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Bands and bonds of $B_{12}As_2$

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Ab initio pseudopotential calculations of the crystal structure, electronic structure, cohesive energy, and formation enthalpy of $B_{12}As_2$ have been calculated using a large plane-wave expansion. We compare the bonding with that of B_{12}, $B_{13}C_2$, and $B_{12}O_2$, which have nearly or exactly identical structures as well as with that of elemental As.

I. INTRODUCTION

This is the sixth paper of a series of B_{12} and compounds formed from the B_{12} icosahedron. Except for tetragonal[1] $B_{50}C_2$ all have rhombohedral symmetry. B_{12} is[2] a simple rhombohedral lattice of B_{12} icosahedra, whereas[3-5] $B_{12}C_3$, $B_{13}C_2$, and $B_{12}O_2$ consist of the lattice of icosahedra plus interstitial chains which consist of two or three atoms lying along the threefold axis. Figure 1 of Ref. 3 is a model of the $B_{11}C(CBC)$ structure which x-ray analyses indicate has rhombohedral symmetry only because the icosahedral carbon atom occupies sites randomly on the top and bottom triangles of the icosahedra. In Ref. 5 we noted that as one went from B_{12} to $B_{12}O_2$ to $B_{13}C_2$ the lattice constant a, lattice angle α, unit-cell volume, chain-icosahedral and intericosahedral bond lengths, as well as icosahedral distortion, all increased, while the CBC chain is shorter than the O-O. Noting that the atomic radii[6] of the chain atoms which bond to the icosahedra in the above sequence go from zero to $r_{\rm O}=1.247$ bohr to $r_{\rm C}=1.455$ bohr, one may ask if the established pattern extends to $B_{12}As_2$ where $r_{\rm As}=2.230$ bohr.

The boron pseudopotential used in the $B_{12}As_2$ calculated is identical to that used in all five previous calculations. It is well known that because the Kohn-Sham[7] exchange-correlation (xc) potential is nonlinear in the charge density, $v_{\rm xc}\neq v_{\rm xc}(\rho_{\rm val})+v_{\rm xc}(\rho_{\rm core})$. In constructing the ionic pseudopotential from the atomic, it has become[8] common to subtract off $v_{\rm xc}^{\rm val}=v_{\rm xc}(\rho_{\rm tot})-v_{\rm xc}(\rho_{\rm core})$; however, for first row atoms (for reasons we do not understand) we have found that taking $v_{\rm xc}^{\rm val}=v_{\rm xc}(\rho_{\rm val})$ yields results in no worse and sometimes in better agreement with experiment.[9] Thus our B, C, and O pseudopotentials have not used the core correction. We[10] have recently developed a pseudopotential which eliminates the need for the core correction in the heavier elements. We tested this pseudopotential, which is based on Hartree-Fock cores, on Na and GaAs and found it far superior to ordinary local-density-approximation (LDA) pseudopotentials and of equal quality to the core-corrected LDA pseudopotential both with respect to comparison with experiment and to the independence of the calculated results on the atomic configuration used to construct the pseudopotential. The As scalar relativistic pseudopotential generated in Ref. 10 and the B pseudopotential used in Refs. 1–5 are used in this calculation.

We expand in all plane waves with kinetic energy less than 44.005 Ry at the five points in the irreducible wedge of the Brillouin zone (BZ) which reduce to the two special **k** points[11] of the fcc lattice when $\alpha=60°$ and use the same

TABLE I. Rhombohedral lattice constant, angle, and interatomic bond lengths of $B_{12}As_2$ compared with experiment. (Lengths in bohrs.) The first four bond lengths are intraicosahedral; the last is intericosahedral. The symbols t, $\hat{t}$, e, and $\hat{e}$ represent atoms in the top, bottom, and two equilateral triangles of the icosahedron.

	Calc.	Expt.
a	10.054	10.078
α	70.18°	70.50°
t-t	3.584	3.594
t-e	3.361	3.377
t-$\hat{e}$	3.428	3.464
e-$\hat{e}$	3.266	3.305
As-As	4.526	4.515
As-$\hat{e}$	3.761	3.770
t-$\hat{t}$	3.346	3.347

iterative technique to diagonalize the self-consistent Hamiltonian that we used in all papers in this series.

