measure of the precision of theory and experiment.

This work will be described in detail elsewhere with an assessment of research areas opened up by this significant development. The same experimental principle may be applied to creep strain rather than creep-strain rate. The power of the technique is not limited to linear viscoelastic solids but to any slow rate process governed by an analogous first order differential equation.

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A calculation of the surface energy of α-rhombohedral boron

In a preceding investigation, Vega *et al.* [1] applied the Griffith criterion for the fracture of brittle materials to tensile failure in boron fibres. The application was restricted to fractures initiated at a particular type of imperfections, the geometry of which was observed to be similar to that of a Griffith crack, i.e. the proximate voids existing in the vicinity of the core–mantle interface. The application of the Griffith equation permitted the authors to estimate experimentally the surface energy γ for boron with a Young's modulus of $4.4 \times 10^5\,\text{N mm}^{-2}$ as calculated by Talley [2]. The values of the surface energy obtained were 2.77 to $6.43\,\text{J m}^{-2}$, which is of the same order as available values in the literature for bulk tungsten [3, 4]. As neither experimentally measured nor theoretically calculated values of γ have earlier been reported, it is the purpose of the present work to calculate γ by some simple fundamental considerations.

Elemental boron can exist in three different allotropic forms: α-rhombohedral, tetragonal and β-rhombohedral. The structure of boron in fibres has most commonly been referred to as amorphous [5–7]. Others have interpreted the amorphousness of boron in terms of a fine grained polycrystalline structure with crystallite sizes of 20 to 30 Å [8–10]. By now there is some agreement on the microcrystalline nature, but on the other hand, it has not yet been possible to determine the exact crystal structure of the microcrystallites.

Considering the uncertainty in crystal structure, and the fact that tetragonal and β-rhombohedral boron are relatively more complicated structures, we have decided to make our calculations on the simpler α-rhombohedral allotrope.

A complete description of the three allotropic forms of boron can be found in [11] and [12]. Data for α-rhombohedral boron have been taken from a textbook by Adams [11]. Only the most relevant data will be summarized here.

All three allotropic forms are characterized by lattice arrangements of B_{12} icosahedra. The B_{12} icosahedral unit is shown in Fig. 1. The α-rhombohedral structure consists of nearly regular icosahedra in a slightly deformed cubic close packing. The rhombohedral unit cell can be more conveniently described in terms of the related hexagonal cell with $a = 4.908$ Å and $c = 12.567$ Å and containing three icosahedra.

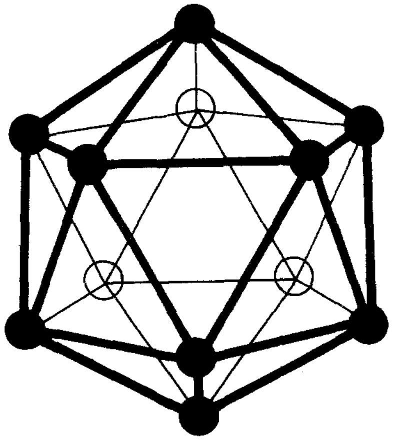

Figure 1 The B_{12} icosahedral unit in boron structures.

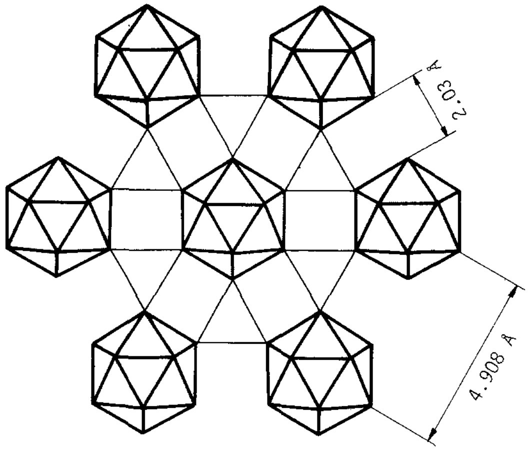

Figure 2 The basal plane in the α-rhombohedral structure of boron.

The bonds within the icosahedral units range from 1.73 to 1.79 Å. The average bond, the so-called intraicosahedral bond, is about 1.76 Å. Of a total of 36 valence electrons available per icosahedron, 26 are used by the intraicosahedral bonds and the remaining 10 for the binding between icosahedra. In the basal plane, the icosahedra are arranged in a close-packed array with nearest neighbour distance 4.908 Å (Fig. 2). The icosahedra are bonded by means of delta bonds, in which two electrons are shared between three atoms in the vertices of an equilateral triangle. Each icosahedron utilizes 4 electrons to be shared among the six delta bonds for the binding in the basal plane. Due to this electron defficiency, the bonds are relatively long; 2.03 Å.

Finally, the basal planes are stacked one above the other. The corresponding intericosahedral distance centre-to-centre is 5.056 Å. Each icosahedron is bonded between the planes by six bonds, three on the top and three on the bottom, which utilize the remaining 6 electrons. These bonds have a length of 1.71 Å.

We now consider the relative strengths of the three different bond types of α-rhombohedral boron. Their absolute strengths will subsequently be related to the energy of sublimation of boron, for which experimental values are available. The physical basis of our analysis is given by the Hellmann–Feynman theorem [13, 14], in the form stating that the total force acting on an atomic nucleus in a cluster of atoms (in a stable state) may be calculated as the classical electrostatic force exerted by all other nuclei and all electron density in the cluster. The force on nucleus i is defined as

$$\mathbf{F}_i = -\nabla_i E(\ldots \mathbf{r}_i \ldots), \qquad (1)$$

where E is the total system energy as a function of all nuclear co-ordinates $\mathbf{r}_i$. The Hellmann–Feynman theorem expresses the remarkable fact that all terms of $\nabla_i E$, except the electrostatic term, exactly cancel when the system is in a stable state.

