

Bipolarons in boron-rich icosahedra: Effects of carbon substitution

I. A. Howard and C. L. Beckel

Department of Physics and Astronomy, University of New Mexico, Albuquerque, New Mexico 87131

David Emin

Sandia National Laboratories, P.O. Box 5800, Albuquerque, New Mexico 87185-5800

(Received 29 December 1986)

Analysis of electronic-transport and magnetic measurements on boron carbides has indicated that charge transport occurs via bipolaron hopping between the twelve-atom icosahedral structural units of these solids. Two types of isoelectronic icosahedral units are neutral icosahedral boron clusters (B_{12} icosahedra) and positively charged clusters of eleven boron atoms and a carbon atom [$(B_{11}C)^+$ icosahedra]. In particular, the transport analysis assumes that it is energetically favorable for an electron pair to occupy a $(B_{11}C)^+$ icosahedron rather than a B_{12} icosahedron. Here, we study the energy changes and atomic displacements associated with adding two electrons to a $(B_{11}C)^+$ icosahedron in neutral surroundings and compare our results with our previous study of two electrons added to an analogous B_{12} icosahedron. We find that the addition of the two electrons reduces the $(B_{11}C)^+$ system's energy by about 18 eV. Most of this energy reduction, ≈ 16 –17 eV, is associated with the two electrons filling bonding orbitals associated with all of the atoms of the positively charged icosahedron. The remainder of the energy reduction is associated with the polaronic displacements, the contraction of the icosahedron induced by the placing of the two electrons in icosahedral bonding orbitals. Indeed, the energy reduction associated with adding two electrons to form a $(B_{11}C)^-$ icosahedron is greater than that associated with adding two electrons to form a B_{12}^{2-} icosahedron by about 14 eV. This is because the increased Coulombic attraction of the two electrons arising from the extra positive charge provided by the carbon nucleus exceeds the increases in electronic kinetic energy and electron-electron repulsion energy associated with the icosahedron's reduced symmetry. Thus, it is energetically preferable for an electron pair to occupy a $(B_{11}C)^+$ icosahedron rather than a B_{12} icosahedron. This supports the notion, arising from analysis of electronic transport experiments, that bipolaron hopping occurs between $B_{11}C$ icosahedra.

I. INTRODUCTION

As shown in Fig. 1, boron carbides are solids composed of coupled 12-atom icosahedral clusters of atoms. Here, boron-rich icosahedral structures reside at the vertices of a rhombohedron. In addition, there is a carbon-containing three-atom chain along the longest diagonal of the rhombohedron. In particular, in one structural model¹ the intericosahedral chains primarily contain either one or two carbon atoms, while the icosahedral units primarily have either one carbon atom or none. With such carbon substitutions, single-phase boron carbides exist with carbon concentrations between $6\frac{2}{3}\%$ and 20%. At 20% carbon, the icosahedra each contain a single carbon atom (forming $B_{11}C$ units) and the three-atom chains each have a boron atom bridging two carbon atoms (forming C—B—C chains). At the idealized low-carbon extreme, $6\frac{2}{3}\%$ carbon, B_{12} icosahedra are linked by C—B—B chains. At intermediate carbon compositions, there is a distribution of $B_{11}C$ and B_{12} icosahedra and C—B—C and C—B—B chains.

There are thirteen internal bonding orbitals of a boron icosahedron.² These can accommodate 26 electrons. With all of the atoms of an icosahedron linked to other structural units (icosahedra or chains) by two-center bonds, a neutral B_{12} icosahedron has only 24 second-shell

electrons (36–12) available for internal bonding. Thus, such a boron icosahedron requires the addition of two electrons to fill its internal bonding orbitals.

The substitution of a carbon atom for a boron atom within an icosahedron provides an additional electron for the icosahedron's internal bonding. We assume that a $B_{11}C$ icosahedron has the same number of bonding orbitals as a B_{12} icosahedron. Then, a $B_{11}C$ icosahedron requires the addition of only one electron to fill its internal bonding orbitals. In addition, an electron can be donated to the internal bonding orbitals of an icosahedron from the nonbonding state of the central atom of an C—B—C intericosahedral chain. Thus, ideally at the 20% carbon concentration, with $B_{11}C$ icosahedra and C—B—C intericosahedral chains, all of the system's bonding orbitals will be filled. However, at lower carbon concentrations there are an insufficient number of electrons to fill the system's bonding orbitals.

