Equation of State and Pressure Induced Amorphization of β-Boron from X-Ray Measurements up to 100 GPa

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The equation of state of boron has been measured up to 100 GPa by single-crystal x-ray diffraction with helium as the pressure transmitting medium. Rhombohedral β-boron is the stable structure up to 100 GPa under hydrostatic conditions. Nonhydrostatic stress stabilizes a different rhombohedral structure. At about 100 GPa a pressure-induced amorphization is observed. The amorphous phase can be quenched to ambient pressure. An explanation is proposed based on the different stability under pressure between intraicosahedra and intericosahedra bonds.

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Owing to its unusual chemical bonding, elemental boron is a material with remarkable features [1]. Boron also occupies an important place in the field of materials science. Boron-rich compounds have technologically interesting properties such as superhardness [2] or high-temperature superconductivity [3]. The properties of boron at ambient pressure have been extensively studied, and they are still of great interest [4]. Boron can exist under four crystalline modifications and an amorphous one. All these polymorphs have the same structural unit: a boron icosahedron, B_{12}. However, boron is not a molecular solid because the B_{12} cluster is not stable by itself. With only three valence electrons, boron can fulfill the fivefold bonding within the icosahedra and the intericosahedra bonding by developing an uncommon covalent bond. There are three-center (3c) bonds on the 20 triangular planes of the icosahedron and two-center (2c) covalent bonds between icosahedra. It has been recently established that the 2c bonds is as strong as or weaker than the 3c bonds [4,5]. The simplest structure, α-boron, is constructed from only one icosahedron in a rhombohedral unit cell. The energetically favored structure, β-boron, has a much larger rhombohedral unit cell with 105 atoms. It consists almost entirely of icosahedra in a rather complicated array, and with, along the main diagonal of the unit cell, a partial condensation of icosahedra [6].

Compared to other low-Z elements, the properties of boron at high pressure have hardly been studied. High enough pressure should destroy covalent bonds favoring a more uniform electron density. In a recent conductivity measurement, β-boron has been observed to transform from a nonmetal to a superconductor at 160 GPa, with a pressure dependence of the resistance showing visible steps that could be attributed to structural changes [7]. But these structural changes and their driving mechanisms are unknown, and many questions arise. In particular, are the 2c covalent bonds more affected by pressure than the 3c metalliclike bonds? Which pressure are the icosahedra stable up to? The determination of the equation of state (EOS) is certainly an important measurement to progress in the understanding of boron. In a recent study, x-ray diffraction was performed on β-boron up to 31 GPa and 3500 K. At high-temperature, a transition to the tetragonal phase (T-192) was observed at ~10 GPa, and this tetragonal phase was proposed to be the stable boron phase at high pressure [8]. We report here an accurate determination of the equation of state up to the 100 GPa range. Interesting structural changes are observed that are related to the resistance steps observed in Ref. [7]. Under hydrostatic conditions, β-boron is stable up to 98 GPa. But under nonhydrostatic conditions, an intermediate rhombohedral phase appears. At ~100 GPa, the disappearance of the diffraction peaks indicate a transition to an amorphous phase which has been quenched to ambient pressure.

With the use of third generation synchrotron sources and the single-crystal x-ray diffraction technique, the structural properties of most low-Z systems can now be extended in the 100 GPa range [9]. In the case of boron, the complicated structure and the hardness of the material enhance the difficulties arising from its low-Z value ($Z = 5$). For a complicated structure such as β-boron, the diffracted intensity is distributed in many peaks. That is tantamount to say that measuring the x-ray pattern of β-boron is as difficult as studying an element with $Z = 1.7$ and a simple fcc structure. Also, boron needs to be nested in a quasihydrostatic pressure medium, helium, in order to keep the hydrostatic conditions while compressing. In the 100 GPa range, the boron crystallite should not be of larger dimensions than 6 μm. Therefore, the structural study of boron in the 100 GPa range is almost of the same order of difficulty as the one of hydrogen.

Four experiments have been performed so as to cover different pressure ranges (runs *A–D*), to test the influence of nonhydrostatic pressure and to characterize phase transitions. The boron sample (0.996 purity), powder or single crystal, was loaded in membrane diamond anvil cells (DAC) equipped with boron seats for a large x-ray aperture [9]. Helium was used as the pressure transmitting medium in all the experiments. The pressure was measured with the hydrostatic ruby scale [10]. In runs *A* and *B*, boron powder was loaded in the DAC. A typical spectra measured by angle-dispersive diffraction with a 0.533 96 Å monochromatic beam and a MAR image plate detector is shown in Fig. 1. A structural refinement with the hexagonal setting of β-boron (320 atoms in the hexagonal cell) reproduces very well the diffraction pattern.

