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Bipolarons in boron icosahedra

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Small-bipolaron hopping has been proposed as the mechanism of electrical transport in the boron carbides, compounds composed of boron-rich icosahedra linked by carbon-containing chains. We present a simple model of small-bipolaron formation and of the small-bipolaron hopping activation energy. We then consider, by means of a molecular-orbital calculational technique, a cluster model of bipolaron formation in a boron icosahedron set in charge-neutral surroundings. A lower limit of 3.7 eV is calculated for the bipolaron formation energy, of which 1.0 eV is related to site distortion and 2.7 eV to filling of icosahedral bonding orbitals. We have therefore established within our model that small-bipolaron formation will be energetically favored in the boron carbides.

I. INTRODUCTION

Boron carbides, $B_{1-x}C_x$, exist as a single phase over a wide range of carbon content, corresponding to $0.07 \lesssim x \leq 0.20$. Their structures in the single-phase region are based on that of rhombohedral α-boron. In the α-boron unit cell, B_{12} icosahedral units, slightly deformed, sit at the corners of a rhombohedron. When carbon is added, three-atom carbon-containing chains are formed. These run along the long diagonal of the unit cell. In addition, carbon may substitute for one of the boron atoms in an icosahedron. Thus, as carbon concentration is varied between 7% and 20%, boron carbide crystals may contain a distribution of B_{12} and $B_{11}C$ icosahedral units, and of CBC and CBB chains. A perfect crystal of the composition B_4C would contain, presumably, solely $B_{11}C$ icosahedra and CBC chains. Electronic transport measurements (electrical conductivity, Seebeck coefficient, and Hall mobility) at temperatures between 70 and 1300 K have established that electronic motion is via small-polaronic hopping.[1-3] Magnetic susceptibility measurements have subsequently shown that the density of paramagnetic spins is only $\sim 10^{-2}$ the carrier density.[4,5] Thus, the picture that has been developed involves spin-paired electrons hopping between sites. The unit comprised of a singlet electron pair and the associated distortion at the site occupied by the pair is a bipolaron.

There is abundant evidence at the molecular level that the icosahedral borane, $B_{12}H_{12}{}^{2-}$, is stable as a dianion; two extra electrons are needed to fill the molecular bonding orbitals.[6] It is believed, therefore, that the bipolaron sites in boron carbide are the icosahedra rather than the carbon-containing links. The extra electrons needed to fill the bonding orbitals of the icosahedral units are supplied by the carbon atoms, either in the chains linking the icosahedra or in the icosahedra themselves. At the composition $B_{0.8}C_{0.2}$ ($B_{12}C_3$) there would be in a perfect crystal two electrons donated to each icosahedron. In this hypothetical situation, all the bonding orbitals in each icosahedron would be filled. In fact, $B_{12}C_3$ has the lowest conductivity of any homogeneous boron carbide composition; as carbon content is decreased from $B_{12}C_3$ there is an increase in conductivity. In the bipolaron model, this increase is due to the increase in the number of holes, that is, electronically unoccupied icosahedral sites among which electron pairs can hop. The high-temperature transport process in single-phase boron carbide can therefore be summarized as involving the hopping of holes between bipolaron sites located in the icosahedra. While either B_{12} or $B_{11}C$ icosahedra could be bipolaron sites, it is to be expected that the $B_{11}C$ sites will be energetically favored, since the "extra" positive nuclear charge on the C will considerably decrease the electron-nuclear interaction below that in the B_{12} icosahedron. Since the tendency of a carbon-containing chain such as CBC will be to *donate* electrons to the icosahedra, we do not consider the inter-icosahedral chains to be potential bipolaron sites. (In addition, the large spatial extent of an icosahedron allows delocalization of added electrons and thus minimization of the Coulomb repulsion; this, too, makes the icosahedra favorable as bipolaron sites.)

