Electronic structure and optical properties of the $B_{12}O_2$ crystal

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The electronic structure and the optical properties of the icosahedral $B_{12}O_2$ crystal are studied by means of first-principles calculations. The results are compared with the other B_{12}-based compounds with the same rhombohedral crystal structure. $B_{12}O_2$ is a semiconductor with a direct band gap of about 2.40 eV at Z. It is shown that intericosahedral bonding is stronger than the intraicosahedral bonding in $B_{12}O_2$. There is no covalent bonding between the O atoms and a net charge transfer from the B_{12} icosahedron to the O atoms. From the calculated complex dielectric function and energy-loss function, the static dielectric constant and bulk plasmon frequency in $B_{12}O_2$ are estimated to be 3.4 and 26.9 eV, respectively, which are smaller than that of other B_{12}-based compounds. [S0163-1829(96)02527-1]

Recently, we have investigated the electronic and optical properties of some icosahedral boron-rich compounds.[1,2] The band structures, the density of states (DOS), the effective charges, the bond orders, the bulk moduli, and the optical conductivities of α-r-B_{12}, $B_{12}As_2$, $B_{12}P_2$, $B_{11}C(CBC)$, and $B_{13}C_2$ crystals were reported. In this paper, we extend our calculation to another icosahedral crystal $B_{12}O_2$. Boron oxides are the basic components of independent and dependent boron ores on Earth[3] and exist in many phases such as B_2O_3, B_xO ($x=6$, 6.5, or 7), B_2O, $(BO)_x$, and BO_2.[4] The exact composition of icosahedral boron suboxide B_6O or $B_{6.5}O$ was not sure. Based on the calculated density of 2.65 g/cm³ and the measured density of 2.64 g/cm³, Post[5] had proposed the structural composition of the compound to be $B_{12}O_2$. More recently, x-ray-diffraction experiments were carried out and the atomic positions and the lattice parameters of $B_{12}O_2$ were determined.[6,7] Oxygen $K\alpha$ x-ray emission spectroscopy,[8] in conjunction with $X\alpha$ discrete-variation calculation suggested the O-O separation in the crystal to be in the 2.5- to 3.5-Å range.

Theoretically, Lee, Kim, Bylander, and Kleinman[9] used the first-principles pseudopotential method to calculate the crystal and electronic structures of $B_{12}O_2$. Beckel *et al.* studied the vibrational modes in $B_{12}O_2$ using a central force model and also the electronic structure by means of the Hartree-Fock method.[10] In this paper, we report the calculation of the electronic structure and optical properties of the $B_{12}O_2$ crystal using the first-principles orthogonalized linear combination of atomic orbitals (OLCAO) method[11] based on the crystal parameters of Ref. 6. $B_{12}O_2$ has the same space group $r\bar{3}m$ ($a=5.15$ Å, $\alpha=62.90°$) as B_4C. Figure 1 shows the rhombohedral unit cell of the crystal structure of $B_{12}O_2$. Each of the two oxygen atoms links to three B_{12} icosahedral while the separation between the O atoms is quite large. The B atoms can be divided into two groups, B_1 and B_2, according to the different bonding status. B_1 are the top or bottom B atoms in the icosahedron that bond to the B atoms of another icosahedron, while B_2 are the equatorial B atoms bonding to the O atom. In the present calculation, the basis sets for B atoms are the same as in the $B_{12}As_2$ and $B_{12}P_2$ calculations.[1] For the O atoms, a similar basis set con-

sisting of O $2s$, O $3s$, O $2p$, and O $3p$ orbitals, in addition to the core orbitals, is chosen. The computational procedures for $B_{12}O_2$ are the same as for the other B and B-rich compounds.[1,2]

