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Neutron- and x-ray-diffraction measurements of the bulk modulus of boron

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The bulk modulus of β-boron has been measured up to 10 GPa by neutron powder diffraction using an opposed-anvil pressure cell. The bulk modulus of α-boron has also been measured to 5 GPa by single-crystal x-ray techniques. The values have been determined to be 185(7) GPa for β-boron and 224(15) GPa for α-boron. These values are markedly smaller than those measured for other hard materials, but total-energy calculations for α-boron are in reasonable agreement.

I. INTRODUCTION

Boron and some boron-rich compounds form a structurally unique class of materials. In almost all cases, the common structural unit is a B_{12} icosahedron in which each boron atom has five nearest neighbors within its own icosahedron. If the bonding were the conventional covalent type, in which two atoms each contribute one electron to the bond which is formed by an accumulation of negative charge between the atoms, then each boron atom would have to contribute five electrons to bonding within the icosahedron. However, boron has only three valence electrons and it is thought that bonding is achieved by the formation of so-called three-center electron-deficient bonds where the charge accumulation occurs at the center of a triangle formed by three adjacent atoms. Electron-density studies support this model.[1,2]

The electron-deficient nature of the bonding within the icosahedra is accentuated in a crystal structure by the need to form conventional covalent two-center bonds to link the icosahedra together. This leads to an antimolecular structure where the bonds linking the icosahedra are shorter and hence thought to be stronger than those within the units.

The icosahedra may be linked together in many different ways, and as a consequence, boron exhibits the most varied polymorphism of any of the elements: Sixteen crystalline forms have been reported to date.[3] Of these, the most commonly found is the rhombohedral β form, while the rhombohedral α form has the simplest structure.[3-5] Both forms adopt the space group $R\bar{3}m$ which has two alternative settings; the hexagonal setting has been chosen for this study. The structure of α-boron may be described as a trigonally distorted cubic close-packed array of icosahedra, while β-boron has a short-range structure that is closely related to the amorphous form and consists of a complex three-dimensional array of atoms. Individual icosahedral units in this structure are harder to identify than for the α form, but the arrangement can be classified into three types of interpenetrating icosahedra.[3] These icosahedra share atoms with other icosahedra, and so β-boron has a greater proportion of three-center bonds than α-boron.

Boron is exceptional among the more common elements in that its compression properties have not been studied in any detail. At present, the only published measurement of the bulk modulus is that by Bridgman,[6] who determined the linear compressibility of an unknown phase, thought to be the β form as it is the most common. This gave a value of $B_0 = 181$ GPa based on the assumption that the sample behaved isotropically. This assumption needs to be checked as β-boron has since been shown to have a rhombohedral unit cell. Also, the value of B_0 is considerably smaller than that measured for other hard materials. For example, the bulk moduli of diamond and boron nitride are 440 and 369 GPa, respectively.[7,8]

Rather more theoretical than experimental studies exist, the most recent being by Mailhiot, Grant, and McMahan,[9] who performed total-energy calculations using both the linear muffin-tin orbital (LMTO) and the pseudopotential method. The energies of several simple structures were calculated, but, among the structures considered, that of α-boron was the only one that boron is known to adopt. The calculations for α-boron gave values for B_0 of 249 and 266 GPa for the pseudopotential and LMTO methods, respectively.

The accuracy of these values may be judged from the calculated equilibrium atomic volumes 7.05 and 6.93 Å^3 compared with a measured value of 7.34 Å^3 (Ref. 5). Of the two methods of calculation used, the pseudopotential approach is expected to be the more accurate because it is better able to take account of directional bonding and nonflat electron-ion potentials in the interstitial regions—effects that are likely to be significant in boron. The values of the atomic volume reflect this in that the value calculated by the LMTO method differs by 5.5% from the measured value, while that calculated by the pseudopotential method differs by 4%. The remaining

4% difference (which is greater than the difference between the two methods) must be assumed to be due to the complexity of the structure and the difficulty of constructing appropriate pseudopotentials for elements at the top of a group in the periodic table.

