## Crystal structure, formation enthalpy, and energy bands of $B_6O$

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We have performed *ab initio* calculations of the crystal structure and electronic structure of  $B_6O$  using an expansion in over 11 700 plane waves. The crystal structure is compared with recent x-ray data; contour plots show the two oxygen atoms in the unit cell do not bond to each other, and the heat of formation is calculated to be 11.37 eV per unit cell.

### I. INTRODUCTION

Boron and its compounds based on the  $B_{12}$  icosahedron are a fertile field for the performance of electronicstructure calculations. Because of the extreme difficulty in obtaining good stoichiometric single crystals, many experimental results are contradictory while many other simple facts have been unobtainable from experiment. An example of the latter is  $B_{13}C_2$  where x-ray data can determine where the atoms are but not what they are, i.e., it cannot distinguish between the  $B_{12}(CBC)$  and  $B_{11}C(BBC)$  structures. Chemical coordination number arguments favor the CBC chain; whereas Emin and coworkers<sup>1</sup> had given indirect but not unconvincing arguments based on a comparison of the  $B_{12}C_3$  and  $B_{13}C_2$ electrical conductivities, Raman spectra, and a theoretical free-energy analysis which favored the BBC chain. Ab initio calculations<sup>2</sup> of the internal and free energies as well as a comparison of the calculated lattice constant and angle with x-ray results, however, unequivocally favor  $B_{12}(CBC)$ . An example of the former is tetragonal  $B_{50}$  which was shown by x-ray analysis to really be  $B_{50}C_2$ or  $B_{50}N_2$  some 33 years after its first discovery. Our preliminary unpublished calculations indicate that only one of two possible  $B_{50}C_2$  structures is stable while  $B_{48}C_2$  and  $B_{50}$  are unstable.

It was not that long ago that  $B_6O$  was listed<sup>3</sup> as  $B_{6,6}O$ and it was unclear whether the stoichiometry of the perfect crystal was B7O, B13O2, or B6O. It is only very recently that reliable x-ray data<sup>4</sup> have become available which show that the structure is  $B_{12}O_2$ , i.e., the structure is identical to that<sup>2</sup> of  $B_{12}(CBC)$  with the chain-centered boron removed. In this paper we perform calculations for  $B_6O$  identical to those we performed for<sup>5,2</sup>  $B_{12}$ ,  $B_{13}C_2$ , and<sup>6</sup>  $B_{12}C_3$  using the method described in the Appendixes of Ref. 6. Because the oxygen pseudopotential is much deeper than the carbon, we use all plane waves with  $(\mathbf{k}+\mathbf{G})^2 < 100$  Ry (compared to 43.946 Ry for the carbides) which results in 11704-11729 plane-wave expansions at the five k points sampled in the irreducible wedge of the Brillouin zone (BZ). [These k points are identical to those described for  $B_{12}(CCC)$  in Appendix C of Ref. 6.] The s and p pseudopotential cutoff radii were taken to be 1.1 bohr for both B and O and the local pseudopotentials were chosen identical to the p.

#### II. CRYSTAL STRUCTURE

We adjust the atomic positions and lattice constants until the calculated Hellmann-Feynman forces and stresses become sufficiently small that the total energy has converged to its minimum value. Table I lists, in order, the calculated lattice constant and angle, the four independent intraicosahedral bond lengths, the oxygenoxygen separation, and oxygen-icosahedral and intericosahedral bond lengths<sup>7</sup> and compares them with the x-ray results of Higashi *et al.*<sup>4(a)</sup> It should be noted that we are comparing calculations for an ideal crystal at 0 K with measurements on a powder at room temperature containing an estimated 93% occupancy of the oxygen sites. The local-density approximation (LDA) for exchange and correlation typically causes 0.5-1 % errors in the lattice constant so the agreement here between theory and experiment is excellent. The discrepancy in lattice angle is larger than for  $B_{12}$  or the carbides but in the direction one would expect from oxygen vacancies. The discrepancy in individual bond lengths d is worse than for  $B_{12}$  and very much worse than for the carbides. Our results seem to be closer to those of Ref. 4(b) where d(O-O)=5.78 bohrs and  $d(O-\hat{e})=2.84$  bohrs have been quoted.<sup>8</sup> Higashi et al. point out that the lattice constant, angle, and unit-cell volume all increase on going from  $B_{12}$  to  $B_{12}O_2$  to  $B_{13}C_2$ . We show that this is generally true also for the calculated values in Table II. We note that  $B_{12}O_2$ has the smallest discrepancy between calculated and mea-

TABLE I. Rhombohedral lattice constant, angle, and interatomic bond lengths of  $B_{12}O_2$  compared with experiment.