II. RESULTS

In Table I the calculated lattice constant, lattice angle, and bond lengths are compared with the x-ray analysis of Morosin *et al.*[12] The agreement is extremely good except for α, where it is better than we obtained for $B_{12}O_2$ but not nearly as good as for B_{12} or the carbides. It is interesting to note that the As-$\hat{e}$ bond is actually shorter than the sum of the covalently bonding atomic radii[6] of B and As (3.893 bohr) while the As—As bond is slightly longer than twice the As radius (4.460 bohr). The boron icosahedron is said[13] to be two electrons short of fulfilling its bonding requirements while each As has one more electron than needed for its tetrahedral bonding requirements. Thus there is expected to be some transfer of electronic charge from the As to the icosahedra. The As-As ionic repulsion and As-$\hat{e}$ ionic attraction can account for the small differences from ideal covalent bond lengths. This repulsion between chain atoms also occurs in $B_{12}O_2$, where, because the oxygens do not bond to each other, it bends the boron-oxygen bonds perceptibly off the icosahedral radial direction.

In Fig. 1 contours of constant pseudocharge density in the three independent faces of the icosahedron are plotted. That there is more charge around the e and $\hat{e}$ equatorial atoms which bond to the As than about the top atoms t is obvious. Contours of constant charge density in the reflection plane containing the threefold rotation axis along its long diagonal are shown in Fig. 2. This is the first case in which the chain is covalently bonded. In $B_{12}O_2$ the oxygen atoms seem to repel each other strongly and the charge density drops to 8ζ (where ζ=millielectrons/bohr^3) midway between them. In the carbides the CBC chain is more nearly hydrogen bonded with the boron ion playing the usual role of the proton.

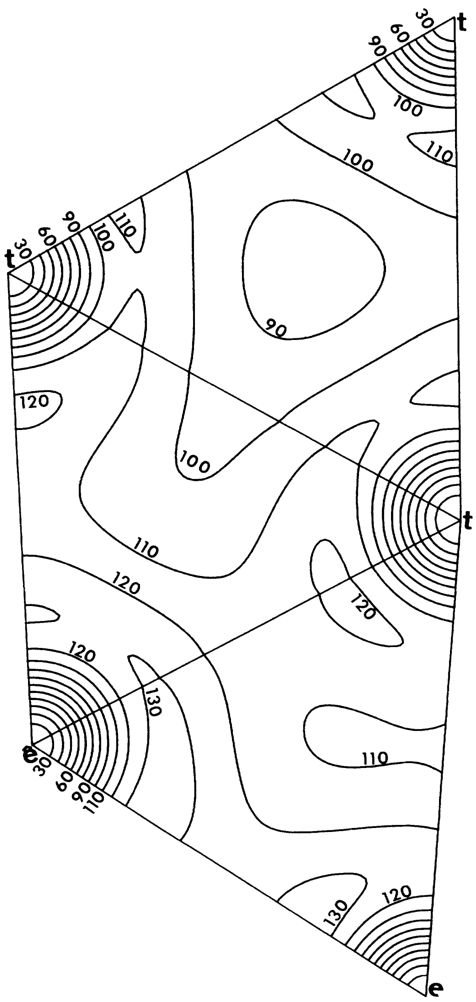

FIG. 1. Contours of constant pseudocharge density in units of millielectrons/bohr^3 in the three independent faces of the B_{12} icosahedron of $B_{12}As_2$. Atoms t, e, and $\hat{e}$ belong to the top and two equatorial triangles of the icosahedron.

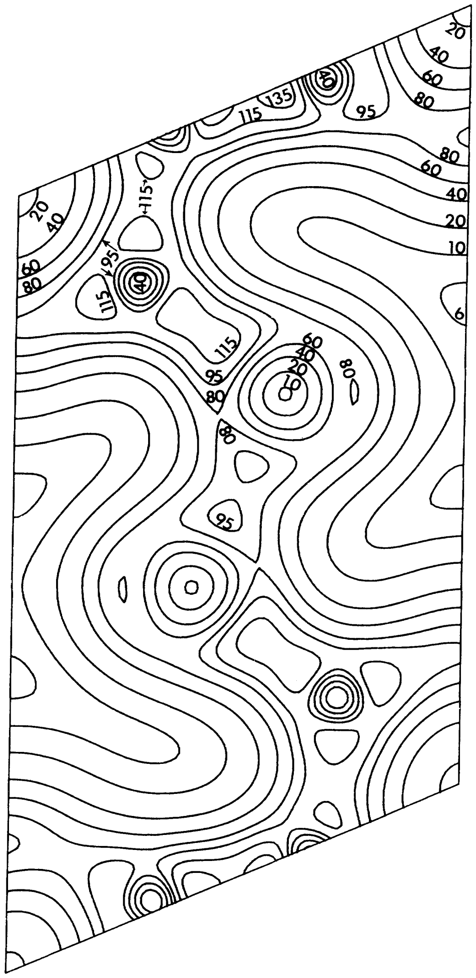

FIG. 2. Constant pseudocharge density contours in units of millielectrons/bohr^3 in the reflection plane of $B_{12}As_2$. Boron icosahedra are centered at the four corners of the figure and two covalently bonding As atoms lie on either side of the center of the long diagonal.