Given the unique bonding and structure of boron, there is clearly a need to investigate the isotropy of its compression and to obtain accurate measurements of the bulk modulus as a basis for further theoretical studies. Diffraction-based methods offer an ideal means as they measure directly both the magnitude and isotropy of the unit-cell compression.

Boron has a relatively low x-ray-scattering power, and the obvious technique to use for its study is neutron diffraction as boron has a large neutron-scattering cross section. This requires the use of ^{11}B-enriched boron to avoid the prohibitively high absorption of natural boron. ^{11}B-enriched β-boron is quite readily available. But it proved impossible to obtain a sufficiently large sample of ^{11}B-enriched α-boron for neutron diffraction (~ 100 mm^3), and natural boron single crystals of a suitable size for x-ray studies were obtained instead.

Thus two parallel studies were performed. A recently developed high-pressure cell (the Paris-Edinburgh cell), designed for pressures up to 10 GPa, was used for a neutron-powder-diffraction study of β-boron and x-ray single-crystal techniques were used to measure the bulk modulus of α-boron.

II. EXPERIMENTAL DETAILS

A. Powder-diffraction studies of β-boron

The neutron-powder-diffraction experiments used the Paris-Edinburgh pressure cell shown in Fig. 1. This cell employs a novel opposed-anvil design and is described in detail by Besson *et al.*[10–12] Its principal features are the toroidal anvil design (Fig. 1) and the compact hydraulic ram which makes *in situ* variation of the sample pressure possible. The anvil profile is based on the work of Khvostantsev[13] and consists of a spheroidal sample space surrounded by a toroidal gasket indentation. These modifications allow a sample volume of 80 mm^3 to be taken to pressures in excess of 10 GPa.

Samples were prepared from a supply of 98.6% ^{11}B-enriched β-boron purchased from Centronic Limited, England. The sample was a mixture of boron and NaCl pressure calibrant in the proportions 70:30 by volume, and the material was precompressed to approximately 1 GPa prior to loading to produce a pellet of the correct size.

The pellet was placed in the cell, and pressure was applied without a pressure fluid as it was assumed that the NaCl, which has a low shear strength, would give adequately quasihydrostatic conditions. However, measurements at an applied load of 40 tonnes showed marked pressure broadening of diffraction lines, which was thought to result from bridging between grains within the sample. To reduce this problem, subsequent loadings included fluorinert in the sample volume. This is a liquid at low pressures and so fills any voids efficiently. Fluorinert solidifies at approximately 1.7 GPa,[14] but it was expected to remain sufficiently soft to ensure good quasihydrostatic conditions. Measurements at loads of 70 tonnes and above showed that this procedure appreciably reduced the pressure-induced broadening.

Neutron-diffraction measurements were performed on the POLARIS diffractometer of the U.K. spallation source, ISIS, at the Rutherford Appleton Laboratory using time-of-flight techniques. These are well suited to high-pressure work because a fixed scattering geometry can be employed, which allows scattering from the pressure cell materials around the sample to be eliminated by careful collimation of both the incident and diffracted beams.

For the Paris-Edinburgh cell, a multistage approach to collimation is used. The incident beam is initially reduced to 2×1 cm^2 by elements placed in the beam line. A collimator placed on the front of the cell (see Fig. 1) then reduces the cross section to a circle of diameter 4–6 mm according to the sample size. Collimation of the beam diffracted at $2\theta = 90°$ is provided by covering the faces of the anvils with neutron-absorbing paint (Gd_2O_3-

