FINAL TECHNICAL REPORT

"ANALYSIS OF BORON CARBIDES' ELECTRONIC STRUCTURE"

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Abstract

An extensive study has been undertaken of the electronic properties of boron-rich icosahedral clusters as a means of understanding the electronic structure of the icosahedral borides such as boron carbide. We have estimated a lower bound on bipolaron formation energies in B_{12} and $B_{11}C$ icosahedra, and the associated distortions. While the magnitude of the distortion associated with bipolaron formation is similar in both cases, the calculated formation energies differ greatly, formation being much more favorable on $B_{11}C$ icosahedra.

We have also investigated the stable positions of a divalent atom relative to an icosahedral borane ($B_{12}H_{12}$), with the result that we find a stable energy minimum when the atom is at the center of the borane, internal to the B_{12} cage. If incorporation of dopant atoms into B_{12} cages in icosahedral boride solids is feasible, novel materials might result.

In addition, we have calculated the normal modes of a $B_{12}H_{12}$ cluster, of the C_2B_{10} cage in para-carborane, and of a B_{12} icosahedron of reduced (D_{3d}) symmetry, such as is found in the icosahedral borides. The nature of these vibrational modes will be important in determining, for instance, the character of the electron-lattice coupling in the borides, and in analyzing the lattice contribution to the thermal conductivity.

INTRODUCTION

The icosahedral borides, that is, borides based on linked B_{12} icosahedra, are of considerable interest for their potential in high-temperature thermoelectric power generation and in high-temperature semiconductor devices. Boron carbide, for example, has a high carrier concentration ($\sim 10^{21}/cm^3$), a low thermal conductivity ($\sim 10^{-2}$ W/cm^2-K) and an anomalous thermopower (Seebeck coefficient) of $\sim$100-200 μV/K which increases linearly with temperature. In addition, boron carbide and other icosahedral borides are structurally stable to very high temperatures ($\sim$2600 K melting point for boron carbide, for example). All these factors make borides such as boron carbide an important subject of study; while boron carbide has long been used for its mechanical properties, very little investigation of its electronic properties has been carried out. It was pointed out by Wood and Emin[1] that the conductivity and Seebeck coefficient of boron carbide are consistent with hopping of electrons between polaron states localized on the boron icosahedra. Magnetic susceptibility measurements of Azevedo et al.[2] indicate that only $\sim 10^{-2}$ of the carriers have a net spin; this has led to the hypothesis[3] that hopping between bipolaron states, on which a singlet pair of electrons is localized, is the transport mechanism in boron carbide.

Our work during the contract period has had the aim of studying the electronic and vibrational structure of the icosahedral borides, with particular emphasis on boron carbide.

The boron carbide lattice structure is based on the α-rhombohedral boron structure. In this structure, icosahedral B_{12} units are linked together in a plane by triangular ("three-center") bonds, and held together between planes by direct two-center bonds between icosahedra. In boron carbides a certain (variable) amount of carbon is added to this lattice, and three-membered carbon-containing chains are formed perpendicular to the planes of icosahedra. Carbon may also be substituted for boron at a site within the icosahedron. In this way, single-phase compositions from B_9C to B_4C can be formed.

We have studied both the electronic and vibrational structure of the B_{12} units that are the basis of the boride structure. Electronic studies were carried out by several quantum-chemical calculational methods, including Extended Huckel theory and Partial Retention of Diatomic Differential Overlap (PRDDO), which will be summarized in the following section. Vibrational studies employed classical force-field methods. One result of our electronic calculations was a simple but flexible representation for bipolaron formation in terms of a single B_{12} icosahedron plus appropriate terminal "tieoff" atoms. The normal modes of an icosahedron were analyzed for the first time by means of the force-field calculations. Since polaron-type defects involve a distortion of the icosahedron in response to the presence of the localized electron(s), it is important to consider icosahedral distortions simultaneously with electronic structure.

METHODS

Several calculational techniques were used in studying the electronic structure of boron icosahedra. Since our goal was to study a solid in which localized states are of prime importance, calculations involving a finite cluster of atoms were more suitable than band-structure techniques, which assume a perfect lattice. Accordingly, we made use of the Extended Huckel method and the PRDDO method applied to clusters of one or more icosahedra. The first is a non-iterative method suitable for quickly producing a qualitative picture of cluster orbitals. The second is a self-consistent-field approximation of an _ab initio_ Hartree-Fock calculation.

The Extended Huckel method[4] approximates diagonal matrix elements of the Hamiltonian by the ionization potentials of the atomic levels involved; off-diagonal elements are taken to be proportional to the overlap between atomic orbitals, with an empirically determined proportionality constant. Since this method is not iterative, it uses very little computer time and is suitable either for a qualitative idea of cluster properties or for dealing with clusters whose size makes a self-consistent-field calculation impractical.