	Calculated	Expt.
a (bohrs)	9.709	9.732
$\alpha$ (deg)	63.22	62.90
d(t-t) (bohrs)	3.363	3.42
d(t-e) (bohrs)	3.361	3.40
$d(t-\hat{e})$ (bohrs)	3.417	3.50
$d(e-\hat{e})$ (bohrs)	3.311	3.46
d(O-O) (bohrs)	5.695	5.82
$d(\mathbf{O} \cdot \hat{e})$ (bohrs)	2.826	2.70
$d(t-\hat{t})$ (bohrs)	3.199	3.17

TABLE II. Comparison among  $B_{12}$ ,  $B_{12}O_2$ , and  $B_{13}C_2$  of calculated and experimental (in parentheses) lattice constant, lattice angle, rhombohedral unit-cell volume (Å<sup>3</sup>), chain length, chain-icosahedral bond, intericosahedral bond, and two intraicosahedral circumferences with their ratios. (All lengths in bohrs.)

	<b>B</b> <sub>12</sub>	<b>B</b> <sub>12</sub> <b>O</b> <sub>2</sub>	<b>B</b> <sub>13</sub> <b>C</b> <sub>2</sub>
a	9.512(9.556)	9.709(9.732)	9.824(9.823)
α	58.12°(58.06°)	63.22°(62.90°)	65.54°(65.62°)
Ω	582.31(589.72)	693.38(693.76)	751.08(751.90)
d(C-C)		5.695(5.82)	5.450(5.435)
$d(\mathbf{C} \cdot \hat{\mathbf{e}})$		2.826(2.70)	3.044(3.056)
$d(t-\hat{t})$	3.155(3.231)	3.199(3.17)	3.297(3.279)
c(1)	18.371(18.352)	18.479(18.80)	18.602(18.625)
c(2)	18.307(18.403)	18.273(19.07)	18.323(18.328)
c(1)/c(2)	1.0035(0.9972)	1.0113(0.9858)	1.0152(1.162)

sured unit-cell volumes. This may be a consequence of LDA errors making all the calculated volumes too small, while the measured  $B_{12}O_2$  volume is also too small because of the O vacancies. In Table II we also compare calculated and experimental chain lengths, chainicosahedron, and intericosahedron bond length. It is interesting to note that the O-O chain is longer than the C-B-C chain so that the oxygens truly are not influenced by each other. We also note that the calculated  $t \cdot \hat{t}$  intericosahedral bond lengths are in the canonical order but the measured ones are not. The  $B_{12}$  bond length seems to be the culprit here because of its large deviation from the calculated value.

The individual intraicosahedral bond lengths have no discernible pattern. In the last three rows of Table II we list two different circumferences of the icosahedra and their ratio, c(1)/c(2). The first is the intersection of the reflection plane and the icosahedron, which is given by

$$c(1) = \sqrt{3}d(t-t) + 2d(t-\hat{e}) + [4d^{2}(t-e) - d^{2}(t-t)]^{1/2}$$
(1)

and the second is the intersection of the icosahedron with a plane containing two  $e \cdot \hat{e}$  bonds and the inversion center of the icosahedron, which is given by

 $c(2) = 2d(e \cdot \hat{e})(1 + 2\sin\theta)$ (2)

with

$$\theta = \cos^{-1} \{ [d^2(e \cdot \hat{e}) + d^2(e \cdot t) - d^2(t \cdot \hat{e})] / 2d (e \cdot \hat{e}) d (e \cdot t) \} .$$
(3)

For the regular icosahedron c(1)/c(2)=1; our calculated ratios are all >1 and like c(1) increase from  $B_{12}$  to  $B_{12}O_2$  to  $B_{13}C_2$ . The calculated c(2) are not in the standard order but differ from each other by only a small amount. The experimental values are not only all out of standard order but the deviation of the  $B_{12}O_2$  values from the  $B_{12}$  and  $B_{13}C_2$  is very large whether compared with the experimental deviation of  $B_{12}$  from  $B_{13}C_2$  or with the calculated deviations among all three crystals. There is no reason to expect the calculated structure for  $B_{12}O_2$  to be any worse than that for  $B_{13}C_2$ , which is in near perfect agreement with experiment. We therefore assert that our calculated structure for  $B_{12}O_2$  is a better representation of the zero-temperature perfect crystal than the structure obtained from the x-ray data. If it were easy to obtain



FIG. 1. Energy bands of  $B_{12}O_2$ . The solid (dashed) lines represent states even (odd) under reflection. The dot-dashed lines along the threefold  $\Gamma Z$  rotation axis are the doubly degenerate representation. The + and - at symmetry points represent the symmetry under inversion.  $\Gamma_1$  and  $Z_1$  ( $\Gamma_2$  and  $Z_2$ ) become solid (dashed) lines in any direction whereas  $\Gamma_3$  and  $Z_3$  become either a dot-dashed line or a pair of solid and dashed lines.

good samples from which good data could be obtained, the structure of  $B_{12}O_2$  would have determined long ago.