TABLE II. Comparison amongst B_{12}, $B_{12}O_2$, $B_{13}C_2$, and $B_{12}As_2$ of calculated lattice constant, lattice angle, rhombohedral unit-cell volume, chain length, chain-icosahedral bond, and ratio of polar-to-equatorial circumferences of the B_{12} icosahedron. (Lengths in bohrs.)

	B_{12}	$B_{12}O_2$	$B_{13}C_2$	$B_{12}As_2$
a	9.512	9.709	9.824	10.054
α	58.12°	63.22°	65.54°	70.18°
Ω	582.31	693.38	751.08	870.22
C-C		5.695	5.450	4.526
C-$\hat{e}$		2.826	3.044	3.761
t-$\hat{t}$	3.155	3.199	3.297	3.346
$c(1)/c(2)$	1.0035	1.0113	1.0152	1.0364

The chain-icosahedral bond is here also clearly covalent whereas the C and O $2p$ pseudocharge densities are so sharply peaked near the atom that in those cases all one sees in the bonding region is a monotonically decreasing charge density from the chain atom to the boron.

In Table II B_{12}, $B_{12}O_2$, $B_{13}C_2$, and $B_{12}As_2$ are listed in order of increasing atomic radius of the interstitial (chain) atoms which bond to the icosahedra. We see that the calculated lattice constant, lattice angle, unit-cell volume, chain-icosahedron bond length, intericosahedral bond length, and icosahedral distortion all follow this ordering. The distortion is the deviation from unity of the ratio of the polar to equatorial circumferences of the icosahedron, formulas for which are given in Ref. 5. The chain lengths run in inverse order to the atomic radii, with the three atom CBC chain being shorter than the O-O and the As-As being by far the shortest. In order to calculate the heat of formation of $B_{12}As_{12}$ we had to calculate the cohesive energy of elemental As which also crystalizes in a rhombohedral lattice but with two atoms

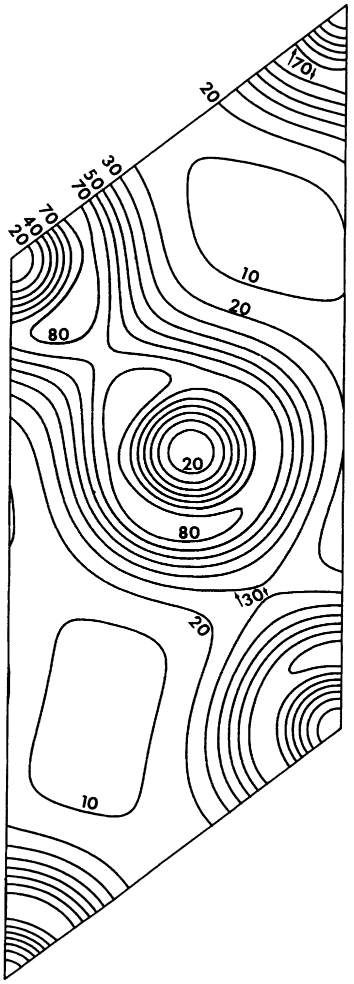

FIG. 3. Constant pseudocharge density contours in units of millielectrons/bohr^3 in the reflection plane of As. There are two As per unit cell, one shared between the four corners of the figure and the other in the center.

