Observation of Inverted-Molecular Compression in Boron Carbide

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High-pressure neutron diffraction studies of boron carbide, B_4C, to 11 GPa show that the icosahedral structural units are 23(4)% more compressible than the structure between them. This inverted-molecular compression is in accordance with qualitative predictions based on models of the bonding, but had not previously been observed directly. The results show the effect of the structural compression on the electrical resistivity to be more complex than present, semiquantitative models suggest.

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The boron-rich solids (BRS) have attracted considerable experimental and theoretical interest because of their unusual bonding and transport properties [1–6]. The refractory nature of these materials suggests that they may also have important applications in high-temperature electronic devices [7]. Many BRS have a molecularlike structure, based on 12-atom icosahedra, but the nature of the bonding within and between the icosahedra appears to lead to a form of structural compression that is the inverse of that found in normal molecular solids [6]. This is interesting in itself as a manifestation of a distinctive form of bonding, and is also believed to be important to the understanding of the electronic transport properties [8].

Boron has one of the most varied structural chemistries of all the elements [9]. A common feature of its structures and those of the related BRS is the icosahedral structural units [9,10]. The hardness and refractory nature of these materials [6] shows they are strongly bonded, and the ability to form strongly bonded networks of linked icosahedra is unique to the BRS [6,11]. An example is the group of solids whose structures are based on that of α-boron [10], shown on the right in Fig. 1. This structure is composed of icosahedra formed by two sites (labeled 1 and 2) with coordinates $(x, -x, z)$ and $(x', -x', z')$ in space group $R\bar{3}m$. The icosahedra are covalently linked together to form a rhombohedral array. The principal variation in structure among the group is the chain that is sometimes found cross-linking this rhombohedral array. In α-boron the chain is absent; B_6P, B_6As and B_6O have a two-atom chain; and boron carbide (shown on the left in Fig. 1) has a three-atom C-B-C chain with atoms located at 0,0,1/2 and $0,0,\pm z$ (labeled 3 and 4) [10]. The icosahedra are enclosed units, and have come to be regarded as molecularlike structural components [6].

An icosahedral boron atom in these structures has five neighboring boron atoms within the icosahedron and one additional nearest neighbor outside the icosahedron (Fig. 1). Boron is trivalent and so has insufficient electrons to form six conventional "two-center" covalent bonds to its neighbors [6]. Electron-density studies [10] have provided evidence to support the view that, instead, intraicosahedral bonds are formed by an accumulation of charge at the center of a triangle of adjacent atoms [6]. This bonding model is also supported by calculations [2]. Such bonding is referred to as "electron deficient" (Ref. [6]) and has been likened to that found

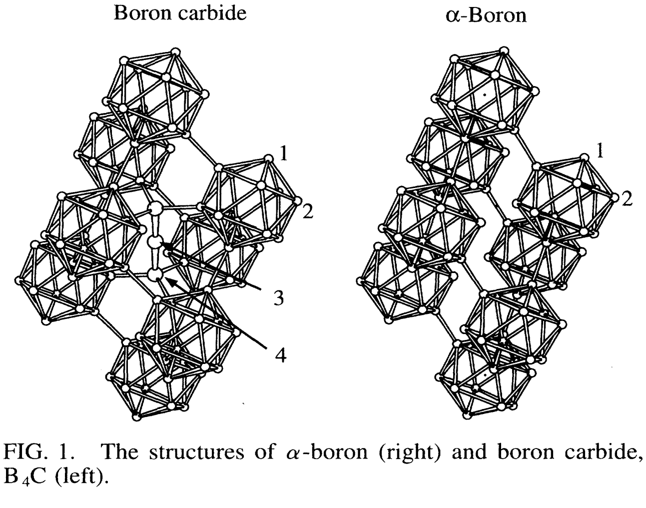

FIG. 1. The structures of α-boron (right) and boron carbide, B_4C (left).

in metals [2,6,12]. In contrast, the bonds between icosahedra—which are shorter than the intraicosahedral bonds [13]—are believed to be more like conventional covalent bonds [6,11]. Based on the expectation that any electron deficiency of the intraicosahedral bonding relative to the intericosahedral bonding will make the icosahedra more compressible than the structure surrounding them, the BRS have been termed as "inverted-molecular" solids [6]. Inverted-molecular (IM) compression is believed to be a distinctive characteristic of BRS, and is believed to play an important role in determining their bulk properties.