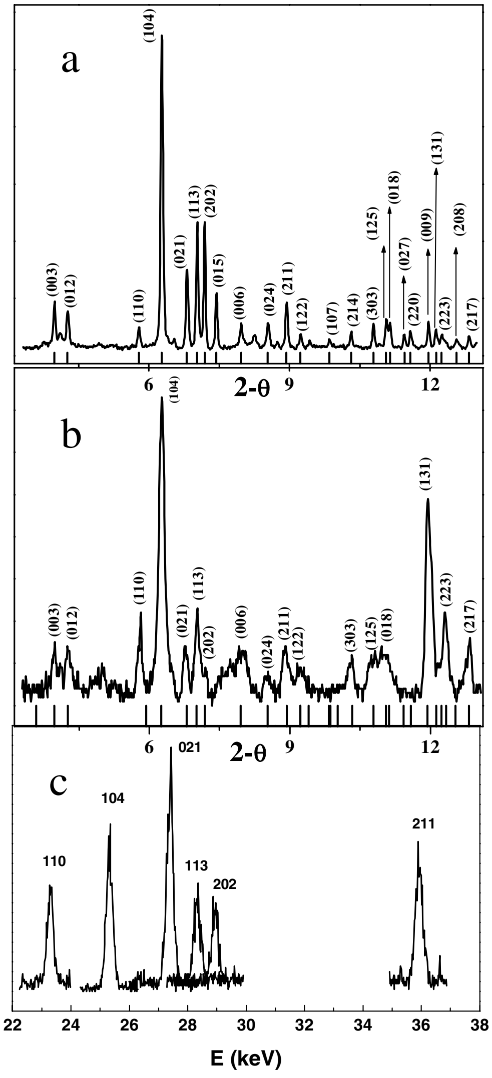

FIG. 1. Selected examples of the x-ray diffraction spectra of boron with different techniques: (a) Angle dispersive x-ray (ADX) powder diffraction of β-boron powder in helium at 21 GPa; (b) ADX powder diffraction of the stress stabilized rhombohedral phase of boron at 31 GPa; (c) Energy dispersive single-crystal x-ray diffraction peaks of β-boron at 60 GPa. The vertical lines at the bottom of each ADX spectra mark the predicted position of the reflections.The *hkl* indices are indicated above each peak and correspond to the hexagonal setting of the rhombohedral structure.

In run *A*, the DAC was equipped with 400 μm culet diamond anvils and good hydrostatic conditions were achieved only up to 26 GPa. In run *B*, 150 μm culet diamond anvils were used so as to reach the 100 GPa range. But the large amount of boron powder required to have good diffraction patterns occupies too much volume in the sample chamber, and the hydrostatic conditions deteriorate above 20 GPa. Therefore, in the next experiments single-crystal x-ray diffraction was used to obtain diffraction data under hydrostatic conditions up to the maximum pressure. In run *C*, a single crystal of 7 μm dimensions was loaded in a DAC equipped with 85 μm culet diamond anvils. With the energy-dispersive single-crystal technique, seven diffraction peaks, and their harmonics, could be measured within the x-ray aperture of the DAC, as shown in Fig. 1. The peaks were well correlated with the hexagonal orientation matrix of β-boron. The width of the rocking curves of the peaks was smaller than 0.1°, which is an indication of good quality single crystals, but it suddenly broadened above 65 GPa. This indicated a deterioration of the hydrostatic conditions, probably ascribed to a bridging of the single-crystal between the two diamond anvils. As it will be seen below, a phase transition was observed subsequently. In run *D*, a smaller single crystal, 5 μm in dimensions, was loaded in the DAC with slightly bigger culets of the diamond anvils, 100 μm. Angle-dispersive single-crystal x-ray diffraction (ADX) was performed. This technique is more efficient than energy dispersive single-crystal x-ray diffraction to determine the new structure when a phase transition takes place. Eight diffraction peaks were identified and correlated using the hexagonal orientation matrix of β-boron. The sample was under good hydrostatic conditions up to at least 97 GPa, a pressure above which the intensity of the diffraction peaks dramatically decreased down to disappearance, probably because of the amorphization of the sample, as it will be discussed below.

The x-ray data of the equation of state of β-boron obtained from 2 to 97 GPa under hydrostatic conditions in the runs *A*, *C*, and *D* are collected in Fig. 2. The zero pressure volume of the hexagonal cell, V_0, was obtained to be equal to 2460 Å^3, which is in very good agreement with the JCPDS 31-0207 database value ($a_0 = 10.92$ Å, $c_0 = 23.81$ Å, and $V_0 = 2461.5$ Å^3). The $P(V)$ data were fitted to the Vinet formulation of the equation of state [12]. The Vinet equation has been found to be the most accurate one to fit the EOS at very high pressure. In addition, it gives a better determination of the two compression parameters, the bulk modulus, B_0, and its pressure derivative, B_0' [13]. We thus propose the following form for the EOS of β-boron: $P(\mathrm{GPa}) = 3B_0(1 - X)X^{-2}\exp[3(B_0' - 1)(1 - X)/2]$ with $X = V/V_0$ and the following values for the parameters, $V_0 = 2460$ Å^3, $B_0 = 210(6)$ GPa, and $B_0' = 2.23$. The pressure dependence of the hexagonal lattice parameters is also plotted in the inset of Fig. 2. An almost identical compressibility is observed for the *a*