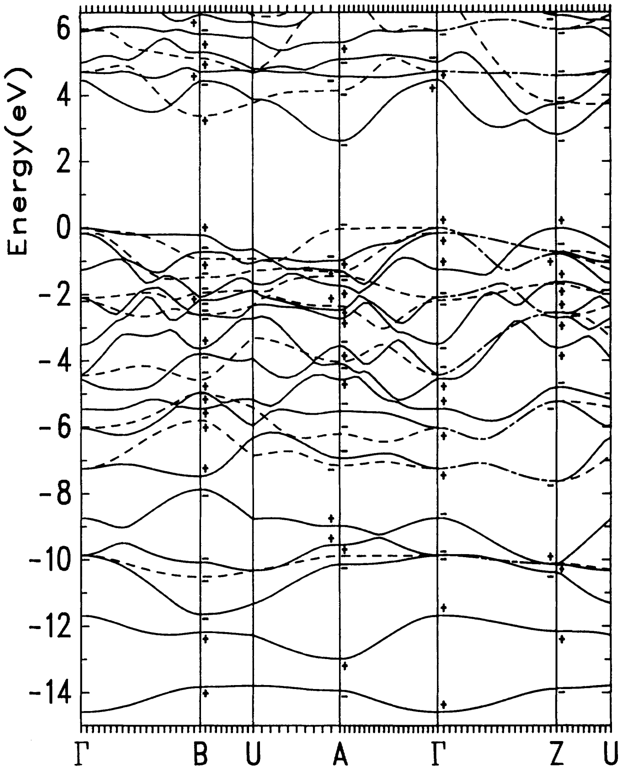

FIG. 4. Energy bands of $B_{12}As_2$. The solid (dashed) lines represent states that are even (odd) under reflection in a vertical plane. Along the threefold rotation axis from Γ to Z the alternating long- and short-dashed lines represent twofold degenerate states. The symmetry under inversion is shown by a + or − at symmetry points Γ, B, A, and Z.

TABLE III. Calculated lattice constant, lattice angle, inner displacement parameter, unit-cell volume, nearest-neighbor (NN) distance, and cohesive energy of As compared with NMN (Ref. 15) and MHW (Ref. 16) and experiment.

	MBK	NMN	MHW	Expt.
a (bohr)	7.559	7.591	7.718	7.751
α	56.799°	56.28°	55.9°	54.554°
u	0.2297	0.230	0.2294	0.2276
Ω (bohr^3)	282.80	282.68	294.19	282.68
NN (bohr)	4.790	4.790	4.839	4.755
E_{coh} (eV/atom)	3.775		3.78	2.96

per unit cell. It is interesting to compare the contours of constant As charge in the reflection plane shown in Fig. 3 with those of $B_{12}As_2$. The first- and second-neighbor distances (from the central atom to the upper-left-hand and lower-right-hand corner atoms, respectively) are 4.790 and 5.715 bohr. Only the first neighbor bond could be called covalent and it is longer and weaker than the As-As bond in $B_{12}As_2$, in the sense that its charge density is less in both the bond maxima and central minimum.

Our $B_{12}As_2$ energy bands are plotted in Fig. 4, labeling points with the Slater[14] notation. $B_{12}As_2$ has two electrons per unit cell less than $B_{12}O_2$ or $B_{12}C_3$ but also has one fewer band below the gap and so, like them, is a semiconductor. Its indirect gap from Γ to A is 2.609 eV, and the direct gap at A is 2.636 eV but is a dipole forbidden transition. The 2.819-eV direct gap at Z is dipole allowed. The x-ray data in Table I was obtained[12] from a clear, colorless sample so we may be fairly certain that these gaps, like most calculated using the local-density approximation for exchange and correlation, are underestimates.

In Table III we compare our calculated lattice constant, lattice angle, unit-cell volume, inner displacement parameter u, cohesive energy, and nearest-neighbor distance for elemental As with those of Needs, Martin, and Nielsen[15] (NMN) and Mattheiss, Hamann, and Weber[16] (MHW) and with the experimental values listed by MHW. Because of the semimetallic nature of As and the smaller unit cell resulting in a larger BZ than $B_{12}As_2$, we used a 30-point sample of the irreducible BZ wedge corresponding to the fcc 10 special **k**-point sample.[11] The agreement with NMN is remarkably close considering the fact that their pseudopotential calculation did not use the xc core correction. The all-electron calculation of MHW gives a and α in better agreement with experiment but for the two most important quantities in determining the total energy, i.e., the unit-cell volume and the nearest-neighbor distance,[17] our results are actually in better agreement with experiment than theirs. Remarkably, the two calculations yield identical cohesive energies which, as usual, due to the LDA, are too large.[18]

TABLE IV. Comparison of various B_{12} compounds calculated cohesive energies (in eV/atom) and heats of formation (in eV/unit cell).