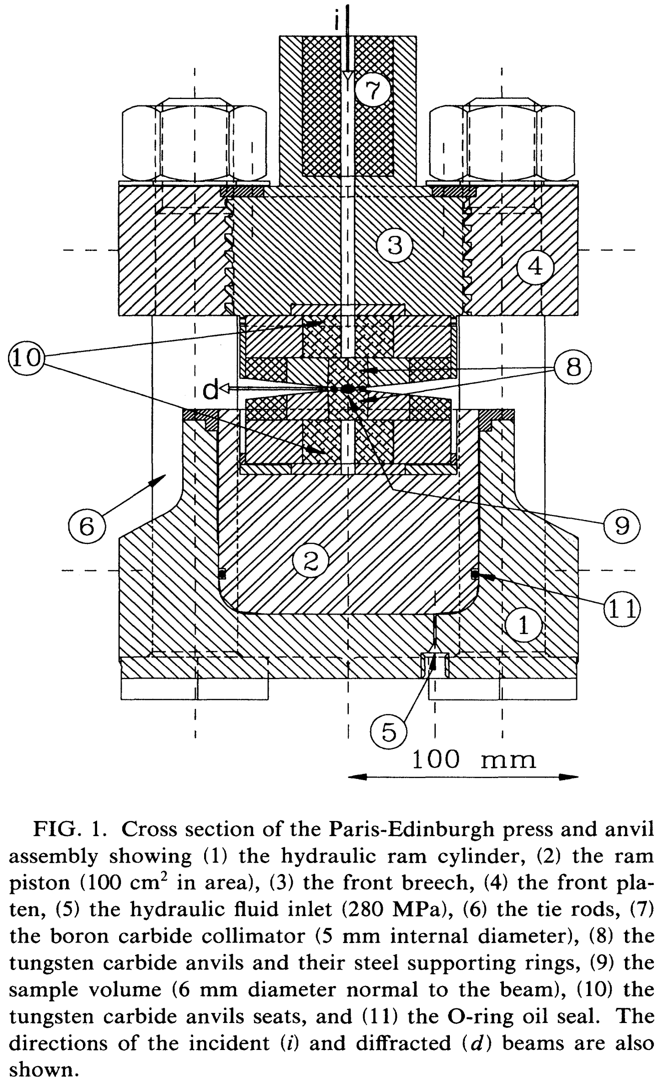

FIG. 1. Cross section of the Paris-Edinburgh press and anvil assembly showing (1) the hydraulic ram cylinder, (2) the ram piston (100 cm^2 in area), (3) the front breech, (4) the front platen, (5) the hydraulic fluid inlet (280 MPa), (6) the tie rods, (7) the boron carbide collimator (5 mm internal diameter), (8) the tungsten carbide anvils and their steel supporting rings, (9) the sample volume (6 mm diameter normal to the beam), (10) the tungsten carbide anvils seats, and (11) the O-ring oil seal. The directions of the incident (*i*) and diffracted (*d*) beams are also shown.

doped epoxy). Finally, a slit is placed on the side of the cell to restrict the region viewed by the detectors to that immediately around the sample. The shielding enables spectra to be collected that are almost totally free from scattering by the anvils and with a signal-to-background ratio of 1:2 for the strongest peaks of β-boron (Fig. 2).

Data were collected from three different loadings of the cell—at 40 tonnes without fluorinert, and at 70 and 80 tonnes with fluorinert, and finally at 120 tonnes (and then downloaded to ambient pressure) with fluorinert. To correct for any variation in the cell position, a zero-pressure measurement was made for each loading. The diffracted signal was detected by a bank of twenty 2×13-in. ^{3}He detectors placed 2 m from the sample at $2\theta=90°$. This gave a total flight path from the source of 14 m and a resolution $\Delta d/d=0.5\%$.

The time-of-flight spectra collected were normalized for the incident spectral function by the use of a spectrum collected from a vanadium sample. The normalized spectra were used for Rietveld profile refinement using the program TF14LS.[15] Prior to the pressure experiments, a pattern was collected from a test sample placed in a standard sample can to verify that a pattern as complex as that of β-boron could be refined successfully (see Fig. 2). Remarkably, it proved possible to refine all of the 33 variable atomic coordinates together, and the values obtained were in agreement with previous single-crystal work.[4] At high pressures it was not possible to refine the atomic coordinates because of the poorer signal to background; they were fixed at the measured ambient-pressure values,[4] and only the lattice parameters were refined in addition to the scale, background, and a peak-width parameter to model the effects of pressure-induced broadening. Examples of profile refinements at ambient pressure and 6.9 GPa are shown in Fig. 2.

