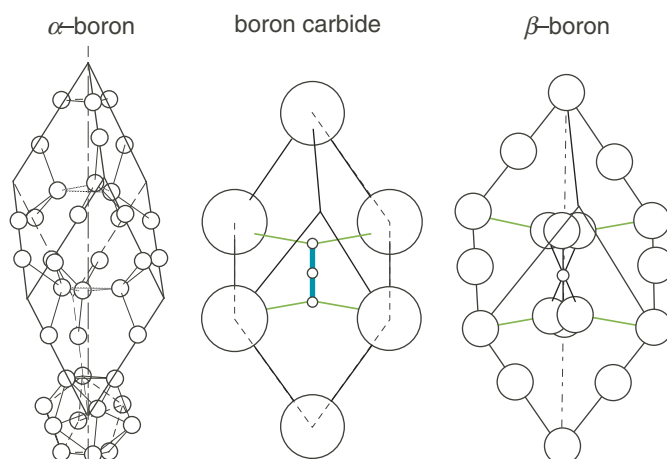

Fig. 1 Crystal structure of α-, β-boron, and boron carbide. The icosahedral units B_{12} are symbolized by large open spheres for boron carbide and β-boron. The lattice parameter of β-boron is twice of that of α-boron. The orientation of adjacent icosahedra is different between α- and β-boron.
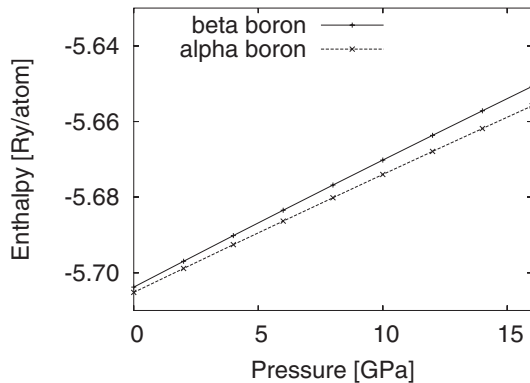
Fig. 2 Calculated enthalpy H of α- and β-boron as a function of pressure p.

(ii) High-temperature properties; At high temperatures, β-boron is more stable than α-boron. The predominant mechanism of this stability comes from the phonon contribution. In terms of phonons, β-boron is soft, which reduces the free energy at high temperatures.

High-pressure study of solid boron has significance on the stability of various polymorphs. We have calculated enthalpy $H = E + pV$ of α- and β-boron as a function of pressure p at $T = 0$ K. Here, E is the total energy evaluated with the optimized structure at each p. As seen in Fig. 2, stability of α-boron is increased with increasing p. The relationship between H and p is almost linear. The pressure dependence of H is expressed as

$$\frac{\partial H}{\partial p} = V\left(\frac{p}{B} + 1\right), \tag{1}$$

where B is the bulk modulus. In the pressure range examined, the p dependence of H is dominated by the second term of the right-hand side of Eq. (1); that is, the stability under pressures is dominated by the volume, or the density. Therefore, it is reasonable to see the stability of α-boron at high pressures, because of its dense character as shown in Table 1.

From this dependence, it is seen that β-boron is stabilized at negative pressures. The situation of negative pressure is realized by thermal expansion. What is inferred by this is that, at high temperatures, low-density phases are thermodynamically stable. This is consistent with the fact that all high-temperature phases, β and tetragonal phases, are dilute compared to the α phase. When finite temperature is involved, however, careful analysis is required, which is given elsewhere [11].

4 Interpretation of high-pressure experiments

High-pressure experiment is an abundant source of our understanding for condensed-matter physics. In the following, we select topics of high-pressure experiments which are useful to study physical properties of boron.

4.1 Comparison of *inter* and *intra*icosahedral bonds

As described at the beginning, the traditional understanding of the nature of bonds in boron is that the *inter*icosahedral bond is stronger than the *intra*icosahedral bond. This is proven by electronic structural and phonon calculations [3, 10, 12]. The force constant of the *inter*icosahedral bond f_{rh} is thee times as large as that of the *intra*icosahedral bond f_{in} [12].

An objection to this understanding is repeatedly stated on the basis of the volume compressibility. In Table 2, available data for compressibility K are compared. Numeric values depend on how to define. It is seen that in most cases the compressibility is less in the *intra*icosahedron than the unit cell. From this, the authors of Refs. [14, 15] state that the traditional understanding is wrong.