An understanding of transport in boron carbide will involve an understanding of bipolaron formation. In this paper, we begin with general considerations of bipolaron and polaron formation energies. We then present a series of quantum-chemical molecular-orbital calculations that illustrate the application of these ideas to bipolaron formation in systems of boron icosahedra. We consider, in this paper, only bipolaron formation on B_{12} icosahedra. This is a point of reference for calculations in progress which will consider as a separate issue the effects of carbon substitution in the icosahedron. A demonstration that bipolaron formation is energetically favorable in B_{12} icosahedra would suggest the probability of bipolaron formation on $B_{11}C$ icosahedra in the boron carbides.

II. POLARON AND BIPOLARON FORMATION: GENERAL CONSIDERATIONS

A polaron is the unit comprised of a self-trapped electron and the atomic deformation pattern associated with its presence on a site. The formation energy of the polaron depends on the stiffness of the lattice and the strength of the electron-lattice interaction. A small polaron is a polaron that is essentially confined to a single site. Likewise, a small bipolaron involves a pair of self-trapped electrons on a site. In the case of boron carbide, the site is an icosahedron, with the charge distributed over all the twelve atomic sites of the icosahedron. The associated lattice distortion involves displacements of these twelve atoms. For the small bipolaron, the formation energy depends on the lattice stiffness, the electron-lattice interaction strength, and, in addition, on the magnitude of the Coulomb repulsion due to the localization of two electrons on a site. This Coulomb repulsion will itself vary with the lattice distortion.

In a simple model one can write the energy, E, of a small polaron in a static lattice as

$$E = kx^2/2 - Ax \ , \tag{1}$$

where the electron's energy is taken to be zero in the absence of distortion. Here x is the configuration coordinate associated with deformation of the occupied site (icosahedron), k is the site stiffness constant, and A the site's electron-lattice coupling constant. It is assumed that the electron-lattice interaction energy can be taken linear in the distortion. Thus, the first term is the strain energy at the site, and the second is the change in the electron's energy due to the electron-lattice interaction. Minimization gives

$$x^P_{\min} = A/k \ , \tag{2a}$$

$$E_P = -A^2/2k \ , \tag{2b}$$

where $x^P_{\min}$ is the configuration coordinate at the energy minimum, E_P. Thus, the formation energy E_P for the polaron is $-A^2/2k$.

In the same simple model, we will represent the static system's energy E with two electrons on a deformable site as

$$E = kx^2/2 - 2Ax + U \ . \tag{3}$$

Here the factor of 2 in the second term arises because the bipolaron is composed of two electrons; U is the effective Coulomb repulsion between the two electrons. We take the repulsion to vary with configuration coordinate as $U = U_0 - Cx$. U_0 is the repulsion in the absence of distortion, and C is the rate of change of U with distortion coordinate x. Minimization of E now gives

$$x^{\mathrm{BP}}_{\min} = (2A + C)/k \ , \tag{4a}$$

$$E_{\mathrm{BP}} = -(2A + C)^2/2k + U_0 \ . \tag{4b}$$

Thus the formation of one small bipolaron is energetically favored over the formation of two isolated small polarons only if $E_{\mathrm{BP}} < 2E_P$, or

$$-(2A + C)^2/2k + U_0 < -A^2/k \ . \tag{5}$$

The distortion-related decrease in energy of the system (which we will call the binding energy) for the bipolaron is $-(2A + C)^2/2k$. Consequently, within this model the small-bipolaron binding energy will be greater than the small-polaron binding energy, $-A^2/2k$, *unless* $|C| > |A|$ if A and C are of opposite signs. If A and C are both positive or both negative, the bipolaron binding energy will always be larger.

A semiclassical small-bipolaron hop occurs when the electronic energy of the occupied site equals that of the final site. The minimum distortion energy necessary to achieve equality of the electronic energies—a "coincidence event"—then determines the hopping activation energy ΔE. For the small polaron case, such a calculation results in a hopping activation energy $\Delta E_p = A^2/4k$.[7] For the small bipolaron, the requirement of coincidence of electronic levels is that

$$-2Ax_0 - Cx_0 + U_0 = -2Ax_1 - Cx_1 + U_0 \tag{6}$$

for two sites labeled by 0 and 1, i.e., $x_0 = x_1 \equiv x_c$. The total distortion-related energy for sites 0 and 1 is then

$$E^{\mathrm{dis}}_{\mathrm{BP}} = k[x_c - (2A + C)/k]^2/2 + kx_c^2/2 \ . \tag{7}$$