The PRDDO method[5,6] developed by the Lipscomb group and subsequently applied to boranes, carboranes, and other boron-containing molecules, is considerably more sophisticated. It is a self-consistent calculation which uses a minimum basis set of Slater-type atomic orbitals. Since some of the three-center integrals in the Hamiltonian matrix are retained and

approximated, PRDDO can be considered intermediate in complexity between methods like MNDO and CNDO, which retain only two-center integrals, and an _ab initio_ Hartree-Fock calculation. PRDDO was our method of choice for clusters consisting of one or two icosahedra.

A large number of clusters was considered with the above methods. Among single-icosahedral clusters, B_{12}^0, B_{12}^{2-}, $B_{12}H_{12}^0$ and $B_{12}H_{12}^{2-}$ were considered, as well as $(B_{12}^0)(H_{12}^0)$, $(B_{12}^{2-})(H_{12}^0)$, $(CB_{11}^{1+})(H_{12}^0)$ and $(CB_{11}^{1-})(H_{12}^0)$, in which the hydrogens radially bonded to the icosahedral B_{12} cage were held neutral. Icosahedral "dimers," i.e., two linked icosahedra, were also considered, as $[B_{12}-B_{12}]^0$, $[B_{12}-B_{12}]^{2-}$, $[B_{12}H_{11}-B_{12}H_{11}]^0$, and $[B_{12}H_{11}-B_{12}H_{11}]^{2-}$. While initial calculations were "static," i.e., were not geometry-optimized, later calculations incorporated total configuration energy minimization.

Vibrational calculations were performed by classical force-field methods which require only specification of atomic masses and force constants. Results of such calculations are important for several reasons. A knowledge of the normal modes of B_{12} and $B_{11}C$ cages is useful in predicting the distortions that may accompany bipolaron formation or understanding the transfer of thermal energy in the boron carbides. In addition, calculations of this sort which incorporate carbon substitution can be correlated with ir and Raman spectra of carborane crystals and boron carbides in interaction and structure determinations.

RESULTS

A. <u>Bipolaron Formation in B_{12} and $B_{11}C$ Icosahedra</u>

The bulk of our electronic structure work has focussed on the
question of bipolaron formation in B_{12} and $B_{11}C$ cages. As a
preliminary to considering bipolaron formation, we calculated the
electronic structures of a number of single-icosahedral clusters,
including B_{12}^0, B_{12}^{2-}, $(B_{12}H_{12})^0$ and $(B_{12}H_{12})^{2-}$. This was done
partly as a check on the calculational methods used, since a
number of calculations of the electronic states of B_{12}^{2-} and $B_{12}H_{12}^{2-}$
have previously been carried out. Since bipolaron hopping
involves movement of a singlet electron pair between icosahedra
in a boride, however, a comparison of the neutral and doubly
negative charge states of B_{12} and $B_{12}H_{12}$ was of interest.

The $B_{12}H_{12}$ unit can be thought of as a "building block" of
the boride lattice, since it is a B_{12} icosahedron connected to
"external" atoms by two-center bonds, and in this respect is of
interest. The stable form of the icosahedral borane molecule is
the dianion, $B_{12}H_{12}^{2-}$, in which the extra two electrons serve to
fill the internal cage bonding orbitals of the molecule and lower
its total energy.

We find an optimum B-B bond length of 1.74 Å for $B_{12}H_{12}^{2-}$, in
agreement with Lipscomb's[6] previous results. For this structure,
we find that charge is distributed such that each boron has
-.095e associated with it, while each hydrogen has -.071e, based
on a Mulliken population analysis. The gap between occupied and
unoccupied levels is 13.1 eV; the topmost occupied orbitals have
g_u (4-fold), h_g (5-fold) and t_{2u} (3-fold) symmetry, from higher
to lower energy.

It is of interest to contrast this with the results for B_{12} clusters. Here we find that, for B_{12}^{2-}, the optimum B-B bond length is about 1.76 Å, while for B_{12}^{0}, it is ~ 1.75 Å. Thus, not only is the cage larger in diameter (by ~ .02 Å) for B_{12}^{2-} than for B_{12}^{0} -- this is understandable on the basis of increased Coulomb repulsion -- but the B_{12} cage is <u>larger</u>, by ~.04 Å in diameter, in B_{12}^{2-} than in $B_{12}H_{12}^{2-}$. Furthermore, while $B_{12}H_{12}^{2-}$ is a closed-shell configuration, neither B_{12}^{0} nor B_{12}^{2-} is closed-shell; one has to go to B_{12}^{4-} to find a closed shell state for B_{12}, and this is energetically unfavorable due to the increase of Coulomb repulsion. The size differential between B_{12}^{2-} and $B_{12}H_{12}^{2-}$ can be explained by considering the filling of the 13 internal (icosahedral) bonding orbitals which exist for both B_{12} and $B_{12}H_{12}$.