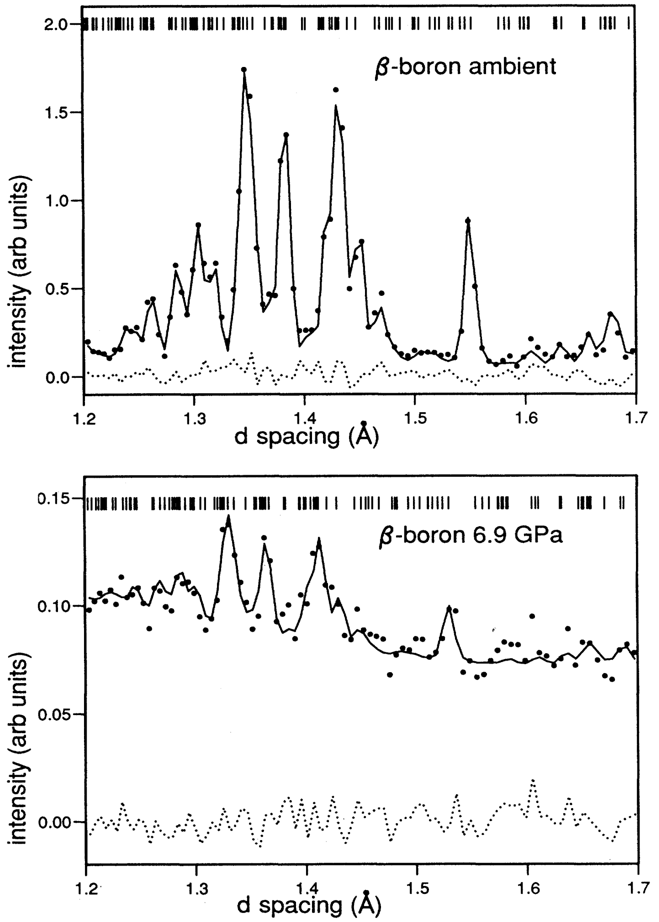

FIG. 2. Part of the profile of β-boron around the strongest peaks, showing the results of profile refinement on data taken at ambient pressure (upper plot) and 6.9 GPa (lower plot). The observed values are plotted as solid circles, and the calculated values are joined into a solid line; the lower dotted profile shows the difference between the observed and calculated profiles, and the vertical lines at the top of each plot mark the predicted positions of reflections.

The same spectra were also refined separately to obtain the lattice parameter of NaCl. The problems of peak overlap were avoided by inspection and the elimination of regions of the spectrum where strong NaCl and β-boron peaks coincided.

The thrust axis of the cell is parallel to the incident beam, and so application of force results in a displacement of the sample that alters both the flight path length and the 2θ angle. This movement was estimated to increase linearly to 1.5 mm at a load of 100 tonnes, and the measured values of the lattice parameters of NaCl and β-boron were corrected accordingly. In addition, the values were corrected for a zero offset along the cell axis by assuming an ambient-pressure lattice parameter of 5.640 Å for NaCl (Ref. 16) in the ambient-pressure reference measurement.

The corrected values of the lattice parameter of NaCl were used to obtain a pressure from the Decker equation of state which has an accuracy of 0.05–0.1 GPa in the range 0–10 GPa.[16,17] The pressures corresponding to the applied loads of 40, 70, 80, and 120 tonnes were found to be 3.7, 6.8, 7.8, and 9.0 GPa, respectively.