Minimization with respect to x_c gives $x_c = (2A + C)/2k$; the minimum coincidence distortion x_c is just half the equilibrium distortion for small bipolaron formation. Thus

$$(E^{\mathrm{dis}}_{\mathrm{BP}})_{\min} = (2A + C)^2/4k \equiv \Delta E_{\mathrm{BP}} \ . \tag{8}$$

We have studied cluster models which allow us to investigate the changes in energy and optimal geometry that occur when charge is placed on a boron icosahedron in otherwise neutral surroundings. In the remainder of this paper we discuss the results of these calculations.

III. SMALL BIPOLARONS IN BORON ICOSAHEDRA

Here, we study the formation of small bipolarons on B_{12} icosahedra in neutral surroundings. Since we are interested in a localized distortion of a boron icosahedron, we have made use of a finite-cluster approach. Our model consists of a single deformable B_{12} icosahedron in which each atom is connected by a radially-directed two-center bond to a hydrogenic atom. The average charges on these hydrogenic "external" atoms are constrained to zero to simulate the presence of a neutral lattice surrounding the B_{12} icosahedron. Furthermore, we restrict our consideration to "breathing mode" type deformations. That is, the atoms of the cluster move in or out in unison. This corresponds to a scaling of the inner icosahedral "radius."

We have taken the initial geometry for our clusters from Yakel's x-ray analysis[8] for the low-carbon end of the boron carbide single-phase range. Thus, we have broken the symmetry of the B_{12} cage from the full icosahedral (I_h) symmetry to the D_{3d} symmetry exhibited by icosahedra in the boron carbide lattice. There are three distinct B—B bond lengths, as illustrated in Fig. 1, in our D_{3d} cluster symmetry: the B(1)-B(1) distance between atoms (shown as open circles) in the equatorial puckered hexagon; the B(2)-B(2) distance between atoms (shown as dotted circles) in the top and bottom polar triangles; and the B(1)—B(2) bonds connecting these two sets of atoms. For simplicity, we use an average starting B(1)—B(2) bond length instead of the two distinct lengths seen by x-ray diffraction. In particular, our starting bond lengths are $l[B(1)—B(1)]=1.781$ Å, $l[B(2)—B(2)]=1.822$ Å, and $l[B(1)—B(2)]=1.804$ Å. The distances from the icosahedral center to a B(1) and B(2) atom are 1.695 and 1.734 Å, respectively. The optimum distance from a boron atom to its associated hydrogenic "tie-off" atom was determined in a preliminary calculation to be 1.09 Å. This was done by initially assigning to the H 1*s* basis function the Slater exponent appropriate to a second-shell B electron, and finding the energy minimum for the B-H distance; in this way the H tie-off mimics, to some extent, the presence of external atoms (B or C) bonded to the B_{12} cage. The B-H distance was held fixed at 1.09 Å throughout the present set of calculations. Thus, during energy minimization of the cluster geometry, a B atom and its associated hydrogen atom move as a unit. The average charge on all the H atoms is held to zero by adjustment of the 1*s* Slater exponent.

To calculate the formation energy of the bipolaron we add two electrons to the B_{12} cage, and minimize the energy of the cluster within the constraint of a completely symmetric "breathing mode" distortion. Thus, we simulate the presence of a small bipolaron on a B_{12} cage in an otherwise neutral lattice. The uncharged and doubly negative clusters are denoted as $(B_{12}^0)(H_{12}^0)$ and $(B_{12}{}^{2-})(H_{12}^0)$ to emphasize that the excess charge is confined to the B_{12} cage.

To carry out those calculations, we have used the partial retention of diatomic differential overlap (PRDDO) method developed by Lipscomb and co-workers.[9,10] This technique has been used extensively in studies of the boranes and carboranes. It is a self-consistent technique which approximates an *ab initio* Hartree-Fock calculation, using a minimum basis set of Slater atomic orbitals. PRDDO approximates and retains one- and two-center Coulomb integrals, one-, two-, and three-center hybrid integrals, and one- and two-center exchange integrals.