Several systems of icosahedral dimers were considered. These represented an attempt to correlate icosahedral distortion with charge transfer between icosahedra. We took as the base point for these calculations two directly linked icosahedra, each having a B-B internal bond length of 1.77 Å. Distortions of both icosahedra were then imposed such that one icosahedron was expanded, the other contracted, around the 1.77 Å mean. Initial calculations used only $[B_{12}-B_{12}]$ clusters, with no tieoff atoms present. In its dianionic state, this cluster has a closed-shell configuration. When this cluster was distorted, such that one icosahedron had a B-B bond length 0.05 Å or more longer than the other, it was found that two or more electronic charges were transferred toward the larger B_{12} group. Cluster orbitals were

such that the highest occupied orbital was localized on the larger B_{12}, while the lowest unoccupied orbital, identical in form, was localized on the smaller B_{12}. The gap between the two was ~.3 eV. This would appear at first to be evidence of a bipolaron state resulting in expansion of the associated B_{12} group.

When terminal hydrogens were attached, however, so that the cluster became $[B_{12}H_{11}-B_{12}H_{11}]^{2-}$, a different picture emerged. Distortion of the icosahedra around the 1.77 Å mean B-B bond length was accompanied, for small bond length charges, by a slight (several tenths of an electron) charge transfer toward the smaller icosahedron. This apparent contradiction was resolved by considering several factors which led us to a more appropriate model for the boride lattice. First, we are particularly interested in charge distributions in our clusters as a representation of charges in a lattice. Thus, it is important to preserve as far as possible the crystal symmetry "seen" by an icosahedron in the lattice. The dimer model, obviously, does not do this well. For instance, charge distributions are such that the atom in each icosahedron that links it to the other icosahedron has a net positive charge. Atomic charges become progressively more negative as one moves away from the link toward the far side of the icosahedron.

A second defect of the dimer models we have used lies in our taking the 1.77 Å B-B bond length as our base point. While this is indeed the experimentally determined B-B distance in α-boron, in the context of a cluster model which lacks the crystalline

environment, it is not accurate to impose this value as the mean bond length about which bond lengths in the icosahedra must fluctuate symmetrically. In fact, the mean bond length for B_{12}^0 and B_{12}^{2-} will not necessarily be the same as that for $B_{12}H_{12}^0$ and $B_{12}H_{12}^{2-}$.

The dimer models provided important indications of what is necessary to model the boride lattice. Specifically, the equilibrium geometries of boron icosahedra depend critically on the presence or absence of tieoff atoms; and the preservation, insofar as possible, of crystal symmetry is crucial in predicting atomic charges. Both these considerations were taken into account in our subsequent calculations.

To model as realistically as possible the energetics of bipolaron formation in B_{12} cages, we investigated the optimal geometry as a function of charge state for a boron icosahedron whose atoms are linked by two-center bonds to twelve "external" atoms. In this way, we can simulate a localized bipolaron-like distortion in a lattice of icosahedra connected by 2-center bonds. A comparison of total energies for the neutral (uncharged) icosahedron and the doubly negative icosahedron then gives us an estimate of bipolaron formation energy in such a system.

The lattice outside the 13-atom cage is simulated by the twelve "tieoff" atoms around the icosahedron, whose atomic parameters are varied to mimic the environment that would be seen by an icosahedron in a neutral lattice. This is a fairly accurate representation of the coordination seen by an

icosahedral unit in a 2-center-bonded network of icosahedra (although for such a network, as in boron carbide, the bonding to external atoms will not be radial for six of the twelve icosahedral atoms). To provide a simulation of the true situation in the lattice, we have imposed several conditions on our 24-atom cluster (B_{12} + 12 tie-off atoms):

1) We have broken the full B_{12} icosahedral symmetry (point group I_h) and retained the 3-fold symmetry as found in the crystal lattice, so that the cluster has point-group symmetry D_{3d}. We retain three different bond lengths within the icosahedron: the B(1)-B(1) distance between atoms in the equatorial "puckered hexagon"; the B(2)-B(2) distance between atoms in the polar triangles; and the B(1)-B(2) distance between polar and equatorial atoms. (We neglect the two distinct B(1)-B(2) distances observed with x-ray diffraction.) Starting geometry for the geometry optimization is taken from Yakel's[7] x-ray diffraction data for low-carbon boron carbide. The initial bond lengths are therefore: [B(1)-B(1)] = 1.781 Å, [B(2)-B(2)] = 1.822 Å, and [B(1)-B(2)] = 1.804 Å, the latter an average over the 1.802 Å and 1.805 Å measured by Yakel. The distance from the center of the icosahedron to a B(1) atom is therefore 1.695 Å, and from the center to a B(2) atom, 1.734 Å.

2) The 12 tieoff atoms radially bonded to the B_{12} cage are hydrogenic, that is, they are single-electron atoms. However, we have constrained the average (Mulliken) charge on these hydrogenic atoms to be zero, since our initial interest is in studying the behavior of a network of charge-neutral icosahedra.

This has been accomplished in our calculations by varying the Slater 1s exponent to ensure average neutrality of the atoms. We have started by taking the Slater exponent to be that of the B 2s (or 2p) orbital, and have then adjusted it downward to achieve neutrality.

