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Elastic moduli of B_{12} and its compounds

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We have calculated the bulk modulus and all the elastic moduli that can be obtained from uniaxial strains of B_{12}, $B_{12}C_3$, $B_{13}C_2$, $B_{12}O_2$, and $B_{12}As_2$. All atoms are allowed to relax to their equilibrium positions under strain and the errors incurred by failure to do so are revealed.

I. INTRODUCTION

Boron and B_4C are, diamond and perhaps cubic BN excluded, the two hardest substances known. Boron is listed at 9.5 on the original Mohs scale where diamond is 10 and B_4C is listed at 14 on the modified Mohs scale where diamond is 15 and cubic SiC is 13; B_4C is listed immediately below diamond and above SiC on the Knoop scale.[1] Although there is no direct connection between hardness and bulk modulus, the hardest substance, diamond, has the largest bulk modulus known and, in general, hard substances have large bulk moduli. We therefore determined to calculate the bulk moduli of rhombohedral B_{12}, $B_{12}C_3$ (commonly referred to as B_4C), $B_{13}C_2$, $B_{13}O_2$, and $B_{13}As_2$ for which we[2-6] have previously performed electronic structure calculations. Although the stable polymorph of elementary boron is rhombohedral B_{320}, it is likely that metastable B_{12} is slightly harder because it has a reciprocal density[7] of 51.1 bohr^3/atom compared with[8] 52.0 bohr^3/atom for B_{320}. Diamond and graphite are, of course, an extreme example of the metastable polymorph being denser and harder.

Typically, bulk moduli are obtained by fitting the total energy of the crystal as a function of uniform compression and dilation with the relative positions of the atoms kept fixed. Liu and Cohen[9] obtained remarkable agreement with the experiment for β-Si_3N_4 in this manner. Interestingly, they also found that the hypothetical compound β-C_3N_4 has a bulk modulus comparable to diamond. The only calculation of which we are aware in which the internal parameters were allowed to relax to equilibrium is one by Chelikowsky *et al.*[10] for $(SiO_2)_3$. They took fixed volume changes and allowed c/a as well as the atomic positions to relax. In order to obtain elastic constants as well as bulk moduli, we have chosen to apply $\pm 3\%$ uniaxial strains ε_{xx} and ε_{zz} where z is the threefold rotation axis direction and y is the direction of the normal to the reflection plane. After allowing the atoms to relax to their equilibrium positions using the Hellmann-Feynman forces as a guide, we calculate the stresses σ_i induced by these strains. The calculations in the strained case are identical to those in the unstrained[2-6] except that in every case, except $B_{12}C_3$, the ε_{xx} strain reduces the symmetry so that the number of independent **k** points to be sampled in the Brillouin zone is increased. From

$$\sigma_i = \sum_j c_{ij}\varepsilon_j , \tag{1}$$

and the fact that we apply only one ε_j, at a time, we have $c_{ij}=\sigma_i/\varepsilon_j$ yielding c_{11}, c_{21}, c_{31}, c_{51}, c_{33}, c_{13}, and c_{23}. Using $c_{22}=c_{11}$, $c_{32}=c_{31}$, $c_{52}=-c_{51}$, $c_{46}=c_{52}$, and $c_{66}=\frac{1}{2}(c_{11}-c_{12})$ we are able to obtain every nonzero elastic constant except for $c_{44}=c_{55}$. Incorrect versions[11] of these relationships appear in the literature and so we calculated them independently and found they agreed with Fumi's[12] version.

Note that we obtain independent values for c_{31} and c_{13}. We report their average value and take their difference as an estimate of the computational error. Now, $B_{12}C_3$ consists of $B_{11}C$ icosahedra plus CBC interstitial chains and is rhombohedral only because the icosahedral carbon is randomly situated on the top and bottom triangles of the icosahedra. In our calculations, however, we must assume a particular site is occupied and this reduces the symmetry from D_{3d} to C_{1h}. Thus for $B_{12}C_3$ we apply ε_{yy} as well as ε_{xx} and ε_{zz} and obtain all c_{ij} with $j \le 3$. The only nonzero elastic coefficients we do not obtain are c_{44}, c_{55}, and c_{66}. The bulk moduli B are obtained from

$$P/B=\Delta V/V=(s_{11}+s_{22}+s_{33}+2s_{12}+2s_{13}+2s_{23})P , \tag{2}$$

where P is the pressure, V is the volume, and s_{ij} are components of the elastic compliance matrix. The s_{ij} are then obtained in terms of the c_{ij} by inverting the elastic modulus matrix to obtain, in the rhombohedral case,

$$B=\frac{c_{33}(c_{11}+c_{12})-2c_{13}^2}{c_{11}+c_{12}-4c_{13}+2c_{33}} . \tag{3}$$

Note that the c_{ij} with i or j or both ≥ 4 do not in general cancel out of the expression for B, so in the case of $B_{12}C_3$, which is macroscopically but not microscopically rhombohedral, we average c_{11} with c_{22} and c_{13} with c_{23} and then apply Eq. (3).

II. RESULTS

In Table I we display elastic moduli for $B_{13}C_2$ calculated for both positive and negative strains together with their average both before and after the atoms were allowed to relax to their equilibrium positions. The c_{11}, c_{21}, c_{31}, and c_{51}, were calculated with $\varepsilon_1 \equiv \varepsilon_{xx}=\pm 0.03$ while c_{13} and c_{33} were obtained with $\varepsilon_3 \equiv \varepsilon_{zz}=\pm 0.03$. The first thing we notice is the large asymmetry between

TABLE I. Elastic moduli of $B_{13}C_2$ calculated for positive and negative uniaxial strains, without and with atomic relaxation in units of 10^{11} N/m^2.