Table 2 Comparison of compressibility of α-boron and boron carbide in 10^{-3} GPa^{-1}. Compressibility K is defined by $\partial \ln \xi / \partial p$, where ξ is defined differently among available data. Distinction of model and *ab initio* (ab) calculations is made. For the icosahedron, the deformation is described by the change in the height (H) and width (W), if possible.

ξ	α-boron		boron carbide		
	model [10] r	ab [15] V	exp. [13] V	ab [15] V	ab (this study) r
cell		−4.50	−4.9	−4.03	−1.16
inter	−2.1				
intra	−1.8	−3.36	−6.1	−3.64	(H/W) −0.96/−1.20
chain					−0.60

This argument, however, overlooks a large difference in the number of bonds. For the macroscopic deformations, the elasticity is determined by balance between how strong the individual bond is and how many such bonds are involved. The number of the *intra*icosahedral bonds N_{in} is 10 times larger than that of *inter*icosahedral bonds N_{rh}. Because of this large difference, even by assuming large *inter*icosahedral bond, i.e., $f_{rh} \approx 3f_{in}$, we can get a conclusion that the compressibility of *intra*icosahedral bond K_{in} is larger than that of *inter*icosahedral bond K_{rh} as seen in Table. 2. Therefore, *the fact that K_{in} is comparable to K_{rh} or even slightly larger than that, itself indicates the strong character of the* inter*icosahedral bond!* In phonon spectra, we observe the strength of individual bonds, whereas in macroscopic elastic properties we observe the effect of all of the bonds together.

4.2   Elastic response under uniaxial stress

The icosahedron of boron is stiff as a whole *for uniform deformation,* as seen in the preceding subsection. However, it is relatively deformable for other types of deformation, like balloon. A balloon is quite deformable, but is relatively stiff when it is uniformly compressed. In this subsection, the effects of this deformity of icosahedron are examined.

In α-boron, the strongest *inter*icosahedral bonds are aligned nearly along the c-axis. From this, it is easily expected that the component of elastic constant C_{33} is stronger than C_{11}. This is confirmed by calculations [9]. For boron carbide, a more strong bond of the CBC chain is inserted in the main diagonal of the unit cell. Surprisingly, the calculated C_{33} is even smaller than C_{11} [9].

This unexpected result is a consequence of the atom relaxation for externally applied stress. The *inter*icosahedral bonds are slightly deviated from the lattice vector of the rhombohedral unit cell, as shown in Fig. 3. For α-boron, these bonds are slightly upright. When a compression is applied along the c-axis, the icosahedra become more flat, and the *inter*icosahedral bonds become more upright. This way of deformation is in which the external stress is applied. Hence, the relaxation is not efficient, and the crystal exhibits stiff in this direction. On the other hand, for boron carbide, the *inter*icosahedral bonds slightly lie down. When a compression is applied along the c-axis, the icosahedra are elongated in this direction,
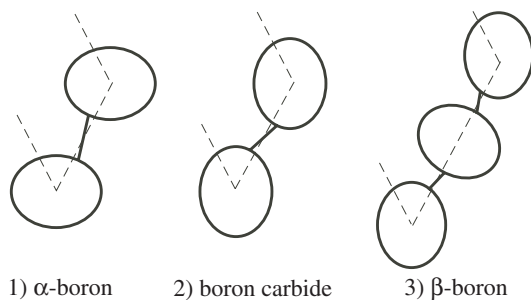

1) α-boron   2) boron carbide   3) β-boron

Fig. 3 Comparison of deformation of icosahedra under hydrostatic pressures. The dashed lines indicate the lattice vectors of the rhombohedral unit cell, and the solid lines indicate the *inter*icosahedral bonds. Note that there is a little deviation in the orientation of the *inter*icosahedral bonds from the lattice vector. The deviation is different from crystal to crystal.

Table 3 Variation of the cell angle α_0 against p obtained by the present *ab initio* calculations.