The distance between tieoff atom and its associated cage boron has been kept fixed throughout the calculations; that is, the tieoff atom simply moves in the direction of motion of the cage B during geometry variation. The bond length between the two was energy-optimized in a preliminary quantum-chemical calculation to 1.09 $\overset{\circ}{A}$, and set at that value in all subsequent calculations.

3) The above-described cluster was then considered in its neutral $[(B_{12}^0)(H_{12}^0)]$ and dianionic states $[(B_{12}^{2-})(H_{12}^0)]$, and an energy minimization, as a function of geometry, was performed for each. The cage atoms were allowed to move in a breathing mode only; that is, only inward or outward radial movement was permitted. Although this may not be in fact the sort of distortion that corresponds to bipolaron formation, it is certainly the simplest realistic distortion.

Energy minimization was first carried out for the deformable cluster $(B_{12}^0)(H_{12}^0)$. The resultant optimum geometry gave the following bond lengths and distances:

[B(1) - B(1)] = 1.750 $\overset{\circ}{A}$ Center of cluster to B(1) = 1.665 $\overset{\circ}{A}$

[B(2) - B(2)] = 1.792 $\overset{\circ}{A}$ Center of cluster to B(2) = 1.706 $\overset{\circ}{A}$

[B(1) - B(2)] = 1.773 $\overset{\circ}{A}$

The total SCF cluster energy was -8246.1 eV. The gap between the highest occupied orbital and the lowest unoccupied orbital was 6.0 eV. Although the cluster would have a partially-filled degenerate orbital if its symmetry were I_h, the lower D_{3d} symmetry splits this orbital so that resultant cluster orbitals are either filled or empty. Mulliken charges on the "tie-off" hydrogen atoms were averaged to zero within $1.5 \times 10^{-3} |e|$ by setting the 1s Slater exponent to 1.21 for all H atoms. Within the B_{12} icosahedron, B(1) atoms were slightly negative, with charges of $-.038|e|$ each; B(2) atoms were correspondingly slightly positive at $+.041|e|$ each.

The $(B_{12}^0)(H_{12}^0)$ calculation is useful only as a basis for comparison with $(B_{12}^{2-})(H_{12}^0)$. Two calculations were carried out on the doubly-negative cluster $(B_{12}^{2-})(H_{12}^0)$. In the first, the cluster geometry was held fixed at the calculated minimum-energy configuration for the _neutral_ cluster $(B_{12}^0)(H_{12}^0)$. In the second, the cluster geometry was allowed to "relax" to the minimum-energy configuration for a dianion. Comparison of the results of these calculations and of the $(B_{12}^0)(H_{12}^0)$ calculation described in the last section allow one to determine the binding energy and the formation energy of the small bipolaron in a neutral lattice. We will, from this point, denote the calculation for $(B_{12}^{2-})(H_{12}^0)$ in the optimized _neutral_ geometry as $[(B_{12}^{2-})(H_{12}^0)]_{noopt}$, and the calculation for $(B_{12}^{2-})(H_{12}^0)$ in its own optimized geometry as $[(B_{12}^{2-})(H_{12}^0)]_{opt}$.

When two excess electronic charges are placed on the B_{12} cage in our model cluster, we find that for static geometry there is a decrease in total SCF energy as compared to that of the neutral

cluster. Specifically, the $[(B_{12}^{2-})(H_{12}^{0})]_{noopt}$ calculation results in a total SCF energy of -8248.8 eV, a decrease of 2.7 eV from the $[(B_{12}^{0})(H_{12}^{0})]$ result. The 1s H exponents were set to 1.33 to achieve average H neutrality to within $3 \times 10^{-5}|e|$.

This reduction of the cluster energy has three components: a decrease in electron-nuclear energy, which indicates that the two extra electrons have gone into bonding orbitals, an increase in electron-electron repulsion, and an increase in kinetic energy of the electrons. The increase in e-e repulsion is 93.1% of the decrease in electron-nuclear Coulomb energy, while the increase in kinetic energy is 6.6% of the electron-nuclear energy decrease. Thus, there is, in spite of increased Coulomb repulsion and kinetic energy, a slight overall <u>decrease</u> in cluster energy upon addition of two extra charges. This is in large part due to the spatial extent of the unit -- the B_{12} cage -- over which the excess charges are localized. That is, the ~ 3.4 Å diameter of the cage prevents the Coulomb repulsion associated with the presence of the two extra electrons from being prohibitively large.