	Unrelaxed $\varepsilon_j=0.03$	$\varepsilon_j=-0.03$	average	Relaxed $\varepsilon_j=0.03$	$\varepsilon_j=-0.03$	average
c_{11}	5.6297	6.3115	5.9706	4.9662	5.0431	5.0047
c_{21}	0.6238	0.6947	0.6593	1.1821	1.3237	1.2529
c_{31}	0.3052	0.4422	0.3737	0.6714	0.7998	0.7356
c_{51}	−0.2631	−0.2536	−0.2584	0.0937	0.0593	0.0765
c_{13}	0.3617	0.3868	0.3743	0.7033	0.7753	0.7393
c_{33}	5.8934	6.7872	6.3403	4.1883	4.4146	4.3015
B	2.193	2.495	2.344	2.107	2.230	2.169

c_{ij}'s calculated with positive and negative strains. This is a consequence of the rather large ε_j's we used, but their average should eliminate most of the error associated with large ε_j's. We also calculated $c_{11}+c_{12}$ using $\varepsilon_{xx}=\varepsilon_{yy}=0.02$ obtaining 6.1980 × 10^{11} N/m^2 for the average relaxed value, compared with $c_{11}+c_{21}$ = 6.2576 × 10^{11} N/m^2 from Table I, indicating that discrepancies between symmetry-conserving and symmetry-destroying strains are small. The second thing to notice is the huge changes in the individual c_{ij} when the atoms are allowed to relax. For example, c_{33} decreased from 6.34 to 4.30 while c_{21} increased from 0.66 to 1.25. These changes are somewhat muted in the bulk modulus which decreased from 2.344 to 2.169. The last thing to notice is that c_{13} and c_{31}, which were calculated from ε_{zz} and ε_{xx} strains, respectively, are very close to being identical, as symmetry requires they must be. All these discrepancies are typical for the other crystals as well.

In Table II we list the calculated unit-cell volumes and cohesive energies[2–6, 13] together with all the independent c_{ij}'s we have calculated. The bulk moduli are seen to increase with increasing cohesive energy per atom and, if one excludes B_{12} as being inherently different because of the lack of an interstitial chain, they increase with decreasing volume per atom. There does not appear to be any direct correlation between any of the c_{ij}'s. $B_{12}C_3$ with the largest bulk modulus has no individual largest c_{ij}. $B_{12}As_2$ with the smallest bulk modulus has all its c_{ij}'s smaller than any other crystal except for c_{31}, whose relatively large value must be a consequence of the inordinately large value of its rhombohedral angle (70.18° while the other crystals range between 65.54° and 58.12°). Considering the hardness of boron and $B_{12}C_3$, their bulk moduli are exceedingly small. For example a few experimental values are,[14] in units of 10^{11} N/m, 3.72 (for Re), 2.78 (for Pt), 2.70 (for Rh), 1.68 (for Fe), and[9] 2.56 (for β-Si_3N_4). There are no reliable experimental values with which to compare our results, therefore we performed similar calculations for diamond and obtained (with experimental[14] results in parentheses) $c_{11}=10.4356$ (10.76), $c_{12}=1.5955$ (1.25), B = 4.542 (4.43), so that the individual c_{ij}'s are in only fair agreement with the experiment but the bulk modulus is in good agreement. The experimental value of the bulk modulus of boron given in Ref. 14 ($B=1.78\times10^{11}$ N/m^2) can be traced back to a measurement of the compressibility of a boron rod under uniaxial stress made in 1929 by Bridgeman[15] assuming boron to be cubic. Bridgeman suspected it was not cubic and stated that in that case the compressibility could be considerably smaller. Hence our value of 2.072 × 10^{11} N/m^2 is completely consistent with Bridgeman's result. There are a few other results quoted in the literature[16] for boron but it is unclear exactly what was measured and fairly certain that the samples were very impure. We could find no experimental values for any elastic moduli of any of the compounds in Table II, thus the values for the elastic moduli listed in Table II are the best currently available for these crystals.

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TABLE II. Calculated unit cell volumes, cohesive energies, and elastic moduli for B_{12} and its compounds. In addition, for $B_{12}C_3$, $c_{22}=5.3648$, $c_{23}=0.6329$, $c_{52}=-0.3874$, $c_{53}=-0.0103$.

	Ω (bohr^3)	E (eV/atom)	c_{11} (10^{11} N/m^2)	c_{21} (10^{11} N/m^2)	c_{31} (10^{11} N/m^2)	c_{51} (10^{11} N/m^2)	c_{33} (10^{11} N/m^2)	B (10^{11} N/m^2)
$B_{12}As_2$	870.22	6.5733	4.3033	0.9049	0.6565	−0.0231	3.5261	1.817
B_{12}	582.31	6.8314	4.4838	1.1042	0.4110	0.2449	5.8890	2.072
$B_{13}C_2$	751.08	7.1321	5.0047	1.2529	0.7375	0.0765	4.3015	2.169
$B_{12}O_2$	693.38	7.1465	5.8688	1.3319	0.4741	0.2275	4.4387	2.222
$B_{12}C_3$	729.85	7.2508	5.6180	1.2356	0.6959	0.1777	5.1772	2.339

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