The binding energy of two atoms (or clusters of atoms) is usually calculated as a difference in energy eigenvalues. The Hellmann–Feynman theorem supplies us with an alternative approach; the binding energy can be found by integrating the electrostatic forces (acting on the nuclei of one part) over the separation distance, as the two parts are brought together from infinity to equilibrium distance. This approach has been studied by several workers, e.g. Epstein *et al.* [15], who in 1967 investigated the detailed conditions of validity of such calculations, and Slater [16], who in 1972 discussed the $X\alpha$-application of the theorem to molecular and solid state theory. Feynman [14] also demonstrated that a directed covalent bond essentially consists of the attraction between each nucleus and a raised density of valence electrons in the region of the bond; thus the valence electrons serve as directed links between the nuclei.

In view of the fact that the bond energy, in point of principle, may be derived from purely electrostatic interactions, we make two simplifying assumptions:

(i) The energy of a covalent bond is directly proportional to the valence density in the region of the bond, and this density, in its turn, is directly proportional to the number of electrons participating in the bond.

(ii) The energy of a covalent bond is inversely proportional to the length of the bond

It should be emphasized that the approximations (i) and (ii) are too crude to permit a calculation of the absolute bond energies. They merely supply a general idea of the relative strengths of the bonds. The absolute bond energies are then determined from an experimental value of the sublimation energy. The assumption (ii) is of minor importance to the relative strengths, since the bond lengths do not differ much in α-rhombohedral boron.

Some of the interatomic bonds in boron are said to be of normal strength in the sense that two electrons participate in each bond, while other bonds are of less than normal strength since less than two electrons per bond participate. The bonds between neighbouring atoms in an icosahedron (here called I-bonds) are of less than normal strength, since only 26 electrons are shared among the 30 I-bonds of the icosahedron. Thus, according to the assumption (i) above, each I-bond has 26/60 = 43% of normal strength. A bond between an atom in one icosahedron and a neighbouring atom in another icosahedron in the *same* basal plane (here called D-bond) has 8/24 = 33% of normal strength, since 8 electrons (4 from the observed icosahedron and 4 from neighbouring icosahedra) are shared among the 12 D-bonds of one icosahedron. The bond between an atom in one icosahedron and a neigbouring atom in another icosahedron contained in an adjacent basal plane (here called N-bond) is of normal strength, since 12 electrons (6 from the observed icosahedron and 6 from neighbouring ones) are shared among the 6 N-bonds of one icosahedron.

If the energy on one I-, D- or N-bond is denominated ϵ_I, ϵ_D or ϵ_N, respectively, and the energy of sublimation per atom is E_s, then the energy of sublimation per icosahedron (12 atoms) may be expressed as

$$12E_s = 30\epsilon_I + 12\frac{\epsilon_D}{2} + 6\frac{\epsilon_N}{2} \qquad (2)$$

Note that only half of the D- and N-bond energies may be ascribed to the observed icosahedron. If, for a moment, we assume that all bond lengths are equal, the relative bond energies are given by

$$\epsilon_I = 26/60\epsilon_N, \epsilon_D = 8/24\epsilon_N. \qquad (3)$$

These expressions inserted into Equation 2, yield

$$\epsilon_N = 2/3E_s \qquad (4)$$

If the differences in bond lengths are taken into account, according to assumption (ii) above ϵ_I and ϵ_D in Equation 3 must be multiplied by the factors 1.71/1.76 and 1.71/2.03 respectively, which yields a slightly altered value

$$\epsilon_N = 0.69E_s. \qquad (5)$$

At this point it is interesting to observe that the *intra*icosahedral fraction of the cohesive energy (i.e. $30\ \epsilon_I/12E_s$) is large (73%) compared with the *inter*icosahedral fraction (27%). Thus it is pertinent to assume that a crack normally propagates between the icosahedra, and not through them.

If cleavage occurs between two basal planes in α-rhombohedral boron, three N-bonds are ruptured per surface icosahedron. If each surface icosahedron occupies an area A, the cleavage energy per unit area is

$$E_{\text{cleav}} = \frac{3\epsilon_N}{A} = 3 \times 0.69\ \frac{E_s}{A}. \qquad (6)$$

The corresponding surface energy is

$$\gamma = \tfrac{1}{2}E_{\text{cleav}}. \qquad (7)$$

E_s for boron is 5.68 eV per atom [17], and A for a basal plane in α-rhombohedral boron is 20.86 Å^2. From Equation 6 and 7 we finally get

$$\gamma = 0.282\,\text{eV}\,\text{Å}^{-2} = 4.52\,\text{J m}^{-2} \qquad (8)$$

This γ value lies within the range 2.77 to 6.43 J m^{-2}, as experimentally obtained for boron fibres by Vega *et al.* [1].

In a preliminary investigation, Vega estimated the difference in surface energies between the three allotropes of boron, using the simple Orowan function (fitted to experimental values of the Young's modulus and the interplanar distance) for the force between two atomic planes. These estimates indicate that the γ values differ by less than 5%. It then seems reasonable to assume that the γ values for tetragonal and β-rhombohedral boron cannot differ much from the value calculated for α-rhombohedral boron by the present method.

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