Any optimization of the $(B_{12}^{2-})(H_{12}^{0})$ geometry will further lower the energy of the cluster. Thus, we have at this point already shown the existence of $(B_{12}^{2-})(H_{12}^{0})$ to be energetically favored. Optimization none the less allows us to determine the distortion-related energy reduction and to look at the nature of the distortion induced by the two electrons. When a $[(B_{12}^{2-})(H_{12}^{0})]_{opt}$ calculation was carried out, total SCF energy was found to be -8249.8 eV, or 1.0 eV lower than that for

$[(B_{12}^{2-})(H_{12}^0)]_{noopt}$. Slater 1s H exponents were kept at 1.31, so that H charges were again averaged to zero within $4 \times 10^{-4}|e|$. Optimized bond lengths were found to be [B(1)-B(1)] = 1.661 Å, [B(2)-B(2)] = 1.702 Å, and [B(1)-B(2)] = 1.684 Å, with the distances from the center of the cluster to a B(1) and B(2) atom being 1.580 Å and 1.621 Å respectively. The charge distribution over the B_{12} atoms was almost uniform, with $-0.18|e|$ on B(1) atoms and $-0.16|e|$ on B(2) atoms. The highest occupied orbital was 14.0 eV below the lowest unoccupied orbital.

Comparison of $[(B_{12}^{2-})(H_{12}^0)]_{noopt}$ shows that the cluster has contracted upon optimization; all bond lengths are ~ .09 Å shorter, and the diameter of the cage has shrunk by ~ .18 Å. We therefore find that small bipolaron formation leads to a shrinkage of the icosahedron, with a binding energy of ~ 1.0 eV. The total formation energy of the small bipolaron can also be estimated by comparing the total energy of the $(B_{12}^0)(H_{12}^0)$ cluster to that of $[(B_{12}^{2-})(H_{12}^0)]_{opt}$; the result is a formation energy of ~ 3.7 eV. It should be mentioned that a minimum-basis-set calculation such as we have carried out will, as a consequence of the limited flexibility of the basis set, result in an overestimate of electron-electron repulsion. Consequently, we may expect the actual small bipolaron's formation energy to be somewhat larger, i.e., the small bipolaron's energy to be somewhat lower than our estimate.

In addition, we note that as we increase the H1s Slater exponents in going from $(B_{12}^0)(H_{12}^0)$ to $(B_{12}^{2-})(H_{12}^0)$ we have raised the H atom electronic levels and consequently raised the energy

of the dianionic cluster relative to the neutral cluster. This
is necessary to maintain neutrality of the H tie-offs, but again
means that we have somewhat underestimated the bipolaron
formation energy. Thus, all our systematic inaccuracies tend to
diminish the formation energy, and we expect formation of the
small bipolaron to be more energetically favorable than our
calculations indicate.

We note that a preliminary calculation[8] using the same model
gave an estimate of only 1.3 eV for the bipolaron formation
energy, and a contraction of only ~ .01 Å in the cage radius. In
the later set of calculations, averaged charges on the tieoff
hydrogens are held more precisely to zero, and the resulting
formation energy and distortion are much larger.

A second set of calculations was undertaken along the same
lines, this time for $(CB_{11}^{1+})(H_{12}^{0})$ and $(CB_{11}^{1-})(H_{12}^{0})$ clusters. Since
the boron carbides contain CB_{11} icosahedra, this set of
calculations allows us to compare the relative formation energies
for bipolarons on B_{12} and on CB_{11} sites, and to predict which
type of site will be favorable for bipolaron formation in boron
carbide. The symmetry of the $(CB_{11})(H_{12})$ clusters is lower than
the D_{3d} symmetry taken for the $(B_{12})(H_{12})$ clusters, since the
presence of the C atom induces a distortion. Gas-phase electron
diffraction studies[9] of the carboranes have indicated that in
para-carborane (C atoms at opposite poles of the C_2B_{10} cage) the
C-C diameter of the cage is ~ 0.9 of the B-B diameters. The C
atom therefore is "pulled in" toward the center of the cage. In
setting up the starting geometry of our CB_{11} cages, we have first

imposed a D_{3d} symmetry on the cage, as in the B_{12} cages, and then simply contracted the distance of the C atom from the origin to 0.9 times its starting value. The bond lengths for the D_{3d} geometry were those determined previously from the energy-minimization calculations on $(B_{12}^{0,2-})(H_{12}^0)$. The B-H and C-H bond lengths were held fixed throughout the geometry variation of the cages, at 1.09 Å and 1.03 Å, respectively. Subsequently, with these bond lengths, Slater exponents were varied during the calculations to maintain average charge neutrality on the tieoffs.

From the starting geometries described above, we have allowed the $(CB_{11}^{\pm 1})(H_{12}^0)$ clusters to expand or contract in a breathing-mode type distortion, with the constraint of maintaining an average charge of zero on the hydrogenic tieoff atoms. We will describe first our results for the $(CB_{11}^{1+})(H_{12}^0)$ cluster. With a C atom substituted in a B(2)-type position in the cluster, a total energy of -8594.365 eV was calculated at the minimum-energy geometry. In this geometry, the distance from the center of the cage to the C atom is 1.567 Å; that from the center to a B(1) or B(2)-type boron is 1.700 Å and 1.741 Å, respectively. The bond lengths are 1.743 Å from the C to an adjacent B(2), and 1.722 Å from the C to an adjacent B(1).