B. X-ray single-crystal studies of α-boron

A piece $13\times75\times75$ μm^3 was cut from a single crystal of α-boron, provided by B. Morosin and T. L. Aselage of Sandia Laboratories, Albuquerque, New Mexico, and loaded into a Merrill-Bassett diamond-anvil cell.[18] The cell was assembled using a tungsten gasket and a 4:1 methanol-ethanol mixture as a pressure transmitting fluid and was initially taken to 0.5 GPa to provide an "in-cell" measurement at a pressure close to ambient. (The pressure was measured by the ruby fluorescence method,[19] which was based on the Decker equation of state for NaCl and may be assumed to have the same accuracy.)

The cell was then mounted on an Enraf-Nonius CAD4 diffractometer. The sample was carefully oriented using Mo $K\alpha$ radiation (graphite monochromator), and the profiles of several reflections were measured to ensure that the sample was a good single crystal. The lattice parameters were determined from the setting angles of 11 reflections. These setting angles were measured by the four-position method of King and Finger,[20] which corrects for sample miscentering. The results were used

TABLE I. Results of Rietveld profile refinement for β-boron (with NaCl pressure calibrant). The parameters σ_{NaCl} and σ_{B} are the full width at half maximum of the Gaussian component of the line shape described in the text, expressed as a fractional width $\Delta d/d$. The pressure shown as AP is ambient pressure.

a_{NaCl}	P (GPa)	a (Å)	c (Å)	Volume (Å^3)	σ_{NaCl} (%)	σ_{B} (%)	Remarks
	AP	10.934(11)	23.79(3)	2463(5)	0.5(1)	0.5(1)	at AP after the run at 9.0 GPa
5.426(3)	3.66(5)	10.861(6)	23.63(1)	2414(2)	0.8(1)	1.1(1)	no fluorinert
5.306(2)	6.79(5)	10.796(11)	23.52(3)	2374(5)	1.2(2)	0.6(2)	with fluorinert
5.274(2)	7.81(5)	10.780(5)	23.46(1)	2361(2)	1.4(2)	0.8(3)	with fluorinert
5.239(2)	9.00(5)	10.751(7)	23.44(2)	2346(3)	1.4(2)	0.8(3)	with fluorinert

to refine the lattice parameters by the program RAFIN, which allows the constraints imposed by the lattice symmetry to be included. The pressure was then changed and the procedure repeated at 2.65 and 4.00 GPa.

III. RESULTS AND DISCUSSION

The refined values of the lattice parameters of β-boron and NaCl are shown in Table I. Also shown are the linewidths σ for both NaCl and boron. σ is the full width at half maximum (FWHM) of the Gaussian component of the resolution whose width increases linearly with d spacing. This models the strain-induced broadening in the sample as well as the geometric contributions to the instrument resolution function. The geometric contributions to the FWHM were found from measurements at ambient pressure to be approximately 0.5% ($\Delta d/d$), and any increase in width over this value is therefore a measure of the inhomogeneous pressure distribution and hence nonhydrostaticity within the sample. As can be seen, this pressure-induced broadening is significant though the use of fluorinert did alleviate the problem. The consequences for the accuracy of the measurements are not clear. However, the fact that the level of pressure inhomogeneity varies in a nonmonotonic fashion from measurement to measurement, without any apparent systematic effect on the values of the lattice parameters (Figs. 3 and 5), suggests that the effect on the pressure-volume relationship is not significant.

Table II shows the lattice parameters of α-boron as a function of pressure obtained from the x-ray study. In this case the methanol-ethanol mixture gives truly hydrostatic conditions and so no pressure-induced broadening was to be expected.

To simplify the profile refinement procedures, all data were refined in the rhombohedral setting where the three unit-cell edges are equal ($a=b=c$) as are the three interaxial angles ($\alpha=\beta=\gamma$). However, it is conventional to consider the alternative hexagonal setting of the unit cell where ($a=b\neq c$) and ($\alpha=\beta=90°$, $\gamma=120°$), and so the refined values of the lattice parameters are presented in this way.