It is the motion of electrons between filled and unfilled bonding orbitals on different icosahedra which gives rise to electronic charge transport in the boron carbides. Furthermore, conductivity, Hall mobility and Seebeck coefficient (thermoelectric power) measurements indicate that the charge carriers move via thermally activated small-polaronic hopping.³ Thus, charge transport is associated with the small-polaronic hopping of electrons be-

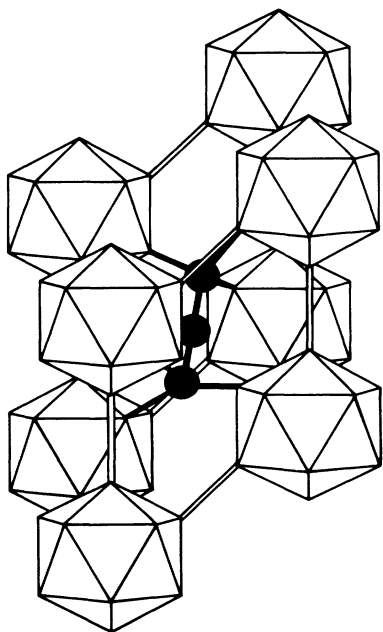
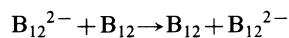


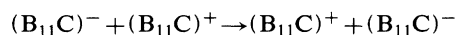
FIG. 1. The structure of boron carbides. Atoms sit at the vertices of the icosahedra and within the three-atom intericosahedral chain.

tween icosahedra. Furthermore, the conductivity taken together with the Hall mobility, as well as the Seebeck coefficient, all yield a charge-carrier density of the order of 10^{21} cm^{-3} at intermediate carbon concentrations.

Magnetic susceptibility and ESR measurements,⁴⁻⁶ however, reveal a temperature-independent density of paramagnetic spins which is 2 orders of magnitude less than the estimated density of charge carriers. Thus, the charge carriers must be spinless. That is, the charge carriers are diamagnetically aligned *pairs* of electrons, i.e., bipolarons, which hop between icosahedra. In particular, this intericosahedral hopping process can be represented as



or



for hopping exclusively between B_{12} or B_{11}C icosahedra, respectively.

Beyond these considerations, it has been observed that the electronic transport in boron carbides is *p* type over the entire range of carbon concentrations which have been studied (between $\approx 9\%$ and 20%).³ This is consistent with bipolaron hopping between B_{11}C icosahedra but not bipolaron hopping between B_{12} icosahedra.¹ This fact implies that it is energetically favorable for a bipolaron to reside on a B_{11}C^+ icosahedron rather than on a B_{12} icosahedron. In other words, the energy lowering of the system upon adding two electrons to form a B_{11}C^- icosahedron is much greater than the energy reduction associated with adding two electrons to a B_{12} icosahedron to

form a B_{12}^{2-} icosahedron.^{1,4}

Previously, we considered the energetics and atomic distortions associated with a pair of electrons being added to a B_{12} icosahedron in which each of the icosahedron's atoms is bonded to a single "external" atom.⁷ We find that tying off the boron atoms is essential to understanding the filling of the internal icosahedral bonds. For simplicity, the external bonding is modeled by having each of the boron atoms radially bonded to a hydrogenic atom. This ties off the external bonds of the boron icosahedron. To simulate the overall neutrality of the environment external to an icosahedron in boron carbides, we constrained the tie-off atoms to be neutral. This is done by adjusting the spatial extent of the atomic orbital of the hydrogenic tie-off atoms. Furthermore, we slightly deformed the icosahedron in accord with the distortion it incurs in the crystalline environment of boron carbides. We found that the addition of two electrons to the neutral cluster lowers the system's energy by about 3 eV. Even without atomic relaxation, the system's energy is lowered by about 2 eV. This is because the two added electrons fill internal bonding orbitals which extend over the entire icosahedron. The dispersal of the two added electrons over the surface of the icosahedron reduces their Coulomb repulsion sufficiently that this doubly negative state remains energetically favored over the neutral icosahedral cluster. The additional 1 eV of the total energy lowering arises from the contraction of the icosahedron which occurs upon filling the icosahedron's internal bonding orbitals.