The calculated band structure of $B_{12}O_2$ along the symmetry lines of the Brillouin zone is shown in Fig. 2. $B_{12}O_2$ is a semiconductor with a direct band gap of 2.40 eV at Z. This gap is about 0.37 eV larger than the value obtained in Ref. 9 using the pseudopotential method. It is possible that the true gap in the $B_{12}O_2$ crystal may be somewhat larger since calculations with local-density approximation generally underestimate the band gap. $B_{12}O_2$ appears to have the smallest gap value among the icosahedral boron compounds
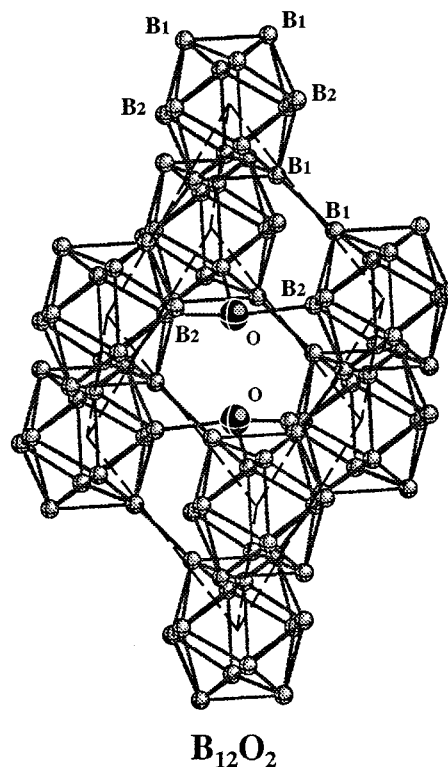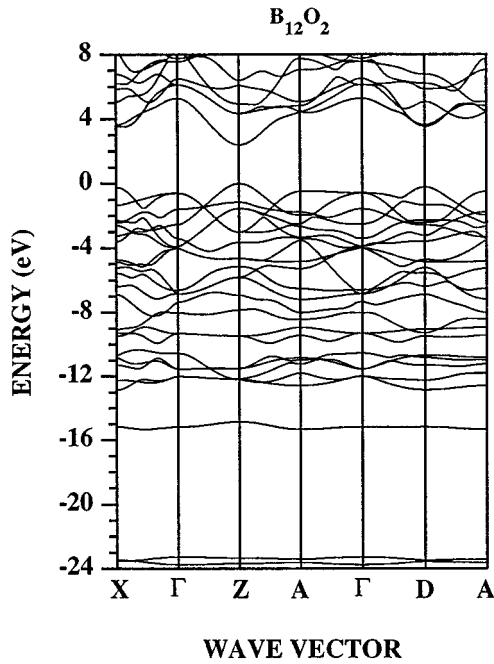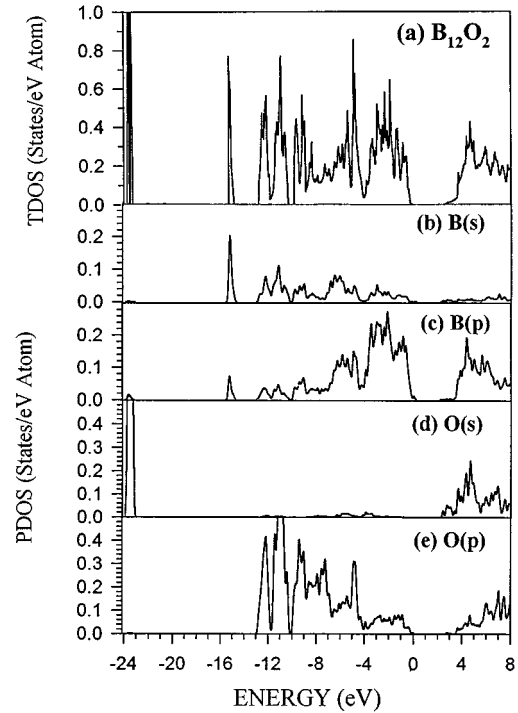

$B_{12}O_2$

FIG. 1. Sketch of the crystal structure of $B_{12}O_2$. The dotted lines show the rhombohedral unit cell.

FIG. 2. Calculated band structure of $B_{12}O_2$

FIG. 3. Calculated total DOS (TDOS) and partial DOS of $B_{12}O_2$: (a) TDOS; (b) B(s); (c) B(p); (d) O(s), and (e) O(p).

[$B_{12}As_2$, $B_{12}P_2$, $B_{11}C$(CBC), and $B_{13}C_2$] with the same crystal structure and using the same method,[1] but is still significantly larger than the α-r-B_{12} crystal, which has a calculated gap of only 1.70 eV. These values are listed in Table I for comparison.