TABLE II. Refined values of the lattice parameters for α-boron.

P (GPa)	a (Å)	c (Å)	Volume (Å^3)
0.50(5)	4.917(1)	12.594(3)	263.7(2)
2.65(5)	4.900(1)	12.552(3)	260.9(1)
4.00(5)	4.891(1)	12.532(4)	259.6(2)

The pressure dependence of the lattice parameters is shown in Figs. 3 and 4. As can be seen, there is a small difference in the rates of compression and the c and a axes in both α- and β-boron. The linear fits give rates of increase in the c/a ratio of 0.010(2)%/GPa in α-boron and 0.020(7)%/GPa in β-boron. Both materials thus appear to exhibit a slightly anisotropic compression. However, the estimated standard deviations of the individual data points shown in Figs. 3 and 4 indicate that the deviation from isotropy may be less certain than the fits imply.

Figure 5 compares the pressure-volume relationship for α- and β-boron. Fits to the data for β-boron using a Murnaghan equation of state yielded a value for B' that was not significantly different from zero, and so the data were fitted with a straight line as shown in Fig. 5. This linear fit gave a value of 185(7) GPa for B, the average bulk modulus, and an ambient-pressure atomic volume $V_0=7.818(6)$ Å^3, which compares with the previously published value of 7.81 Å^3 (Ref. 4).

The same linear fit was applied to the data from α-boron since a free fit to a nonlinear equation of state is not meaningful with only three data points. The linear fit gave $B=224(15)$ GPa and $V_0=7.337(7)$ Å^3, which compares with a published value of $V_0=7.34$ Å^3 (Ref. 5).

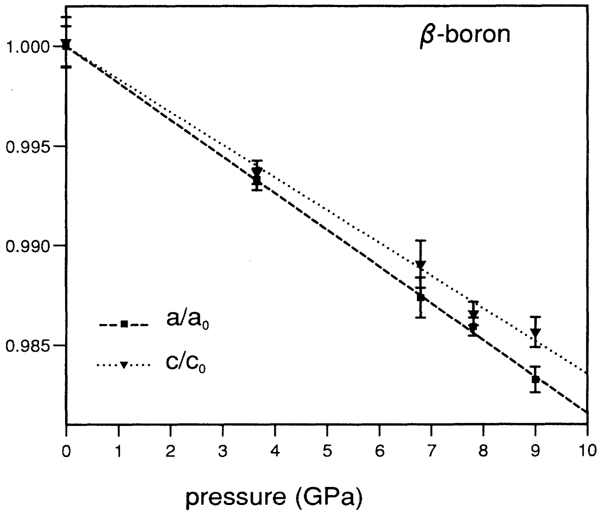

FIG. 3. Pressure dependence of the reduced lattice parameters of β-boron. The squares represent a/a_0 and the triangles c/c_0. The dotted and dashed lines represent linear fits to the data.

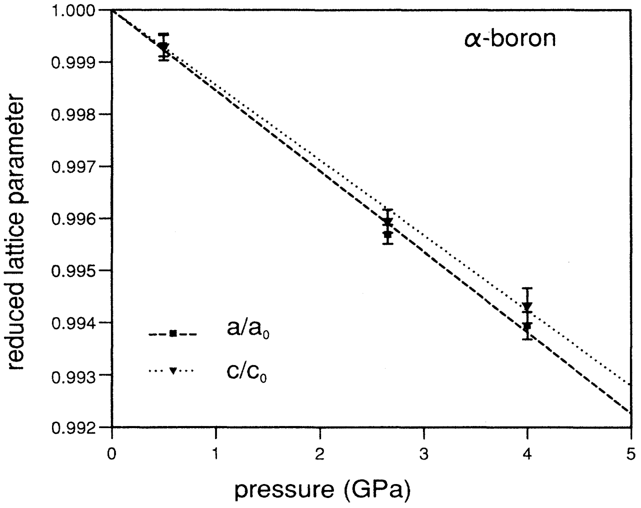

FIG. 4. Pressure dependence of the reduced lattice parameters of α-boron. The squares represent a/a_0 and the triangles c/c_0. The dotted and dashed lines represent linear fits to the data.