	$\alpha_0 - 60$ (°)	$\partial \ln \alpha_0/\partial p$ GPa^{-1}	exp.
α	-1.35	-1.14×10^{-4}	
boron carbide	$+6.4$	$+2.0 \times 10^{-4}$	
β	$+5.22$	$+1.40 \times 10^{-4}$	$+1.39 \times 10^{-4}$ [6]

and the *inter*icosahedral bonds lie down further. This way of deformation is in which the external stress is relaxed. Hence, the relaxation is efficient, and the crystal exhibits soft in this direction.

The presence of soft part could spoil completely the stiff part of crystal. In Ref. [16], the situation is described nicely in a pictorial way by using analogy to magic hand. It is noted that even the presence of stiff bond of the chain does not prevent this relaxation, because the chain is supported by bonds nearly in the *ab* plane, in which situation the stress is completely absorbed in the icosahedron-chain bonds.

4.3   Deformation of icosahedra under hydrostatic pressure

The related subject to the previous one is the deviation of the cell angle under hydrostatic pressures. The primitive unit cell of fcc structure can be regarded as a special case of the rhombohedral cell with the apex angle 60°. The deviation of this rhombohedral angle α_0 from 60° may be a measure how to extent the crystal is anisotropic.

As seen in Table 3, the cell angle α_0 is slightly smaller than 60° in α-boron, while larger in boron carbide. This is a consequence of deformity of the icosahedra of boron, as discussed in Sec. 4.2. The way of deformation is determined by the orientation of the strong *inter*icosahedral bonds. For α-boron, the icosahedron is elongated in the *ab*-plane, while for boron carbide it is elongated in the *c*-axis. Application of pressure makes the deformation process more forward. The positive deviation of the angle α_0 from 60° becomes more positive, and the negative deviation does more negative, as seen in Table 3.

The type of deformation of β-boron belongs to that of boron carbide. In terms of the magnitude of variation, the case of β-boron is an intermediate between α-boron and boron carbide. This is because different types of deformation of icosahedra are involved, as shown in Fig. 3. By observing that the *a*-axis is less compressible than *c*-axis in β-boron, the authors of Ref. [6] claimed that the chain structure $B_{10} - B - B_{10}$ is less rigid than B_{12}. As already seen in Sec. 4.2, *softness of the crystal in the c-direction should not be a sign of softness of the diagonal element, but is a consequence of deformity of the icosahedra.* In fact, the chain of boron carbide is less compressed, even though the unit cell is largely shrunk in this direction, as seen in Table 2.

4.4   Ghost band in Raman spectrum of α-boron

In the Raman spectrum of α-boron [18, 19], it is known that there is a strange band at 520 cm^{-1}. The line width is quite narrow. For this reason, along with others, it was a common practice to treat it differently from usual phonon scattering. Now, it has been clarified that the origin is nothing other than usual phonon scattering [14]. The phonon mode underlying this band is a librational mode of the icosahedron. Their work of this attribution is wonderful. But, their interpretations are inappropriate with some respects.

The frequency of librational modes ω_l is determined by angle forces, and hence the frequency is usually low, less than 100 cm^{-1}. Accordingly, the high frequency of this librational mode seems to suggest unusually large angle forces. Contrary to this simple expectation, the force constants of individual angles are not too large [10]. What makes the frequency so high is again the large number of angles involved in this mode. The interesting properties of this librational mode are not exhausted by this high-frequency property, but further extraordinary properties are involved, with which we proceed our discussion.

4.5 Pressure dependence of the frequency

Pressure dependence of the Raman band of α-boron has been examined both experimentally and theoretically [14]. Pressure dependence of phonon frequency means anharmonicity. In a simple theory, it is directly related to Grüneisen constant $\gamma \equiv \partial \ln \omega / \partial v$, where $\delta v = \delta V / V$. The value of γ is almost the same for all the Raman bands, namely, 0.9. Again, an exception is that of the librational mode. It exhibits almost no pressure dependence. Does it mean negligible anharmonicity for the angle forces? No! Let us analyze the pressure dependence of phonon frequency more closely. The volume dependence comes about through two steps as

$$\frac{\partial \ln \omega}{\partial v} = \frac{\partial \ln \omega}{\partial \ln \xi} \frac{\partial \ln \xi}{\partial v} \, , \tag{2}$$

where ξ is the bond length (angle) which determines the frequency. The first term of the right-hand side of Eq. 2 is the microscopic anharmonicity, i.e., cubic terms in the adiabatic potential. This part is not at all small for the angle force of boron. In Table 1 of Ref. [17], the cubic anharmonicity of boron is compared to those of Si. The reader can see that boron is not unusual. The second term of Eq. 2 bridges the macroscopic variation of the volume to the microscopic variation of the bond length (angle). It is this term which makes the pressure dependence of the librational mode different from what is usually expected. Under uniform deformation, most of angles are not changed. Hence, the second term kills the effects of the microscopic anharmonicity on the pressure dependence.