Due to the low symmetry of the cluster, there are eight types of inequivalent atoms in the CB_{11} cage, and consequently eight types of inequivalent tieoff atoms. Among the cage atoms, only the C has a net negative charge, as might be expected since the electron affinity of C is larger than that of B. Although there

is wide variation of individual charges on the tieoff atoms, the average charge is only $+6.1 \times 10^{-5} |e|$. To achieve this value for the average charge, it was necessary to assign two different Slater exponents to the H1s basis functions: an exponent $\xi_1 = 1.1000$ for the H attached to the C, and an exponent $\xi_2 = 1.0960$ for the remaining H's.

The principal purpose of our calculations is to compare $(CB_{11}^{1+})(H_{12}^0)$ with $(CB_{11}^{1-})(H_{12}^0)$. The energy minimization procedure for $(CB_{11}^{1-})(H_{12}^0)$ resulted in a total SCF energy of -8612.557 eV at the geometry corresponding to the minimum. The C atom for this case is also placed in a B(2)-type position. The distance, at the minimum, from the center of the cluster to the C atom is 1.486 Å. Distances from the center to a B(1) and a B(2)-type boron are 1.610 Å and 1.651 Å, respectively. Bond lengths are correspondingly shorter than in the $(CB_{11}^{1+})(H_{12}^0)$ cluster: from C to a B(1) boron is 1.632 Å, and from C to a B(2) boron, 1.653 Å. We note that the increase in the energy gap between occupied and unoccupied orbitals, from 5.0 eV in $(CB^{1+})(H_{12}^0)$ to 13.0 eV in $(CB_{11}^{1-})(H_{12}^0)$ reflects the increased stability of the cluster when all internal bonding orbitals are filled. If we look at the charge distribution for the $(CB_{11}^{1-})(H_{12}^0)$ cluster, we find that for this case, all the charges on all atoms, with one exception, are negative. The largest negative charge is on the C atom. The average charge on a H tieoff is $+1.50 \times 10^{-5} |e|$; this follows from setting $\xi_1 = 1.3700$ and $\xi_2 = 1.2384$.

A comparison of $(CB_{11}^{1+})(H_{12}^0)$ and $(CB_{11}^{1-})(H_{12}^0)$ yields information on bipolaron formation. Our previous calculations on

$(B_{12}^{0,2-})(H_{12}^0)$ gave a bipolaron formation energy of ~ 3.7 eV, or which 2.7 eV was energy gained through filling the intra-icosahedral bonding orbitals and 1.0 eV was distortion-related. In order to perform the same analysis, we have calculated the total energy of a $(CB_{11}^{1-})(H_{12}^0)$ cluster at the minimum-energy geometry for the $(CB_{11}^{1+})(H_{12}^0)$ cluster. This we will refer to as the $[(CB_{11}^{1-})(H_{12}^0)]_{noopt}$ calculation, as it represents the case in which two electrons have been added to the positive cluster but the geometry has not been optimized, i.e., has not been allowed to "relax" to its new energy minimum. The total energy for the $[(CB_{11}^{1-})(H_{12}^0)]_{noopt}$ cluster is -8610.815 eV. The energy difference between $(CB_{11}^{1+})(H_{12}^0)$ and $(CB_{11}^{1-})(H_{12}^0)$ is 18.19 eV, while that between $[(CB_{11}^{1-})(H_{12}^0)]_{noopt}$ and $(CB_{11}^{1-})(H_{12}^0)$ is 1.74 eV. The total bipolaron formation energy in our model is thus 18.19 eV, of which the distortion-related component is 1.74 eV. This leaves 16.45 eV as the energy reduction achieved by filling the internal CB_{11} bonding orbitals. Accompanying this energy change is an overall "shrinkage" of the $(CB_{11})(H_{12}^0)$ cluster. The contraction in radius of the cluster is ~ .09 Å, close to the value found for the $(B_{12}^{0,2-})(H_{12}^0)$ clusters.

We have now shown that bipolaron formation in $B_{11}C$ cages is a more energetically favorable process than formation on B_{12} cages; placing two electrons on a $B_{11}C^{1+}$ cage results in a shrinkage of ~ .09 Å in radius, while the total energy reduction is ~ 18.2 eV. The distortion-related component of the energy reduction, which was 1.0 eV for the B_{12} cage, is larger, 1.74 eV, for $B_{11}C$.

We gain some insight into why the bipolaron formation energy is larger by comparing the $(CB_{11}^{1+})(H_{12}^{0})$ and $[(CB_{11}^{1-})(H_{12}^{0})]_{noopt}$ calculations with each other and with the analogous $(B_{12}^{0})(H_{12}^{0})$ and $[(B_{12}^{2-})(H_{12}^{0})]_{noopt}$ calculations. We are looking, therefore, at the energy changes caused by adding two electrons to a static-geometry cluster in each case. It was previously found that the reduction in electron-nuclear energy is -987.06 eV in going from $(B_{12}^{0})(H_{1-}^{0})$ to $(B_{12}^{2-})(H_{12}^{0})$. At the same time, the electron-electron repulsion increases by +919.32 eV, and the kinetic energy by +65.06 eV, so that the sum of the energy increases does not compensate for the electron-nuclear energy decrease. Likewise, as we go from $(CB_{11}^{1+})(H_{12}^{0})$ to $(CB_{11}^{1-})(H_{12}^{0})$, the electron-nuclear energy decreases, this time by -1033.57 eV. The electron-electron repulsion and the kinetic energy increase by +937.58 eV and +79.54 eV, respectively.