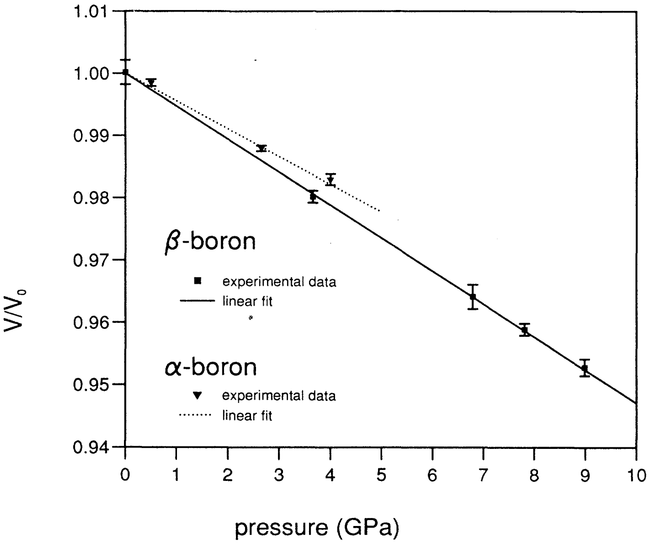

FIG. 5. Pressure dependence of the reduced unit-cell volume for β-boron (squares) and α-boron (triangles). The points show experimental measurements, the solid line represents a linear fit to the data for β-boron, and the dashed line represents a linear fit to the data for α-boron.

For comparison, the data were also fitted with a Murnaghan equation of state with B' fixed at 4, the value expected for a covalently bonded solid. This gave $B_0=213(15)$ and $V_0=7.341(7)$, values which are not significantly different from those obtained from the linear fit.

These results add direct-compression measurements of both the bulk modulus and the anisotropy of the compression to the earlier work on boron, and reveal some significant differences between the α and β forms. The agreement between the value of 181 GPa obtained by Bridgman[6] and that presented in this work for β-boron provides further evidence that the unknown phase studied by Bridgman was indeed β-boron. Although the assumption of isotropy which he used to derive B_0 from his measurements is not generally valid for a rhombohedral lattice, the anisotropy of 0.020(7)%/GPa found in this study is small enough for the assumption to have been a good approximation.

In the case of both α- and β-boron, the values of B are significantly smaller than are found in other comparably hard materials. For example, diamond has a bulk modulus of 440 GPa (Ref. 7) and that for boron nitride is 369 GPa,[8] while the values for both forms of boron are in the range normally observed for metals. The measured value of B is not so very different from the value of 246 GPa calculated for α-boron,[9] and so the calculations must contain an explanation for the relative compliance of boron. The underlying reason for this is not yet clear, but may well lie in the electron-deficient bonding. Further information on this may be obtained from the pressure dependence of the atomic coordinates of α-boron, which we are at present measuring. The remaining discrepancy of about 15% between calculated and measured values of B for α-boron probably reflects the difficulty of the calculations.

The difference in bulk modulus between the two allotropes might be expected to be attributable to the difference in densities in that α-boron, the denser form, is also the stiffer of the two. However, it appears that a difference remains even at the same density. A pressure of 10 GPa makes the density of β-boron the same as that of α-boron at ambient pressure, but B' would have to have a value of 4 in β-boron to make the bulk moduli also the same. The present measurements do not allow an accurate value of B' to be determined, but, as shown, the data suggest that B' is somewhat less than 4. Thus it would appear that the structural differences between the two forms have a significant effect on the compressibility. Work is in progress to extend the pressure range and hence make an accurate measurement of B' for both forms.

These results provide a basis for further theoretical work on both α-boron and (if possible) β-boron.

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