In the present work, we consider the energy and atomic deformation associated with adding two electrons to the isoelectronic icosahedral system which results when one boron nucleus is replaced by a carbon nucleus. Namely, we consider a pair of electrons added to a positively charged B_{11}C icosahedron whose external bonds are tied off with hydrogenic atoms. With the substitution of a carbon nucleus for a boron nucleus, the symmetry of the icosahedron is lowered below that imposed by the crystalline environment of a boron carbide crystal. The carbon atom is pulled closer to the center of the icosahedron than the remaining boron atoms. This effect, as well as the electronic inequivalence of boron and carbon atomic cores, reduces the system's symmetry. As a result, the tie-off atoms experience significantly different environments. Hence, to simulate the overall neutrality of the icosahedron's surroundings, we constrain the net charge on the tie-off atoms to zero.

We find that the addition of two electrons to this cluster results in a contraction of the icosahedron and a much greater energy lowering (≈ 18 eV) than for the B_{12} cluster. The major reason that the $(\text{B}_{11}\text{C})^-$ cluster has a lower energy than the B_{12}^{2-} cluster is that the system's electrons experience the attraction of the "extra" positive charge associated with replacing a boron nucleus by a carbon nucleus. Here, as with the B_{12} icosahedron, the two added electrons are distributed over the entire surface of the icosahedron. However, due to the icosahedron's asymmetry their distribution departs significantly from uniformity. This increases the kinetic energy and electron-electron repulsion of the system's electrons. It is the

predominance of the increased Coulombic attraction over the energy increase arising from asymmetry which results in the $(B_{11}C)^-$ cluster having a lower energy than the B_{12}^{2-} cluster. Here, as for the B_{12} cluster, the energy reduction associated with the icosahedron's contraction (≈ 1.5 eV) is a significant, but relatively minor, portion of the net energy lowering.

In Sec. II of this paper, we present a more detailed account of our model and our computational method. Subsequently, in Sec. III, the results of our calculations are presented in detail. The paper concludes with a brief summary and discussion of our study in Sec. IV.

II. BIPOLARON FORMATION IN BORON-RICH ICOSAHEDRA: MODEL AND METHODS

We consider an atomic cluster composed of a twelve-atom deformed icosahedral unit in which the external bonds are tied off with 12 radially-bonded hydrogenic atoms. Electronic structure calculations are carried out for clusters with the requisite number of electrons to fill all of the bonding orbitals and for clusters which have two fewer electrons. Numerous atomic configurations are considered.

We focus our attention on determining three physically significant atomic and electronic configurations. First, (1) we find the ground-state configuration and energy for a cluster which has two fewer electrons than is needed to fulfill all of the system's bonding requirements. Then, (2) we calculate the energy of this configuration when the two electrons needed to fill the bonding orbitals are added. Finally, (3) we move the atoms of the icosahedron so as to determine the ground-state energy and configuration with the bonding orbitals filled.

The difference between the ground-state energies with and without the two electrons needed to fill the system's bonding orbitals (the first and third calculations) is the formation energy of the bipolaron. The difference between the energies of the unrelaxed and ground-state configurations with the bonding states filled (the second and third calculations) is the bipolaron relaxation energy. The concomitant atomic displacements comprise the bipolaronic deformation.

In carrying out these calculations we must employ several major simplifications. These involve (1) choosing icosahedral clusters to model the icosahedra in crystals, (2) restricting the conformational changes, and (3) utilizing an approximate scheme to calculate the electronic energies.

We develop our model by first considering an average boron-rich icosahedral cluster in the average crystalline environment it encounters in boron carbides. Such an icosahedron experiences a distortion consistent with D_{3d} symmetry. In particular, we take as our starting geometry that found experimentally (from x-ray diffraction) for an icosahedron in boron carbides.⁸ This geometry is an average over icosahedra in a variety of charge states, with different numbers and locations of carbon atoms, and in different surroundings. We then note that the replacement of a boron nucleus with a carbon nucleus leads to a substantial inward puckering of the icosahedron. In particu-

lar, gas-phase electron diffraction studies of the paracarbon boranes (C atoms at opposite poles of the $B_{10}C_2$ icosahedral core of a $B_{10}C_2H_{12}$ molecule) indicate that carbon atoms are pulled in toward the center of the icosahedron such that the C—C diameter of the icosahedron is 90% that of the B—B diameter.⁹ Thus, we consider an icosahedron which initially has D_{3d} symmetry and then has the distance of its carbon atom from the icosahedron's center contracted by 10%. Since the D_{3d} symmetry has two distinct icosahedral positions, labeled as B(1) and B(2) on Fig. 2, there are two possible icosahedral carbon positions in our model.