In essence, the electron-nuclear energy decrease upon adding two electrons to $(CB_{11}^{1+})(H_{12}^{0})$ is larger, due to the additional positive nuclear charge on C, than in $(B_{12}^{0})(H_{12}^{0})$, and this decrease is the factor primarily responsible for the larger bipolaron formation energy. This is in agreement with the hypothesis[3], advanced to explain the p-type conduction of the boron carbides, that $B_{11}C^{-}$ lies below B_{12}^{2-} in energy.

B. Heteroatoms Internal to a B_{12} Cage

We have investigated the stable positions of a magnesium ion relative to an icosahedral borane ion, $B_{12}H_{12}$, with the complex $Mg + B_{12}H_{12}$ neutral. We have included configurations in which the Mg is inside the boron cage.

It is known that several elements (besides carbon) can go substitutionally into the B_{12} cage (e.g., Be, P), and that other atoms can replace H in bonding to the cage[10]. To our knowledge, however, complexes of $B_{12}H_{12}$ plus a divalent atom have not been theoretically investigated (although icosahedral solid borides such as Mg_2B_{14} are known to exist[11]); a divalent metal atom could doubly ionize to supply the two extra bonding electrons required by the boron icosahedron. We have used a self-consistent field (SCF) molecular-orbital computational technique to find the orbitals, one-electron eigenvalues, Mulliken charges and total SCF energies of a complex consisting of a single Mg atom plus $B_{12}H_{12}$. The calculations run over a variety of configurations, including those in which the Mg is inside the B_{12} cage. Magnesium was chosen because its single and double ionization energies are relatively small; as Mg^+ or Mg^{2+} its ionic radius permits it to fit sterically inside the boron icosahedron[12]; and its radius is not so small that it could readily leak through an icosahedral face.

It is of interest to consider such complexes both on a molecular level and as indicators of possible stable configurations in the solid borides based on linked icosahedral B_{12} units. Although none of these icosahedral borides is known to contain heteroatoms internal to the icosahedra, such a configuration exists as a possibility. In addition, a number of compounds (including at least one of the "heavy fermion" superconductors) have a structure which can partially be interpreted in terms of atoms trapped in icosahedral structures, e.g., $NaZn_{13}$, $ThBe_{13}$, and UBe_{13}[13,14].

In our (PRDDO) calculations, we have retained the minimum basis 1s, 2s, and 2p orbitals for boron, 1s for H, and have used a greater than minimum basis for Mg. In two separate sets of calculations, the Mg basis included 1s through 3p and 1s through 3d basis functions. The only coordinate varied in the calculations was the distance of the Mg ion from the center of the $B_{12}H_{12}$ cage. Two different directions of approach of the Mg to the borane cage were also considered.

Self-consistent calculations were performed as the Mg atom was moved along a path from the center of the $B_{12}H_{12}$ group to a point 10 Å from the center (i.e., outside the $B_{12}H_{12}$ cage). This was done either by moving the Mg through the center of one of the triangular faces of the B_{12} cage or by moving it through the center of one of the edges of the cage. Results are qualitatively the same in either case.

We first consider the set of calculations in which there are 1s through 3p basis functions on Mg. If we plot the total SCF energy of the cluster, relative to its total energy when the Mg is at the center, as we move the Mg from the center through a triangular face to its 10 Å position, we find that stable energy minima are at the center and at ~ 3.5 Å from the center (outside the cage); the minimum at 3.5 Å is more stable by ~ 7.6 eV.

When the Mg basis set is increased to include 3d orbitals, movement of the Mg from the center through a triangular face to a position 10 Å from the center produces a variation in total energy, such that there is one stable minimum at the center of the cage, and another outside, at ~ 3.0 Å from the center. In

this case, however, the minimum at the center is 4.7 eV <u>below</u> the one at 3.0 Å. The addition of the extended and highly directional <u>d</u> orbitals has made the central minimum much more stable relative to the farther one. For movement of the Mg through an edge of the cage, features are qualitatively similar: total energy rising sharply as the Mg is displaced from the center, falling outside the cage boundary, and rising somewhat and leveling off as the distance increases to 10 Å.

Since basis set limitations prevent us from obtaining an accurate comparison of the total energies near the B face and away from it, we cannot estimate from our calculations the activation barrier for the Mg to pass through the $B_{12}H_{12}$ cage. What we have shown is that the configuration of the cluster with the Mg at the center is stable, with a total energy comparable to and probably lower than the total energy when Mg is external to the $B_{12}H_{12}$ cage.