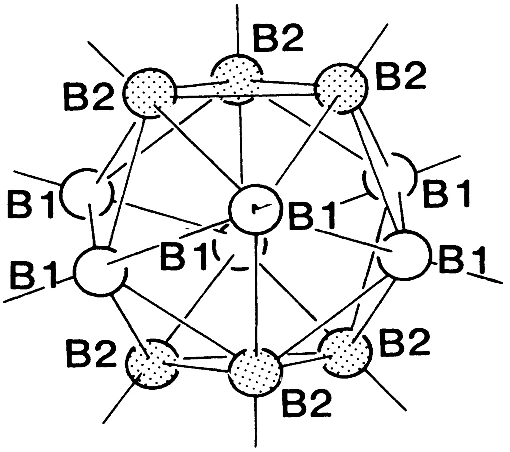

FIG. 1. The B_{12} cage which forms the basis of the clusters considered. Radial hydrogenic tie-off atoms are omitted for clarity. Inequivalent B(1) and B(2) atoms are labeled.

A. The neutral cluster $(B_{12}^0)(H_{12}^0)$

Energy minimization was first carried out for the deformable cluster $(B_{12}^0)(H_{12}^0)$, in which both the B_{12} cage as a whole, and the H atoms as a whole were uncharged. However, charge on every B atom in the cage was not identically zero since B(1) and B(2) type atoms are inequivalent. The resultant optimum geometry gave the following bond lengths and distances:

$$l[B(1)—B(1)]=1.750\ \text{Å},\quad d[\text{center-}B(1)]=1.665\ \text{Å}\ ,$$
$$l[B(2)—B(2)]=1.792\ \text{Å},\quad d[\text{center-}B(2)]=1.706\ \text{Å}\ ,$$
$$l[B(1)—B(2)]=1.773\ \text{Å}\ .$$

The total self-consistent field (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 $1.5\times10^{-3}\,|e|$ by setting the 1*s* Slater exponent to 1.21 for all H atoms. Within the B_{12} icosahedron, B(1) atoms were slightly negative, with charges of $-0.038\,|e|$ each; B(2) atoms were correspondingly slightly positive at $+0.041\,|e|$ each.

The $(B_{12}^0)(H_{12}^0)$ calculation is useful only as a basis for comparison. Since we are primarily interested in the feasibility of bipolaron formation in the boron carbides, we next consider the doubly-negative $(B_{12}{}^{2-})(H_{12}^0)$ cluster.

B. The doubly-negative cluster $(B_{12}{}^{2-})(H_{12}^0)$

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 preceding 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 $[(B_{12}{}^{2-})(H_{12}^0)]_{\text{no opt}}$, and the calculation for $(B_{12}{}^{2-})(H_{12}^0)$ in its own optimized geometry as $[(B_{12}{}^{2-})(H_{12}^0)]_{\text{opt}}$.

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 $[(B_{12}{}^{2-})(H_{12}^0)]_{\text{no opt}}$ 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 1*s* H exponents were set to 1.33 to achieve average H neutrality to within $3\times10^{-5}\,|e|$.

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 *decrease* 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 $(B_{12}{}^{2-})(H_{12}^0)$ cluster geometry will lower the energy of the cluster further. Thus, we have at this point already shown the existence of $(B_{12}{}^{2-})(H_{12}^0)$ to be energetically favored. Optimization nonetheless 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 $[(B_{12}{}^{2-})(H_{12}^0)]_{\text{opt}}$ calculation was carried out, the total SCF energy was found to be -8249.8 eV, or 1.0 eV lower than that for $[(B_{12}{}^{2-})(H_{12}^0)]_{\text{no opt}}$. Slater 1*s* 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 $l[B(1)—B(1)]=1.661$ Å, $l[B(2)—B(2)]=1.702$ Å, and $l[B(1)—B(2)]=1.684$ Å, with the distances from the center of the cluster to a B(1) and B(2) atom being 1.580 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 $[(B_{12}{}^{2-})(H_{12}^0)]_{\text{no opt}}$ shows that the cluster has contracted upon optimization; all bond lengths are ~ 0.09 Å shorter, and the diameter of the cage has shrunk by ~ 0.18 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 $[(B_{12}{}^{2-})(H_{12}^0)]_{\text{opt}}$; 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 *over*estimate 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 H 1*s* 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 *under*estimated 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[11] using the same model gave an estimate of only 1.3 eV for the bipolaron formation energy, and a contraction of only ~ 0.01 Å in the cage radius. In the present set of calculations, averaged charges on the tie-off hydrogens are held more precisely to zero, and the resulting formation energy and distortion are much larger.