### **III. ENERGY BANDS AND COHESIVE ENERGY**

Figure 1 displays the energy bands in the reflection plane of the BZ. The smallest gap is direct and occurs at Z, the center of the hexagonal face of the BZ. This gap of 2.03 eV lies between the  $B_{12}$  and  $B_{13}C_2$  gaps. (These crystals have indirect gaps; the statement is true whether their direct or indirect gaps are considered.) In Figs. 2 and 3 contours of constant charge density are displayed in the reflection plane and on the icosahedral surface. Note that the t- $\hat{t}$  intericosahedral bond along the bottom edge of Fig. 2 peaks at  $155\zeta$  (where  $\zeta$  is millielectrons per cubic bohr) whereas the intraicosahedral  $\hat{t}$ -e bond peaks asymmetrically at 125 $\zeta$ ; this large difference between the two bonds is more similar to the B<sub>12</sub> bonding than to B<sub>13</sub>C<sub>2</sub>. Note also that the *e* and  $\hat{e}$  atoms in Fig. 3 have larger charge-density contours around them than do the *t* atoms. This is similar to B<sub>12</sub> and B<sub>13</sub>C<sub>2</sub> although the effect is largest here and smallest for B<sub>13</sub>C<sub>2</sub>. Thus the O-O and C-B-C chains seem to affect the icosahedral boron charge densities oppositely.

The very deep oxygen potential affects the nature of the occupied bands. We have examined contour plots of the charge density in the reflection plane<sup>9</sup> for some of the low-lying bands at B in the BZ. The lowest two bands are very localized s orbitals which peak on the oxygen sites at<sup>10</sup> 160 $\zeta$ , i.e., of the total charge density of 380 $\zeta$  on the oxygen sites (see Fig. 2) all but 60 $\zeta$  come from these two bands. The contours show the same sort of polarization toward the boron atom that the total charge density does, but the density has decreased to 1 $\zeta$  at the boron site. There is a large region in the middle of the O-O





FIG. 2. Contours of constant charge density plotted in the reflection plane. The  $B_{12}$  icosahedra are centered on the four corners of the figure. The contours plotted are 6, 8, 10, 20–155 in steps of 15, 175, 200, 240, 300, and 380–880 in steps of 100 millielectrons per cubic bohr.

FIG. 3. Contours of constant charge density in steps of 8 millielectrons per cubic bohr plotted in the three independent faces of the icosahedron.

TABLE III. Cohesive energies in eV/atom and heats of formation in eV/cell.

	$E_{ m coh}$	Н
$B_{12}O_2$	7.1551	11.37
$B_{13}C_2$	7.1408	1.41
$\mathbf{B}_{12}\mathbf{C}_3$	7.2588	1.63
B <sub>12</sub>	6.8415	

chain with  $\rho < 1\zeta$  which accounts for the even and odd (under inversion) states being nearly degenerate. The fact that these oxygen s orbitals are polarized toward the borons indicates that even though they are extremely localized, they do contribute to the bonding. The third level is an icosahedral orbital. Its  $\rho = 11\zeta$  at the center of the icosahedron and peaks at  $16\zeta$  well inside the icosahedron. It also contains a single lobe of an oxygen p function peaking at 11 $\zeta$  and pointing toward a boron atom but  $\rho$ falls below  $1\zeta$  on the line joining the O and B atoms. The next eight levels all involve oxygen p orbitals. The eighth level is polarized toward the boron (peaking at 196 $\zeta$  in one lobe and 168 $\zeta$  in the other) but is as localized as the oxygen s orbitals. The other orbitals all hybridize with boron charge but the 7th, 10th, and 11th levels are antibonding. For example, the 11th level at B, which is part of an extremely flat band, peaks at  $119\zeta$  in the oxygen lobe, vanishes on a line (in the plane in which we are plotting the contours) between the icosahedron and the oxygen atom, and then peaks at  $21\zeta$  inside the icosahedron.