Figure 3(a) shows the calculated total DOS for $B_{12}O_2$. There are four band segments within the valence band (VB), similar to that of $B_{12}As_2$, $B_{12}P_2$, $B_{11}C$(CBC), and $B_{13}C_2$.[1] The widths of four band segments are 9.91, 2.47, 0.46, and 0.47 eV, respectively from the top of the VB. The number of electrons in these segments are 32, 10, 2, and 4, respectively, accounting for a total of 48 valence electrons. The orbital-resolved partial DOS (PDOS) for the B atoms is shown in Figs. 3(b) and 3(c) and that for the O atoms is presented in Figs. 3(d) and 3(e). It is quite clear that B $2s$ and B $2p$ hybridize with each other within the first three segments. The single band around -15 eV is the results of collective bonding of all B atoms in the B_{12} icosahedron and is present in all B_{12}-based compounds. Its peak position is affected by the type of other chain elements in the crystal. They are at -14.7, -14.6, -15.3, and -15.0 eV for the $B_{12}As_2$, $B_{12}P_2$, $B_{11}C$(CBC), and $B_{13}C_2$ crystals, respectively.[1] However, in $B_{12}As_2$ and $B_{12}P_2$, this peak has small mixing from As or P, indicating quite different bonding from $B_{12}O_2$. The

fourth segment (23 eV below the top of the VB) originates from the four O $2s$ electrons and all the eight O $2p$ electrons interact with both B $2s$ and B $2p$ electrons with its PDOS distributed over the first two segments.

The valence electron charge density in $B_{12}O_2$ is shown in Fig. 4. The contour plane is chosen to contain the two interstitial O atoms and one B (B_2) atom linked to the O atom (see Fig. 1). The contours show that there is a large empty space between the O atoms. This is related to the fact that the O-O separation in $B_{12}O_2$ is 3.08 Å, about $2\frac{1}{2}$ times larger than that of a free O_2 molecule (1.21 Å). Thus, in contrast to the other B-rich compounds of the same crystal structure, $B_{12}O_2$ does not have a multiatom chain in the $\hat{z}$ direction since the two O atoms do not form a bond. The large O-O separation results in only three directed bondings of the O atom to the three icosahedral instead of forming four tetrahedrally directed bonds as in $B_{12}As_2$ or $B_{12}P_2$.[1] Figure 5 shows the line charge density $\rho(r)$ along the O-O and O-B_2 directions. Obviously, there is no bond formation between the O atoms because of large distance of separation. The lowest charge value along the O-B_2 bond is 0.09 electron, which is comparable to the charge value of 0.10 elec-

TABLE I. Comparison of calculated energy gaps, static dielectric constants ε_0, the major peak positions of $\varepsilon_2(\omega)$, and the bulk-plasmon frequency ω_p.

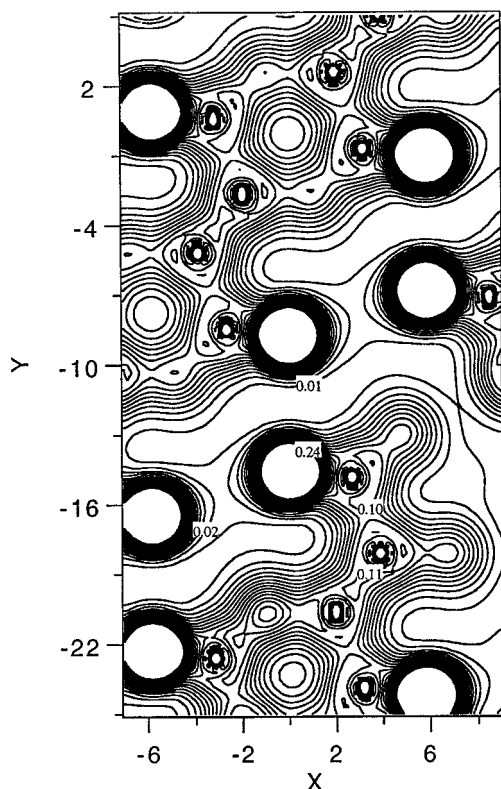| Crystals	$B_{12}As_2$	$B_{12}P_2$	$B_{13}C_2$	$B_{11}C$(CBC)	α-r-B_{12}	$B_{12}O_2$
E_g (eV)	2.78	2.63	3.01	3.04	1.70	2.40
V/V_0	0.990	0.976	0.987	0.955	0.994	0.985
B (Mbar)	2.50	2.66	2.63	2.73	2.45	2.68
ε_0	6.59	5.49		6.35	7.31	3.40
$\varepsilon_2(\omega)_{max}$	6.73	6.37	9.97	7.72	6.90	7.11
ω_p (eV)	33.7	31.7	30.2	32.7	30.3	26.9

FIG. 4. Valence charge-density contour of $B_{12}O_2$. The contour lines are from 0.01 to 0.25 in the interval of 0.01 electron/(a.u.).[3]

tron at the center of the B_1-B_2 bond and the charge value of 0.11 electron at the center of the B_1-B_1 bond. We thus conclude that O and B_2 atoms in the icosahedron form a partially covalent bond in $B_{12}O_2$.