In the boron carbides, each icosahedron is surrounded by a diverse assortment of other icosahedra and intericosahedral chains in a variety of charge states. For example, there will generally be positively charged C—B—C chains and positively charged $B_{11}C$ icosahedra. In addition, there will be negatively charged $B_{11}C$ icosahedra. However, on average the environment surrounding an icosahedron is neutral. Thus, as a crude approximation to this environment, we impose the constraint that there be no net charge on the totality of hydrogenic tie-off atoms of our cluster.

The carbon-containing deformed icosahedra which we study have such low symmetry that there are eight types of tie-off atoms. Thus, there is great latitude in how one could model the tie-off atoms. We have chosen a simple scheme. Namely, despite the diversity of tie-off atoms, each and every tie-off atom of a boron atom is assigned the same bond length and the same spatial extent of its atomic state (Slater exponent). The tie-off atom of the carbon atom is assigned a different bond length and a different Slater exponent. We enforce the net neutrality of the tie-off atoms by adjusting their Slater exponents while keeping their bond lengths fixed.

To crudely mimic bonding of the icosahedral cage to boron atoms, we take the decay length of the atomic state of the tie-off atoms to be that corresponding to the second shell of a boron atom. We choose the atomic positions of the icosahedral cage atoms to be those of a boron-rich icosahedron in a crystal,⁸ then assign the second-shell boron decay lengths to the hydrogenic tie-off atoms, and

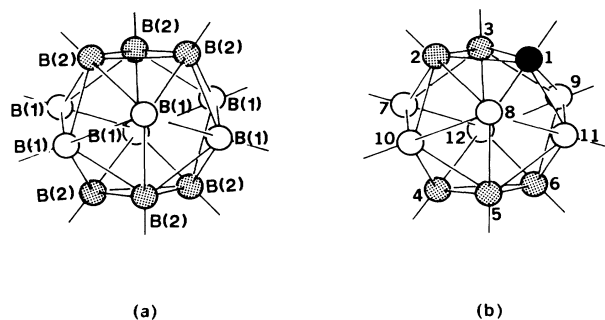


FIG. 2. In (a) an icosahedron of boron carbides as determined by x-ray diffraction is illustrated with the two types of icosahedral sites indicated by B1 and B2. In (b) an icosahedron in which a carbon atom, shown in solid black, substitutes for a boron atom and experiences a 10% inward puckering.

minimize the energy with respect to the tie-off bond lengths. We find the bond length to the boron tie-off atom to be 1.09 Å and to the carbon tie-off atom to be 1.03 Å. These are considerably smaller than those of hydrogen atoms in boron-rich molecules because of our use of such small decay lengths.

For the large clusters with which we are concerned, we cannot consider the totality of potential conformational changes. Hence, we restrict our considerations to "breathing-mode" type deformations, in which the icosahedron and its tie-off atoms are uniformly expanded or contracted. Our procedure is, thus, to choose an icosahedral "radius" and vary the Slater exponents of the tie-off atoms until we obtain their net charge neutrality. The associated electronic energies and wave functions are taken to be those corresponding to this icosahedral radius.

Our electronic calculations utilized the partial retention of diatomic differential overlap (PRDDO) method developed by Lipscomb and co-workers^{10,11} to study boron-rich clusters. It is a minimum-basis-set scheme which yields total self-consistent-field energies, one-electron eigenvalues, molecular-orbital wave functions and Mulliken atomic charges.

III. RESULTS

We first determined the ground state of the tied-off $(B_{11}C)^+$ cluster with the carbon atom in a B(2)-type site. The characteristic distances corresponding to the ground-state configuration are listed in Table I. For comparison, the characteristic distances we previously found⁷ for the tied-off B_{12} cluster are also shown. The Mulliken charges for the cage atoms and their associated tie-off atoms are tabulated in Table II. It is important to note that, even though the cluster as a whole is positively charged, the carbon atom assumes a slightly *negative* charge $-0.164 |e|$. This results from the relatively large electron affinity of carbon. Thus, the boron atoms, rather than the carbon atom, carry the positive charge of the boron-rich cage.