The IM model is supported by measurements of the sound velocity in boron-carbide as a function of carbon composition [14,15]. The longitudinal acoustic velocity is observed to decrease from 14 to 12 mm/μs on going from 13 to 10 at. % (a/o) of carbon [15]. In this composition range, x-ray [13] and Raman [16] measurements suggest that carbon is principally lost from the icosahedra [13,16], and the decrease in ultrasonic velocities is taken to reflect the replacement of relatively stiff $B_{11}C$ icosahedra by more compliant B_{12} units [15]. However, this interpretation essentially assumes the model: The assumptions are made, first, that the icosahedra are the softest structural elements (IM compression) and hence determine the magnitude of the sound velocities, and, second, that removal of carbon makes the icosahedral bonding more electron deficient and hence less stiff [15]. Other support is derived from the fact that the electrical resistivity ρ of boron carbide (B_4C)—a polaronic conductor—shows the unusual behavior of *increasing* with pressure [8], which is taken to reflect the IM character of this material. Here, the argument is based on comparison with the behavior of $\rho(p)$ in normal molecular polaronic conductors like sulphur [17]. In B_4C the increase in ρ with pressure is caused by the increase in the hopping activation energy E_a, and models of the conduction suggest that this results from compression of the hopping sites—thought to be all or part of the icosahedra [8]. In normal molecular solids, ρ decreases strongly with pressure as a result of the increasing electronic overlap as the space between the molecular sites is compressed [17]. However, while the markedly different behavior of ρ clearly reflects the very different compression of the two types of conductor, the present understanding of the conductivity mechanism in B_4C (Refs. [8] and [18]) is not sufficiently precise to establish that the behavior of $\rho(p)$ necessarily entails significant IM compression rather than simply requiring the icosahedra and the space between them to have approximately the *same* compressibility [8].

Thus, although IM compression is of considerable interest and significance both as a signature of an unusual bonding type and also for understanding of the physical properties of boron-rich solids, there is as yet no *direct* evidence for it. There is a clear need for direct measurements of the structural pressure dependence, but this has not hitherto been possible. Boron carbide is a very weak scatterer of x rays and even the pressure dependence of the lattice parameters has so far not been measured. Neutron diffraction is the obvious technique to use as boron and carbon are both relatively strong scatterers of neutrons. However, because of the relatively large sample volumes required, the maximum pressure for neutron diffraction was until recently limited to 3 GPa—too small a range to induce measurable structural changes in a material as incompressible as boron carbide, whose bulk modulus is around 200 GPa [15]. But the recent development of high-pressure neutron diffraction to reach pressures in excess of 10 GPa [19,20] now makes it possible to examine the structural pressure dependence of boron carbide. In this Letter we present the results of such a study using the Paris-Edinburgh high-pressure cell.

The Paris-Edinburgh cell is a novel opposed-anvil design able to achieve pressures in excess of 10 GPa with a sample volume sufficiently large for accurate powder diffraction studies [20]. The sample (volume ~ 100 mm^3) is contained between the opposed anvils by a null-scattering TiZr alloy gasket. Pressure is achieved by the *in situ* application of load to the anvils by a compact 200 ton hydraulic ram. The cell is designed for time-of-flight powder diffraction techniques using the POLARIS diffractometer of the United Kingdom pulsed neutron source, ISIS, at the Rutherford Appleton Laboratory. The incident beam of neutrons passes through one of the anvils along the axis of the cell and the diffracted beam emerges through the gasket at a scattering angle (2θ) close to 90°. Neutron-absorbing collimation enables patterns to be collected that are almost completely free from diffraction peaks due to cell materials, with a good level of signal to background [21].