The calculated effective charges for each type of atom in $B_{12}O_2$ are listed in Table II. Also listed for comparison are the results from the Hartree-Fock calculation,[10] which are quite close. The B_1 atoms gain about 0.04 electron each,
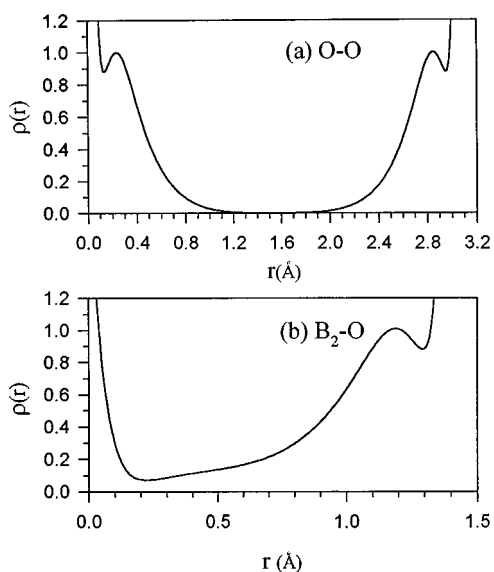

FIG. 5. Charge-density distribution along the lines (a) O-O and (b) B-O.

TABLE II. Calculated Mulliken effective charge for $B_{12}O_2$. The number in the parentheses indicates the number of atoms for the type.

Atom, type	OLCAO results	Hartree-Fock results [a]
B_1	3.04(6)	3.046(6)
B_2	2.79(6)	2.835(6)
O	6.51(2)	6.356(2)

[a]From Ref. 10, where B_1 and B_2 types are just the inverse of B_1 and B_2 in this paper.

while the B_2-type atoms lose 0.21 electron each and the O atoms gain about half an electron each. The effective charge calculation indicates a net charge transfer of 1.02 electron from the icosahedron B atoms to the O atoms. In contrast, the calculations for $B_{12}As_2$ and $B_{12}P_2$ (Ref. 1) showed there is a charge transfer of 1.20 (0.90) electrons from the As (P) atoms to the icosahedron. This shows that the higher electronegativity of the O atom and the fact that the O pair in $B_{12}O_2$ does not form a bond results in a rather different picture of the electronic structure even through the crystal structures of $B_{12}O_2$ and $B_{12}As_2$ are the same.

The calculated overlap populations or bond orders in $B_{12}O_2$ between different pairs of atoms are listed in Table III. We distinguish between the intra- (type A) and inter- (type B) icosahedral bonds. Based on the bond order, it appears that B_1-B_1 intericosahedral bonding is the strongest bond, while the B-O bonding is the second strongest bond. The strength of intericosahedral bonding is about twice as strong as the intraicosahedral bonding. Thus $B_{12}O_2$, like $B_{12}As_2$ and $B_{12}P_2$,[1] also can be classified as the ''inverted molecular solids'' envisioned by Emin.[12] However, the bond order between O and B_2 is 0.17, while that between As (P) and B_2 is 0.21 (0.27), indicating the latter form stronger covalent bonds. Although the absolute values of the bond orders from our calculation are different from those obtained by the Hartree-Fock method,[10] the relative order of the bond strength is the same. These numbers are listed in Table III for comparison.

We have also calculated the total energies for the $B_{12}O_2$ as a function of the crystal volume. The calculated equilib-

TABLE III. Calculated overlap populations for $B_{12}O_2$. The number in the parentheses indicates the number of bonds for the type. A denotes intraicosahedral bonding and B denotes intericosahedral bonding.

Bond	Type	OLCAO	Hartree-Fock results [a]
B_1-B_1	A	0.13(6)	0.204(6)
B_1-B_2	A	0.13(12)	0.216(12)
B_1-B_2	A	0.10(6)	0.176(6)
B_2-B_2	A	0.15(6)	0.227(6)
B_1-B_1	B	0.24(6)	0.417(6)
B_2-O	B	0.17(6)	0.285(6)
O-O		0.00	0.00

[a]From Ref. 10.

rium lattice constant is about 0.993 of the measured one. By fitting the total energy data to Murnaghan's equation of state,[13] a value of 2.68 Mbar for the bulk modulus for $B_{12}O_2$ is obtained. This calculated bulk modulus for $B_{12}O_2$ is larger than the value of 2.22 Mbar obtained by the pseudopotential method.[14] The same was true for other boron-rich compounds.[1] The possible reason for this difference is that our calculation does not optimize the structure parameters of the crystal under pressure. The bulk modulus for $B_{12}O_2$ is comparable to other B_{12} compounds and the results are compared in Table I.