The net charge neutrality of the tie-off atoms is accomplished with the small positive charge of the tie-off of the carbon atom being compensated by the very small negative charges of the tie-offs of the boron atoms. The Slater exponents corresponding to the carbon and boron tie-off atoms are 1.1000 and 1.0906, respectively.

The ground state of the tied-off $(B_{11}C)^-$ cluster with the carbon atom in the B(2) site was also determined (the third calculation described in Sec. II). We find that the addition of a pair of electrons to the icosahedron's bonding orbitals causes a 0.09-Å contraction of the icosahedral radius and a lowering of the cluster's energy by 18.2 eV. The characteristic distances of the contracted icosahedron are presented in Table I along with those of the previously studied isoelectronic tied-off cluster, B_{12}^{2-} . The Mulliken atomic charges for each atom of the cluster and its associated tie-off are listed in Table II. To maintain charge neutrality on the tie-off atoms required Slater exponents of 1.3700 and 1.2384 for the carbon and boron tie-off atoms, respectively. These larger values tend to increase the efficacy of the shielding of the nuclear charges of the

TABLE I. Characteristic distances in Å within our boron-rich icosahedral clusters. Interatomic distances are for nearest neighbors.

Distance	B_{12}	B_{12}^{2-}	$(B_{11}C)^+$	$(B_{11}C)^-$
Center to B(1)	1.665	1.580	1.700	1.610
Center to B(2)	1.706	1.621	1.741	1.651
Center to C			1.567	1.486
B(1)—B(1)	1.750	1.661	1.787	1.693
B(2)—B(2)	1.792	1.702	1.828	1.734
B(1)—B(2)	1.773	1.684	1.809	1.715
C—B(1)			1.722	1.632
C—B(2)			1.743	1.653

tie-off atoms, thereby keeping them from becoming negative.

To obtain the charge distribution associated with the addition of two electrons to the icosahedral cage, we examine the differences between the charges on each cage atom for the $(B_{11}C)^+$ and $(B_{11}C)^-$ clusters. In particular, the change of the charge on each cage atom upon adding two electrons to the icosahedral cage is given in the final column of Table II. It should be noted that the added charge is distributed over all of the sites of the icosahedron, roughly $\frac{1}{6}$ of an electron per atom. Thus, in a first approximation, a carbon substituent acts like a boron. However, on closer examination it is seen that the charge distribution is not uniform. In particular, the changes in the atomic charges range from a minimum of $-0.14 |e|$ for the carbon atom to a maximum of $-0.21 |e|$ for the B(2)-type B atoms adjacent to the carbon atom. As might be expected, the added electrons tend to accumulate on those sites which were most positive on the $(B_{11}C)^+$ cluster. Thus, the presence of the carbon atom at its inwardly puckered position greatly increases the inhomogeneity with which the charge of the added pair of electrons is distributed on the icosahedron.

This increased inhomogeneity increases both the kinetic energy and the Coulomb-repulsion energy of the system's electrons. We find that the increases in the magnitudes of the kinetic energy and the electron-electron repulsive energy upon adding two electrons are greater for the more inhomogeneous $(B_{11}C)^+$ cluster than for the B_{12} cluster by 14.4 and 18.3 eV, respectively. The energy of the attractive interaction of the electrons with the nuclei is also more negative for the $(B_{11}C)^+$ cluster by 46.5 eV. However, the latter is the result of both (1) the additional positive nuclear charge associated with replacing a boron nucleus with a carbon nucleus and (2) the more localized character of the positive charge distribution on the $(B_{11}C)^+$ icosahedron leading to an inhomogeneous increase of the negative charge distribution when the two electrons are added. Finally, we note that the net energy difference between two electrons added to the $(B_{11}C)^+$ cluster and two electrons added to the B_{12} cluster [$-16.5 \text{ eV} - (-2.7 \text{ eV}) = 13.8 \text{ eV}$] is essentially just the interaction energy of a pair of electrons for the extra positive nucleus, $\approx 14 \text{ eV}$.¹²

TABLE II. Mulliken charges on the atoms of our $B_{11}C^+$ and $B_{11}C^-$ clusters in units of $|e|$.