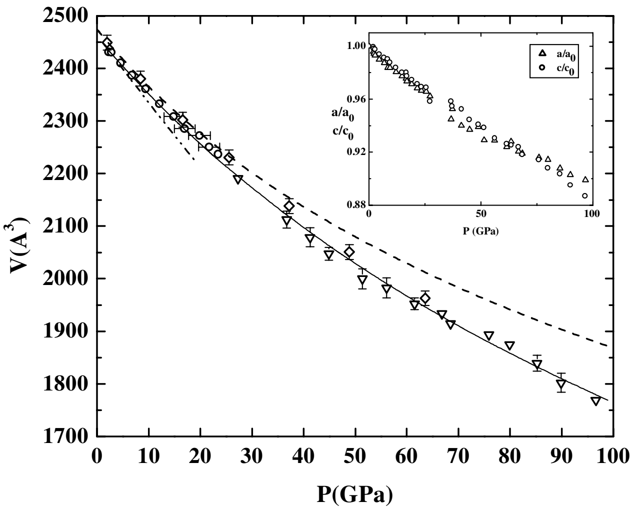

FIG. 2. Volume of the unit cell of β-boron (in the hexagonal setting with 320 atoms in the unit cell) versus hydrostatic pressure. The circles, lozenges, and down triangles indicate, respectively, data points obtained in run *A*, run *C*, and run *D*. The error bars at each data point are indicated when they are larger than the size of the symbols. The full line is the Vinet fit, as given in the text with $V_0 = 2460$ Å^3, $B_0 = 210(6)$ GPa, and $B_0' = 2.23$. The dashed line and the dash-dotted line are, respectively, the fits of the data obtained with x-ray [8] and with neutron [11]. Inset, relative change of the lattice parameters, *a* and *c*, with pressure.

and *c* axes. In Table I, the present values of B_0 and B_0' are compared to other experimental or theoretical determinations. Ma *et al.* performed x-ray diffraction on β-boron powder up to 31 GPa in a DAC with a 4:1 methanol-ethanol mixture as the pressure transmitting medium [8]. The fitted value of B_0 is in very good agreement with the present determination. However, the pressure range covered in that study was not high enough to correctly determine the value of B_0'. It is clearly seen by linearizing the Vinet equation that data points above 40 GPa are essential to correctly constrain B_0'. They obtained a value of $B_0' = 4.2$, which makes a too stiff EOS in the 100 GPa range. Also, they observed that the *a* axis was stiffer than the *c* axis, and this result was used to justify a possible transformation to the tetragonal (T-192) phase at high pressure. However, we do not observe any difference in the compressibility of the *a* and *c* axes in the perfectly hydrostatic case, although we do in the nonhydrostatic compression, which was observed to modify the relative stiffness of the two axes. Nelmes *et al.* performed powder neutron diffraction up to 10 GPa in a large volume press with NaCl as the pressure gauge and fluorinert fluid as a quasihydrostatic pressure transmitting medium [11]. Their B_0 is slightly smaller than ours. Very likely, some error was induced in their measurements due to the mixing of NaCl with boron. The compression was quite hydrostatic and a similar compressibility for the *a* and *c* axes was observed. The pressure range was not large enough to fit B_0'. Yet, Nelmes *et al.* obtained a more accurate value for B_0 of α-boron, as the study was performed by single-crystal x-ray diffraction up to 5 GPa. Surprisingly, this B_0 value for α-boron is identical to ours for β-boron. This similarity indicates that the structural differences between α- and β-boron have a very minor effect on the compressibility of the two phases. Using this statement, we may compare our B_0 with the theoretical estimates on α-boron. Up to now *ab initio* calculations have been performed only on the α-phase, which is much simpler than β-boron. As shown in Table I, the agreement is very good with two calculations [5,15] and reasonably good for the third one [16]. From this, we can state that the microscopic behavior of boron under pressure is expected to be correctly studied by *ab initio* calculations, despite the complex electronic distribution of this system.