The frequency-dependent interband optical conductivity $\sigma(\omega)$ of $B_{12}O_2$ is calculated from the wave functions and is presented in Fig. 6(a). The absorption threshold is at 2.4 eV, which corresponds to the direct gap at Z. We may conclude that the transition between the top of the VB and the bottom of the conduction band at Z is dipole allowed. $\sigma(\omega)$ shows several structures above the threshold at 9.39, 10.24, 12.44, 14.33, and 15.55 eV. The $\sigma(\omega)$ curve gradually decreases after 20 eV. The real $[\varepsilon_1(\omega)]$ and imaginary $[\varepsilon_2(\omega)]$ parts of the dielectric function are calculated from $\sigma(\omega)$. They are shown in Fig. 6(b). The static dielectric constant ε_0 for $B_{12}O_2$ obtained as the zero-frequency limit of $\varepsilon_1(\omega)$ is 3.40, which is much less than the other B_{12}-related compounds we studied. Figure 6(c) shows the calculated energy loss function for $B_{12}O_2$. A bulk-plasmon frequency ω_p at approximately 26.9 eV is obtained, which is also at a much lower energy than the other B_{12}-based compounds.

Table I lists the calculated ε_0, major peak positions in $\varepsilon_2(\omega)$, and the bulk-plasmon frequency ω_p for $B_{12}As_2$, $B_{12}P_2$, $B_{11}C(CBC)$, $B_{13}C_2$, α-r-B_{12},[1,2] and $B_{12}O_2$. $B_{12}O_2$ has the smallest value of ε_0 and ω_p among these boron crystals. There are several possible reasons why $B_{12}O_2$ has a smaller ε_0 than the other B_{12}-based crystals. First, $B_{12}O_2$ is more ionic, as is evidenced by the Mullikan effective charge calculation discussed earlier. Generally speaking, ionic crystals have smaller static dielectric constants. This is supported by the recent calculations on β-Si_3N_4, Si_2N_2O, and α-SiO_2.[15] The ε_0 values obtained are 3.90, 3.34, and 2.45, respectively, correlating with the oxygen content. The second possibility is attributed to the fact that $B_{12}O_2$ does not
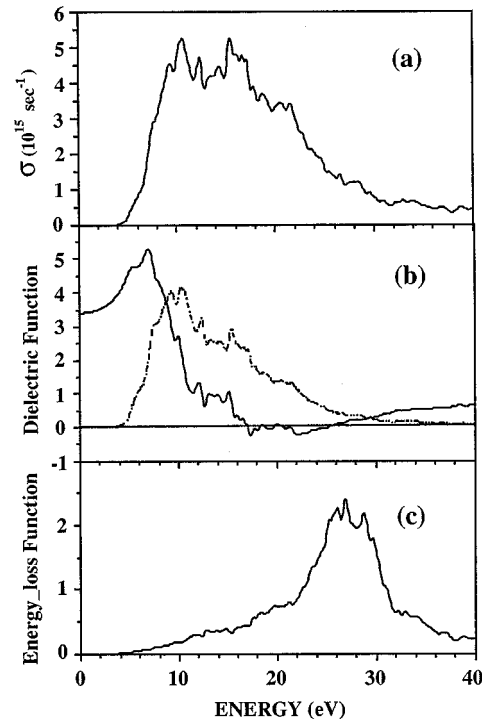

FIG. 6. Calculated optical properties of $B_{12}O_2$: (a) $\sigma(\omega)$, (b) $\varepsilon_1(\omega)$ (solid line) and $\varepsilon_2(\omega)$ (dashed line), and (c) energy-loss function.

have a central O-O chain as in the other crystals that possess a central As-As or CBC chain. There appears to be a larger porous region at the center of the rhombohedral cell. A more porous material generally has a smaller static dielectric constant. We are not aware of any experimental or theoretical results on the optical properties of $B_{12}O_2$ for comparison. We are currently working on the B_2O_3 crystal,[16] which will provide additional insight on the electronic and optical properties of B-related compounds.

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