The samples were taken from material of nominal composition B_4C prepared from 98.6% ^{11}B-enriched boron [22] (obtained from Centronic Ltd.) and graphite powder (obtained from Ultra-Carbon Corp.). The reactants were mixed and pressed into pellets which were heated to 2000 °C for 4 h, and then cooled and ground to a powder. The sample composition was found from Raman spectra and x-ray diffraction measurements of the lattice parameters to be within 0.5 a/o of the stoichiometric composition.

Because no equation of state has been published for boron carbide, two types of sample were used. In the first, a 1:1 by volume mixture of boron carbide and a NaCl pressure calibrant [23] was used to determine the equation of state. In the second type of sample, only boron carbide was used—the pressure for this type of sample being derived from the measured equation of state. Use of pure boron carbide samples allowed diffraction patterns to be collected which contained essentially signals from boron carbide only, and this enabled the structural pressure dependence to be determined accurately. Boron carbide is a hard material, and so, to alleviate the effects of pressure-induced peak broadening, all samples were mixed with fluorinert liquid which has been found to reduce peak broadening in earlier experiments on β-boron [24].

For the study of pure B_4C, three separate sets of measurements were made of the structural pressure dependence (referred to as runs *A*, *B*, and *C*) with a new portion of the sample in each case. This procedure was adopted to provide a check on the reproducibility of the structural changes. Time-of-flight spectra were first collected from the $NaCl/B_4C$ mixture with nine different loads applied to the anvils, ranging from 25 to 110 tons. Spectra were then collected at a total of 13 loads between 10 and 120 tons in runs *A*, *B*, and *C* using pure B_4C. Data acquisition times ranged from $\sim$2 h for the mixed ($NaCl/B_4C$) sample to $\sim$6 h for the pure samples. The spectra were corrected for the effects of the wavelength-dependent attenuation of the pressure cell materials, using a procedure based on the measured attenuation coefficient of the relevant materials and calculations of the relevant path lengths [21,25]. The corrected spectra were then analyzed by Rietveld profile refinement using the GSAS package [26]. The five independent atomic coordinates not fixed by symmetry, an overall thermal parameter, an absorption parameter (to model the sample absorption), a background polynomial, and two peak-width parameters (which model the effects of the instrument resolution and pressure-induced broadening) were refined. Before the pressures could be determined, the refined values of the lattice parameters were corrected for the effects of sample displacement along the beam direction as the cell deformed under load, using a procedure described in Ref. [24].

The inset in Fig. 2 shows a plot of the values of V/V_0 versus pressure obtained from the $NaCl/B_4C$ sample. Also shown are the results of a fit of a Murnaghan equation of state to these data, which gives values of 199(7) GPa for the bulk modulus B_0, and 1(2) for its derivative with respect to pressure B'. The value of B_0 is smaller by $\sim$15% than that found by Gieske, Aselage, and Emin from ultrasonic measurements [15]. This difference probably reflects the fact that ultrasonic measurements are susceptible to microstructural effects and, in this case [15], to an assumption of elastic isotropy which cannot be justified for a rhombohedral lattice. The value of B_0 is comparable with those found in our earlier work for α- and β-boron [24], but is significantly smaller than those of conventional covalently bonded hard materials like boron nitride [27] and diamond [28]. A general picture is thus emerging that relative compliance is a feature of the BRS and their bonding. *Ab initio* calculations, which find B_0 in the range 180–240 GPa for a variety of BRS [1,3], are also in accord with this conclusion.

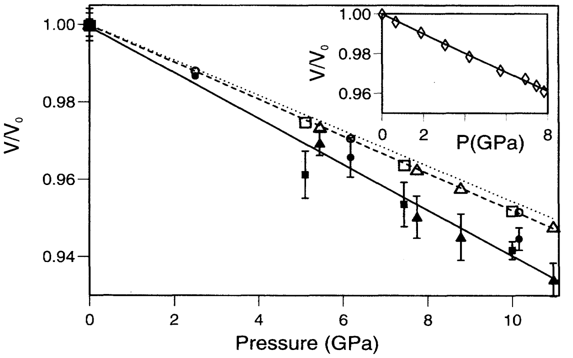

FIG. 2. The pressure dependence of the relative volumes (V/V_0) of the unit cell (open symbols) and the icosahedral volume (solid symbols). The measurements made on three different samples of pure B_4C are represented by triangles, squares, and circles. The solid, dashed, and dotted lines represent linear fits to the behavior of, respectively, the icosahedra, the unit cell, and the intericosahedral space. The inset shows the behavior of V/V_0 for the unit cell as determined from the mixed $B_4C/NaCl$ sample. The solid line in the inset represents the best fitting Murnaghan equation of state.