4.6 Line width

The most interesting issue about this librational mode is why the line width is so narrow. Many effects contribute this line width. The detailed discussion should be referred to [10]. In short, the most important mechanism of the narrow line width is a thermal effect of phonon population. Among the zone-center phonon modes, the librational mode is only such a mode for which the phonon-decay processes are dominated by up-conversion process, i.e., $\omega_l + \omega_1 \rightarrow \omega_2$. This type of decay process is inactivated at very low temperature. This fact itself is common in other materials possessing librational modes. What makes boron distinct from others is that the librational mode is exceptionally high, so that even room temperature can be regarded as low temperature for boron.

5 Summary

Throughout the present discussion, we have seen that high-pressure experiment made important contributions to our understanding of the physical properties of boron. The pressure dependence of enthalpy provides a good guidance for the stability of many polymorphs.

We have also seen that interpretations of high-pressure experiments are sometimes confusing. In many cases, confusion is emerged from difference between the macroscopic applied deformation and the resulting microscopic displacements of atoms. These two are not necessarily identical, nor similar. This is true particularly for complicated crystals, which have a large degree of freedom in the internal coordinates, which could exhibit unexpectedly large relaxation.

References

[1] N. N. Greenwood, in: Comprehensive Inorganic Chemistry, edited by J. C. Bailar, H. J. Emeléus, Sir R. Nyholm, and A. F. Trotman-Dickenson (Pergamon, Oxford, 1973), Chap. 11.
[2] J. L. Hoard, D. B. Sullenger, G. H. L. Kennard, and R. E. Hughes, J. Solid State Chem. **1**, 268 (1970).

[3] D. Emin, Phys. Today **40**, 55 (1987).
[4] M. I. Eremets, V. V. Struzhkin, H. Mao, and R. J. Hemley, Science **293**, 272 (2001).
[5] D. N. Sanz, P. Loubeyre, and M. Mezouar, Phys. Rev. Lett. **89**, 245501 (2002).
[6] Y. Ma, C. T. Prewitt, G. Zou, H. Mao, and R. J. Hemley, Phys. Rev. B **67**, 174116 (2003).
[7] J. Zhao and J. P. Lu, Phys. Rev. B **66**, 092101 (2002).
[8] K. Shirai and S. Emura, J. Phys.: Condens. Matter **50**, 10919 (1996).
[9] K. Shirai, Phys. Rev. B **55**, 12235 (1997).
[10] K. Shirai and H. Katayama-Yoshida, J. Phys. Soc. Jpn. **67**, 3801 (1998).
[11] A. Masago, K. Shirai, and H. Katayama-Yoshida, in preparation.
[12] C. L. Beckel, M. Yousaf, M. Z. Fuka, S. Y. Raja, and N. Lu, Phys. Rev. B **44**, 2535 (1991).
[13] R. J. Nelmes, J. S. Loveday, R. M. Wilson, W. G. Marshall, J. M. Besson, S. Klotz, G. Hamel, T. L. Aselage, and S. Hull, Phys. Rev. Lett. **74**, 2268 (1995).
[14] V. Vast, S. Baroni, G. Zerah, J. M. Besson, A. Polian, M. Grimsditch, and J. C. Chevin, Phys. Rev. Lett. **78**, 693 (1997).
[15] R. Lazzari, V. Vast, J. M. Besson, S. Baroni, and A. Dal Corso, Phys. Rev. Lett. **83**, 3230 (1999).
[16] K. Shirai, J. Solid State Chem. **133**, 215 (1997).
[17] K. Shirai and H. Katayama-Yoshida, J. Solid State Chem. **154**, 20 (2000).
[18] W. Richter and K. Ploog, phys. stat. sol. (b) **68**, 201 (1975).
[19] D. R. Tallant, T. L. Aselage, A. N. Campbell, and D. Emin, Phys. Rev. B **40**, 5649 (1989).