There are a number of ions which, in their doubly-ionized state, will "fit" inside the borane cage. That is, their effective radius will be approximately equal to ~ 0.9 the boron radius. A list of suitable ions under these conditions encompasses more than 20 species, including Ge^{2+}, Nb^{2+}, Fe^{2+}, and Zn^{2+}.[12] It is possible that some ions otherwise suitable will be too small to have a significant stable energy minimum at the center, and if placed inside the borane will be thermally activated over the barrier at its boundaries. Be^{2+}, for instance, may be such an ion.

It seems, however, that there are many ions which could be accommodated inside the borane cage, and quite possibly in the B_{12} units which make up many of the solid borides. Whether such compounds can be synthesized and characterized is a question of considerable interest.

C. Vibrational Modes of Boron-Rich Icosahedra

Normal-mode vibrations of a number of clusters relevant to boron carbide were calculated with classical force-field techniques. As a basis for comparison, the normal modes (frequencies and eigenvectors) of a B_{12} cluster of I_h point-group symmetry were calculated. This was then extended to $B_{12}H_{12}$. Since the symmetry of a B_{12} icosahedron in a boride lattice is D_{3d} (if effects of C substitution are neglected), the modes of a B_{12} cluster of D_{3d} symmetry were subsequently calculated and analyzed in terms of the breakup of the I_h modes.

Since a primary interest is in boron carbides, and therefore in the effects of C substitution at a B site in an icosahedron, vibrational-mode analysis was also carried out for the para-carborane-like unit, $p-C_2B_{10}$, in which C atoms are at opposite "poles" of an icosahedron. Such a cluster has D_{5d} symmetry. The aim is to correlate predicted frequencies with frequencies of the normal modes in the para-carborane $p-C_2B_{10}H_{12}$ and thereby extract B-C interaction strengths. At this point, results of the calculations have been analyzed only for the case of springs along the lines connecting nearest neighbors in the

icosahedron. Inclusion of angular springs also is necessary, and a calculation incorporating these has been performed, although results have not yet been analyzed.

In addition, an explanation has been put forth as to why B-H bond strengths are greater in $C_2B_{10}H_{12}$ than in $B_{12}H_{12}^{2-}$. In essence, in $B_{12}H_{12}^{2-}$ the excess charge (above neutrality) for each B atom induces a dipole moment on each H atom. The charge-dipole interaction decreases bond lengths and spring constants for $B_{12}H_{12}^{2-}$ relative to the case of (uncharged) $C_2B_{10}H_{12}$.

<u>Summary</u>

During the contract period, there have been three principal lines of research on the icosahedral borides. For the most part, we have concerned ourselves with calculation of bipolaron formation energies and the accompanying distortions in B_{12} and CB_{11} icosahedra, as would be found in an icosahedral boride lattice. We have been able to show that, as predicted, the bipolaron in CB_{11} is much more stable than in B_{12}. There is some increase in the distortion-related energy lowering, but for the most part, the difference in formation energies reflects the increased electron-nuclear energy in CB_{11} due to the presence of the extra positive charge in the C nucleus. We also find the bipolaron, either in B_{12} or in CB_{11}, to be accompanied by a shrinkage of the icosahedral cage.

We have also considered stable positions of a divalent heteroatom (in this case, Mg) relative to borane. Results indicate that the center of the borane may be a position of considerable stability. This could be of interest in the design of novel materials based on boron icosahedra.

Finally, we have calculated the vibrational normal modes of a number of boron-rich icosahedral clusters. These are of importance in determining B-C and B-B bond strengths in boron carbide. They will also be important in a consideration of distortions involved in bipolaron formation.

A list of publications and presentations resulting from contract work follows. A number of these are an outgrowth of the International Conference on the Physics and Chemistry of Boron and Boron-Rich Borides, held in Albuquerque, July 29-31, 1985, on the UNM campus. Organizers of the conference were contract personnel C. Beckel (Local Organizing Committee) and I. Howard (Conference Coordinator) in conjunction with D. Emin and T. Aselage, of Sandia Laboratories, and C. Wood, of JPL. The conference brought together research in theory and in experiment on the icosahedral borides, and featured a number of overseas speakers from groups in France, Germany and Japan. In all, 35 invited papers were presented, along with 7 poster papers. Proceedings of the conference were published by the AIP in their Conference Proceedings Series (#140).

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New Technology

Not applicable

Publications

1. D. Emin, T. Aselage, C. L. Beckel, I. A. Howard, and C. Wood, Co-Editors, Boron-Rich Borides, (Proceedings of Conference on the Physics and Chemistry of Boron and Boron-Rich Borides) AIP Conference Proceedings #140, 1986.

2. C. L. Beckel and J. P. Vaughan, Vibrations of Regular Boron Icosahedra, p. 305 in Boron-Rich Borides, eds. D. Emin, T. Aselage, C. L. Beckel, I. A. Howard and C. Wood, (AIP Conference Proceedings #140) 1986.

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6. I. A. Howard, C. L. Beckel and D. Emin, Bipolarons in Boron Icosahedra. II. Effects of Carbon Substitution, manuscript in preparation.

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