Atom Number	Atom Type	$B_{11}C^+$ cluster		$B_{11}C^-$ cluster		Change in cage Atom's charge
		Atom	Tie-off	Atom	Tie-off	
1	C	-0.164	0.162	-0.307	0.192	-0.143
2	B(2)	0.175	-0.003	-0.031	-0.014	-0.206
3	B(2)	0.175	-0.003	-0.031	-0.014	-0.206
4	B(2)	0.080	-0.034	-0.060	-0.023	-0.140
5	B(2)	0.130	-0.013	-0.063	-0.023	-0.193
6	B(2)	0.130	-0.013	-0.063	-0.023	-0.0193
7	B(1)	0.072	-0.020	-0.090	-0.020	-0.162
8	B(1)	0.085	-0.009	-0.059	-0.011	-0.144
9	B(1)	0.085	-0.009	-0.059	-0.011	-0.144
10	B(1)	0.060	-0.025	-0.092	-0.021	-0.152
11	B(1)	0.113	-0.009	-0.055	-0.012	-0.168
12	B(1)	0.060	-0.025	-0.092	-0.021	-0.152

We find the energy reduction associated with adding a pair of electrons to the unrelaxed $(B_{11}C)^+$ cluster is 16.5 eV. However, the total energy lowering of a $(B_{11}C)^-$ cluster upon adding two electrons and allowing atomic relaxation is 18.2 eV. Thus, the bipolaronic relaxation energy of the $(B_{11}C)^-$ cluster is $18.2 \text{ eV} - 16.5 \text{ eV} = 1.7 \text{ eV}$. This is somewhat larger than the bipolaronic relaxation energy we found for the B_{12}^{2-} cluster, 1.0 eV.

The contraction of the icosahedral cluster upon the addition of the pair of electrons is the bipolaronic deformation. From Table I, we see that in our breathing-mode model, the distances from the icosahedron's center to any of the cage atoms are less by $\simeq 0.09 \text{ \AA}$ for the $(B_{11}C)^-$ cluster than for the $(B_{11}C)^+$ cluster. Thus, the bipolaronic deformation of the $(B_{11}C)^-$ cluster is a 0.09- \AA contraction. This magnitude of contraction upon adding two electrons into the icosahedron's internal bonding orbitals is essentially the same as that found in our study of bipolaron formation in an analogous B_{12} cluster.⁷

Thus, we have found that the bipolaronic relaxation energy is somewhat larger for the $(B_{11}C)^-$ cluster than for the B_{12}^{2-} cluster despite their bipolaronic contractions being essentially equal to one another. To understand this, we first recall [see, for example, Sec. II of Ref. (7)] that the bipolaronic relaxation energy ϵ_{BP} in the standard linear electron-lattice interaction model is proportional to the product of the electron-lattice interaction force A and the bipolaronic deformation x_{\min}^{BP} : $\epsilon_{BP} = -Ax_{\min}^{BP}$. Thus, our result implies that the electron-lattice interaction force is greater for the $(B_{11}C)^-$ cluster than for the B_{12}^{2-} cluster. Furthermore, the standard linear electron-lattice interaction model also has the bipolaronic deformation being proportional to the electron-lattice interaction force divided by the stiffness constant appropriate to the icosahedral contraction, k : $x_{\min}^{BP} = 2A/k$. Thus, for equal bipolaronic deformations with an increased electron-lattice interaction force, one must also have the effective stiffness constant comparably greater for the $(B_{11}C)^-$ cluster than for the B_{12}^{2-} cluster. Indeed, the fact that the stiffness of C—B bonds is greater than that of B—B bonds¹³ makes it plausible that the stiffness of the $(B_{11}C)^-$ cluster does exceed that of the B_{12}^{2-} cluster.

Furthermore, from the general principles of polaron formation, we expect the increased localization of the electron pair on the $(B_{11}C)^-$ cluster compared with that of the B_{12}^{2-} cluster to yield a larger effective electron-lattice interaction force for the $(B_{11}C)^-$ cluster than for the B_{12}^{2-} cluster. Nonetheless, our calculations using the PRDDO are not sufficiently accurate for us to obtain meaningful direct confirmation of these effects.