To examine the refined structural parameters for evidence of IM compression, the volume of the icosahedron was approximated by that of an ellipsoid which passes through each atomic site in the icosahedron. This gives a good estimate of the relative volume changes provided the compression is not strongly anisotropic, and there is no evidence of significant anisotropy. The main plot in Fig. 2 shows the pressure dependence of the relative volume of the icosahedra, calculated by this procedure, and the relative volume of the unit cell, up to 11 GPa. [Pressures above 8 GPa were obtained by extrapolation of the best-fitting equation of state. Any errors in this will be very small (<0.3 GPa) over such a small range.] Also shown are lines representing linear least-squares fits to the relative volumes of the icosahedra, the unit cell, and the space between the icosahedra (obtained simply from the difference of the icosahedral and unit cell volumes). The relative volumes of the icosahedra as a function of pressure are self-consistent for the three separate measurements (runs *A*, *B*, and *C*) within the estimated standard deviations, and hence the observed changes appear to be reproducible. The linear least-squares fits yield values of 169(6) and 220(6) GPa, respectively, for the *average* bulk moduli of the icosahedra and the intericosahedral structure, over the range up to 11 GPa. Any errors in the estimated pressures above 8 GPa (see above) would alter the *absolute* values of these average bulk moduli by up to 3% but would not have any effect on the principal result—namely, that the icosahedra are found to be 23(4)% more compressible than the intericosahedral space. This is a direct confirmation of inverted-molecular compression in B_4C.

Our results show that the icosahedra do have the compressibility required by present models of the conductivity mechanism [8,18], and our structural data can now be used to place the modeling of the resistivity under pressure on a more precisely quantified basis. When applied to the simple square-well model used by Samara, Emin, and Wood [8] to estimate the relationship between the structural compression and ρ, our measurements yield a rate of change for the hopping activation energy with pressure $d(\ln E_a)/dp$ of 1×10^{-4} GPa^{-1}, in reasonable agreement with the observed initial $d(\ln E_a)/dp$ of 1.6×10^{-4} GPa^{-1} (Ref. [8]). However, Samara, Emin, and Wood [8] found that $d(\ln E_a)/dp$ increases by a factor of ~10 between ambient pressure and only 2 GPa. Within their model [8], this would imply that the icosahedral compressibility increases tenfold—a behavior that is very improbable and is certainly excluded by our measurements. However, the square-well model was adopted as only an approximate, but tractable, means to make semiquantitative comparisons [8] and hence it is not surprising that it does not describe the complex behavior of the energy levels of the icosahedron over an extended range of compression. Since our results show the icosahedral compression to be almost linear up to 11 GPa, the strong variation of E_a with pressure [8] suggests that this activation energy depends very nonlinearly on the intraicosahedral bond lengths. This clearly needs to be understood and incorporated into the model, and our measurements of the deformation of the icosahedra under pressure provide a secure structural basis for the more sophisticated calculations that are now required for the pressure dependence of the icosahedral energy levels.

This study of B_4C illustrates the effectiveness of neutron-diffraction techniques in providing accurate structural information for low-Z systems. First and foremost, our measurements provide a direct observation of inverted molecular compression and show it to be a significant effect. The results are in accord with qualitative expectations based on models of the unusual bonding of boron-rich solids (BRS) and hence provide support for these models. One manifestation of the bonding is seen in the equation-of-state measurements which, when taken together with our earlier studies [24], show the BRS to have bulk moduli smaller than those of comparably hard materials—a property that is emerging as a feature of this group of materials. The measured compressibility of the icosahedral structural units shows that the effect of the structural compression on the electrical resistivity is more complex than present semiquantitative models suggest.

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