The  $B_{12}$  icosahedron is known to be two electrons shy of filling all its bonding orbitals.<sup>11</sup> The boron in the C-B-C chain needs only two electrons for bonding and according to simple chemical arguments should be able to supply one electron to the icosahedron. On the other hand, we have seen that each oxygen in the O-O chain has two localized *s* and one localized *p* electron leaving three electrons for its three bonds to boron atoms and none to donate to the icosahedra. In addition we have seen that among the occupied hybridizing states there are at least three which are antibonding. Thus one might conclude that  $B_{12}O_2$  has much less cohesive energy than  $B_{13}C_2$ . However a glance at Table III where we compare the calculated cohesive energies<sup>12</sup> shows that  $B_{12}O_2$  has slightly more cohesive energy per atom than  $B_{13}C_2$  but less than  $B_{12}C_3$ .

The heat of formation per unit cell is given by

$$H = 14E_{\rm coh}(B_{12}O_2) - 12E_{\rm coh}(B_{12}) - D_0(O_2) , \qquad (4)$$

where  $D_0(O_2)$  is the dissociation energy of  $O_2$  and the  $E_{\rm coh}$  are given in Table III. The  $D_0(O_2)$  should be calculated using the same set of plane waves used in the  $B_{12}O_2$  calculation. We therefore removed the  $B_{12}$  icosahedra

TABLE IV. Dissociation energy and equilibrium bond length calculated for O<sub>2</sub> in the magnetic  ${}^{3}\Sigma_{g}^{-}$  ground state and  ${}^{1}\Delta_{g}$  first excited state and their difference compared with experiment. (a) Ref. 15, (b) Ref. 16.

	Calculated	Expt.
$\overline{D_0(^3\Sigma_q^-)}$	6.705 eV	5.115 $eV^{(a)}$
$R_e(^{3}\Sigma_{a}^{s})$	1.3323 Å	1.2074 Å <sup>(b)</sup>
$D_0(1\Delta_a)$	5.629 eV	
$R_{e}(^{1}\Delta_{a})$	1.3335 Å	1.2155 Å <sup>(b)</sup>
$\hbar v ({}^{3}\Sigma_{\alpha}^{-} \rightarrow {}^{1}\Delta_{\alpha})$	1.076eV	$0.982 eV^{(b)}$

from the crystal and repeated the calculation (sampling only  $\Gamma$  in the BZ since the O<sub>2</sub> bands were expected to be flat). We were surprised to find that this  $O_2$  crystal had a small but non-negligible stress, indicating that the charge of the O<sub>2</sub> molecules was overlapping. We therefore scaled the lattice constant by a factor<sup>13</sup> of  $\frac{54}{32}$  and repeated the calculation. This eliminated the stress and reduced the dissociation energy by 0.0465 eV. In order to maintain the 100-Ry cutoff, 56339 plane waves were used in the expansion, yielding the results shown in Table IV. Both the magnetic and nonmagnetic molecular dissociation energies were calculated with respect to spin polarized atoms. Thus their difference represents the first excitation energy which along with the  $D_0$  and equilibrium bond lengths is compared with experiment<sup>14,15</sup> in Table IV. It is interesting to note that our  $D_0({}^3\Sigma_g^-)$  is in much better agreement with experiment and our  $R_e({}^{3}\Sigma_{\rho}^{-})$  in much worse agreement with experiment than most previous work.<sup>16</sup> We checked the convergence at the  $B_{12}O_2$ lattice constant, using a cutoff of  $(\frac{54}{32})^2 \times 100$  Ry, and found an increase of 0.2 meV in  $D_0({}^{3}\Sigma_{g}^{-})$  so that most of the difference between our results and previous work must be due to our use of pseudopotentials.  $E_{coh}(B_{12})$  in Table III has been recalculated with the 100-Ry cutoff but is only 1.3 meV greater than previously reported<sup>5</sup> using a 44-Ry cutoff. Thus the three energies in Eq. (4) are calculated with the same cutoff and result in the 11.37-eV heat of formation compared in Table III with those for  $B_{13}C_2$  and  $B_{12}C_3$ . Once the cohesive energy of  $B_{12}O_2$  was found to be of the same magnitude at that of the carbides, it became obvious that its heat of formation would be much larger than theirs because  $E_{\rm coh} = (O)$  $= \frac{1}{2} D_0(\mathbf{O}_2) \ll E_{\mathrm{coh}}(\mathbf{C}).$ 

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- <sup>8</sup>We compare with the experimental values of Ref. 4(a) because Dr. Higashi kindly sent us his work before publication. The two bond lengths attributed to Ref. 4(b) were quoted in Ref. 4(a).

- <sup>9</sup>For functions even under reflection we look in the plane containing **k**; for odd functions we look in one of the other planes.
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