	E_{coh}	H
B_{12}	6.8314	
$B_{12}O_2$	7.1465	11.37
$B_{13}C_2$	7.1321	1.41
$B_{12}C_3$	7.2508	1.63
$B_{12}As_2$	6.5733	2.50

In Table IV are listed our[19] calculated cohesive energies E_{coh} and heats of formation for B_{12} and all the rhombohedral compounds we have studied where $H(B_nX_m)=(n+m)E_{\text{coh}}(B_nX_m)-nE_{\text{coh}}(B_{12})-mE_{\text{coh}}(X)$. The intericosahedral bonding of equatorial atoms in B_{12} is through a weak Δ bond to which each of three icosahedra contributes $\frac{2}{3}$ of an electron. Thus it was completely unexpected that $B_{12}As_2$ would have less cohesive energy (per atom) than B_{12}. In fact, we would have guessed that $B_{12}As_2$ might have more cohesive energy than $B_{12}O_2$ for two reasons: (1) the As bond to each other whereas the O do not; (2) according to the standard model[13] the O and As play the role of cations, donating electrons to the B_{12} icosahedra, but O has a larger ionization energy and electron affinity than As. The only physical reason we can give for the calculated result is a size effect. The large As atom both stretches the $\hat{t}\hat{t}$ intericosahedral bond and, as we have seen, causes an icosahedral distortion more than three times larger than that in $B_{12}O_2$. In all respects in which As is favorable Sb is equally favorable but because of the even larger Sb atomic radius, $B_{12}Sb_2$ does not exist. On the other hand, because of the small As cohesive energy, $B_{12}As_2$ has a larger heat of formation than either $B_{12}C_3$ or $B_{13}C_2$ and is quite stable.

In this last paragraph we summarize what is known about the bonding of crystals based on B_{12} icosahedra. From a chemist's point of view[13] there are 13 internal icosahedral covalent bonds requiring 26 electrons and 12 external covalent bonds requiring 12 electrons from the 36 icosahedral boron electrons. The icosahedron attempts to make up part of this two-electron deficit in one or more of the following ways. It can incorporate a higher valence element into itself such as in $B_{11}C$(CBC). If the interstitial chain has more electrons than required for its bonding as is the case for CBC, As-As, and O-O chains, it can ionize the chain. In the case of tetragonal $B_{50}C_2$, the icosahedra ionize the two interstitial borons which otherwise play no role in the bonding. From a physicist's point of view, because the valence pseudocharge density is fairly constant over the surface of the icosahedron, except in the region of the boron cores where it is expelled, the icosahedral surface may be considered to be a two-dimensional metal. These metal shells then must have a large enough work function to fractionally ionize the other atoms in the crystal. Although the two pictures are equivalent, the chemist's seems more useful. In all the rhombohedral cases, except B_{12}, the six top and bottom atoms of the icosahedron covalently bond to atoms of icosahedra above and below while the six equatorial atoms covalently bond to the chain atoms. The chains themselves may be either bonding (CBC and As-As) or nonbonding (O-O). All this is easily seen in the contour plots. In the case of B_{12} the six equatorial atoms each contribute $\frac{2}{3}$ of an electron to a Δ bond involving atoms from two other icosahedra and in this way reduce the number of electrons required for bonding. In tetragonal $B_{50}C_2$ ten icosahedral atoms bond to other icosahedra and two bond to carbon atoms. Because the two interstitial borons fall far short of making up the eight-electron deficit of the four icosahedra, $B_{50}C_2$ is only metastable;[1] however, we have just completed a calculation of $B_{50}N_2$ where the nitrogens each have one electron they do not need for their bonding and which they can contribute to the icosahedra; we find that $B_{50}N_2$ is stable against decomposing into $4B_{12}+2BN$. Thus the chemists picture holds together very well. In addition, of course there has to be some component of ionic bonding contributing to the cohesion, and finally, we have shown in this paper that size (of the interstial atoms) effects can reduce the cohesive energy.

ACKNOWLEDGMENTS

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[9] Of course, only the *difference* between the atomic and self-consistent crystal v_{xc}^{val} plays any role so that the inclusion of a rigid core correction tends to cancel. Nevertheless this correction becomes moderately important beyond the first row of the Periodic Table.

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[17] The unit-cell volume is given by $\Omega=2a^3[\cos^2(\alpha/2)-\cos^2\alpha]\sin(\alpha/2)$ and the nearest-neighbor distance by $r_{nn}=a[1+4(3u^2-u)(1+2\cos\alpha)]$.

[18] The LDA tends to underestimate the xc energy in both the crystal and the atom but with a larger error in the atom so that the cohesive energy is overestimated.

[19] We found a small error in the boron atomic energy which slightly changes all the cohesive energies previously reported but has no effect on the heats of formation. The atomic energies used here are $E_{As}=-12.350\,563$ Ry and $E_B=-5.171\,663$ Ry.