IV. SUMMARY AND DISCUSSION

When the bonding energy gained in placing two electrons on a site in a deformable lattice exceeds the Coulomb repulsion between the electrons, formation of a bipolaron—a pair of self-trapped electrons—is possible. Bipolaron formation and electrical transport by bipolaron hopping have been proposed for the boron carbides, which are composed of boron-rich icosahedra. We have constructed a deformable cluster model to simulate a B_{12} icosahedron in a neutral environment, and varied the charge state of the B_{12} cage to model bipolaron formation. We find that bipolaron formation is energetically favorable, and calculate a formation energy of ~ 3.7 eV. Of this energy, 2.7 eV results from filling of the B_{12} bonding orbitals, and 1.0 eV is due to the distortion (shrinkage) of the B_{12} cage in response to the added charge.

It is worthwhile to briefly discuss the magnitudes of the energies we find and the size of the distortion associated with bipolaron formation, i.e., a shrinkage rather than an expansion. If we consider a regular icosahedral borane molecule, $B_{12}H_{12}$, in a static geometry such that all B—B bond lengths are 1.74 Å, we find that $B_{12}H_{12}{}^{2-}$ is lower in energy than $B_{12}H_{12}^0$ by ~ 6.4 eV. (The electronic charge is now allowed to spread out over both boron and hydrogen atoms.) As we begin to confine charge on the B_{12} cage itself and demand neutrality on the H atoms, this energy difference shrinks. The energy of $B_{12}H_{12}{}^{2-}$ rises since charge is being confined to the cage. Geometry relaxation effects account for relatively small energy changes. Thus, for $(B_{12}^0)(H_{12}^0)$ and $(B_{12}{}^{2-})(H_{12}^0)$, only 3.7 eV of an energy difference remains between the two clusters. We may expect that in boron carbide itself, charge will not be confined to the icosahedral cage atoms, but will "leak" slightly onto neighboring atoms, resulting in a slightly lower energy for the bipolaronic state. This is a basis for concluding that the bipolaron formation energy we have calculated is a lower bound on the formation energy in boron carbide.

On the basis of Coulomb repulsion, we might have expected an expansion of our $(B_{12}^0)(H_{12}^0)$ cluster on addition of two electrons. Reference to Eq. (4a) shows that this will depend on the relative value of A and C in our simple static-lattice model. In our cluster models, we find that tie-off atoms are very important in determining the sign of the bipolaronic distortion.

Whether the formation of the bipolaron corresponds to a shrinkage or an expansion of the cluster depends on the presence or absence of "tie-off" atoms such as the hydrogens. We find that addition of two electrons to a B_{12} cluster results in a ~ 0.01 Å *elongation* of all bond lengths and a net increase in total energy by ~ 0.8 eV. This can be related to the degree of filling of the internal bonding orbitals of the icosahedron. In the $(B_{12})(H_{12}^0)$ clusters, one valence electron from each B atom is involved in a direct two-center bond to a H atom; this simulates the type of external bonding of the icosahedron seen in a boron carbide lattice, where every atom of an icosahedron is directly bonded either to an atom in another icosahedron or to an atom in a carbon-containing chain. In such an arrangement, the neutral icosahedron needs two more electrons to fill its internal bonding orbitals as we have seen, and the bonding energy thus gained more than compensates for the increase in Coulomb repulsion. In the B_{12}^0 cluster, however, all the B valence electrons are available for internal bonding of the cage; two added electrons will go into lone-pair orbitals and will also increase the Coulomb repulsion. The total energy of ${B_{12}}^{2-}$ will therefore be higher than that of B_{12}^0, and the cluster will expand in an effort to offset the increased electron-electron repulsion.

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