Regarding the experiments in which the hydrostatic conditions were lost, it is important to point out that nonhydrostatic compression favors a displacive structural change in β-boron. This modification was observed by changes in the intensity of the diffraction peaks above 20 GPa in run *B* and 60 GPa in run *C*. Also, by keeping the hexagonal setting of β-boron, the volume calculated for this new phase was larger than in β-boron under hydrostatic conditions and that is thermodynamically impossible. However, the rhombohedral symmetry is still the one to best fit the ADX spectra, as shown in Fig. 1, and a larger unit cell is obtained. The only way to conciliate our measurements with thermodynamics is to add atoms to the unit cell, in order to increase its density. Indeed, by assigning at least 325 boron atoms, the trend of the density with pressure is not anymore in conflict with

TABLE I. Comparison of different determinations of the bulk modulus of boron, B_0, and its pressure derivative, B_0'. The maximum pressure of the various experimental determinations is indicated.

B_0 (GPa)	B_0'	Method	Max *P*	Reference
210(6)	2.23	XRD of β-B in He	97 GPa	This work
201(9)	4.2(0.9)	XRD of β-B in ethanol:methanol	31 GPa	Ma *et al.* [8]
185(7)		Neutron diffraction of β-B	10 GPa	Nelmes *et al.* [11]
213(15)	4.0	Single-crystal XRD of α-B	5 GPa	Nelmes *et al.* [11]
222	3.5	α-B, LDA calculation		Vast [14]
207		α-B, LDA calculation		Lee *et al.* [15]
249		α-B, LDA calculation		Mailhiot *et al.* [16]

thermodynamics. The mechanism of this microscopic reorganization under nonhydrostatic stress is beyond the possibility of the present work, as the quality of the ADX spectra is not good enough to make a refinement of the atomic positions of the boron atoms.

In our three very high pressure experiments, an indication of a pressure-induced amorphization was also observed. The signature of this transition was the disappearance of the diffraction peaks. Unfortunately, the volume of the sample was too small to measure the structure factor, which could have characterized this disordered phase. In run B, the peaks of the sample kept at 80 GPa disappear over one month. The DAC was unloaded and the amorphous phase was recovered at ambient pressure: no diffraction peaks could be measured and the sample had a grey reflecting aspect, different from the black color of β-boron. Also, it seems that nonhydrostatic conditions slightly shift the pressure-induced amorphization to lower values. In runs C and D, the diffraction peaks disappeared above 90 and 110 GPa, respectively. Although amorphous boron exists at ambient pressure, the direct transition from the crystalline to the amorphous phase had never been observed before, even under strong irradiation. This transition is observed here by applying very high pressure. Such a pressure-induced amorphization has been obtained only in two pure elements, sulfur and carbon (in the form of C_{60}) [17]. We can propose a tentative explanation of this pressure-induced amorphization. There are experimental evidences that the icosahedral B_{12} unit is very robust: (i) the icosahedra are not destroyed in the disordered ambient pressure phases, liquid [18] and amorphous [19]; (ii) the interpretation of Raman measurements of α-boron up to 50 GPa by *ab initio* calculations sustains the fact that the intraicosahedral bonds are stiffer than the intercluster ones [5]. Also, since the effect of pressure is to delocalize the electronic density, it is reasonable to assume that pressure should particularly affect the intericosahedra bonds, as these are covalent bonds, while the intraicosahedra ones have a metalliclike character. Pressure should thus break first the intericosahedra bonds and the system would then evolve to a close-packed arrangement of icosahedra. Consequently, the amorphous phase is due to either a kinetically hindered transition to a compact crystallographic structure of icosahedra, or to an icosahedral shell packing. Mackay described a radiating packing of spheres in the Ih symmetry, in which the centers of successive shells of spheres lie on the surface of icosahedra [20]. This Mackay phase has a high packing efficiency and a long range order, but no translational symmetry. Furthermore, its packing unit is a supericosahedra $(B_{12})_{13}$ cluster, with 12 icosahedra at the vertices of the central icosahedron, and that unit already exists in β-boron. The local structure of amorphous boron could hence be based on the first few layers of this hierarchical packing of spheres. *Ab initio* calculations seem now to be the most suitable method to validate this hypothesis for the microscopic mechanism of the pressure-induced amorphization β-boron.

Finally, it is interesting to note that the phase transitions that we have observed match the sequence of resistance steps reported for β-boron at very high pressure [7]. The first step at 30 GPa could correspond to the transition to the rhombohedral phase with a larger unit cell stabilized by nonhydrostatic pressure. The step around 110 GPa could be linked to the amorphization of β-boron. The step around 170 GPa, associated with the transition to the metallic state, should correspond to the breaking of B_{12} clusters and to the stabilization of a close-packed arrangement of boron atoms, as proposed in a recent *ab initio* calculation on the temperature of the superconductivity of β-boron [21]. Certainly, the present structural investigation should now be extended in the 200 GPa range to verify whether boron assumes a simple compact structure in its metallic phase. In summary, the equation of state of β-boron is here accurately determined to 100 GPa under quasihydrostatic conditions and around 100 GPa β-boron undergoes a transition to an amorphous phase.

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