When the two electrons needed to fill the icosahedron's internal bonding orbitals for the $(B_{11}C)^+$ and B_{12} clusters are supplied and the concomitant contraction of the clusters has occurred, the energy gap between bonding and antibonding orbitals should increase. Indeed, we find that these energy gaps do increase from 5 to 13 eV for the $B_{11}C$ cluster and from 6 to 14 eV for the B_{12} cluster. Most of this increase is associated with the filling of the bonding orbitals, rather than the contraction of the icosahedron.

So far, we have only discussed a carbon nucleus replacing a boron nucleus at a B(2) site. We have also considered substitution of a carbon nucleus for a boron nucleus at a B(1) site. Within our model, there should be no major effects of carbon substituent site occupancy since the difference in the distances of a B(1) and B(2) site from the icosahedron's center is only $\simeq 0.04 \text{ \AA}$. Indeed, with a shift of carbon location we find that the energies of the $(B_{11}C)^+$ and $(B_{11}C)^-$ clusters are increased by only modest amounts ($\simeq 0.3$ and $\simeq 0.1$ eV, respectively), making the B(1) site the (slightly) favored site for carbon substitution. In addition, the magnitude of the polaronic contraction is essentially unaltered when the carbon atom is moved from the B(2) site to the B(1) site.

We stress, however, that our model does not adequately distinguish between B(1) and B(2) sites in a boron carbide crystal. This is because in the solid, the atoms at these sites are involved in quite different bonding external to the icosahedra. In particular, atoms in the B(1) site are bonded to the tetrahedrally bonded terminal element of a three-atom intericosahedral chain, most often a carbon atom. An atom in the B(2) site, however, is bonded to an atom of another icosahedra, most often a boron atom, which is involved in the three-center bonding characteris-

tic of the internal bonding orbitals of an icosahedron. In fact, the smallness of the effects we find suggest that the ignored environmental effects are indeed paramount.

IV. SUMMARY AND DISCUSSION

As a step to understanding bipolaron formation in the boron carbides, this paper has considered the effect of adding two electrons to a $(B_{11}C)^+$ icosahedron. The $(B_{11}C)^+$ icosahedron results from the replacement of a boron nucleus with a carbon nucleus within a 12-atom boron icosahedral structural unit upon which the boron carbides are based. To simulate the overall neutrality of the environment surrounding the icosahedron in a boron carbide crystal, we have tied off the icosahedron's atoms with hydrogenic atoms which are constrained to net charge neutrality.

We find that the greater electron affinity of the carbon atom than the boron atoms causes the carbon site in the $(B_{11}C)^+$ icosahedron to become charged slightly negative. The remaining boron atoms of the icosahedron therefore carry the icosahedron's net positive charge. As a result, when two additional electrons are added to the $(B_{11}C)^+$ icosahedron, they are distributed over the entire icosahedron.

The added electrons occupy the molecularlike bonding orbitals of the icosahedron and the icosahedron contracts upon their addition. The magnitude of the bipolaronic deformation is essentially equal to that we have previously calculated⁷ for an electron pair added to a B_{12} icosahedral cluster. However, the bipolaronic relaxation energy we calculate is somewhat larger than what we previously⁷ found for an electron pair added to the B_{12} icosahedral cluster. This result can be plausibly explained by noting that (1) the nonuniform charge distribution of the electron pair on the heterogeneous $(B_{11}C)^+$ icosahedra should enhance its effective electron-lattice interaction, while (2)

the substitution of a boron atom with a carbon atom should increase the icosahedron's stiffness.

Despite the similarities in the charge distribution and the bipolaronic deformation induced by a pair of electrons added to $(B_{11}C)^+$ and B_{12} icosahedral clusters, the energies associated with adding a pair of electrons to them are substantially different. Namely, the energy lowering for the relaxed $(B_{11}C)^-$ cluster is about 14 eV more than that of the B_{12}^{2-} cluster. This energy difference is essentially equal to what is estimated to be the additional Coulombic binding an electron pair would experience on an icosahedron as a result of its attraction to an additional positive charge.

It had previously been noted that bipolaronic hopping between $B_{11}C$ icosahedral units provides a consistent model of the electronic transport over the entire range of carbon compositions of boron carbides, while bipolaronic hopping between B_{12} icosahedra does not.^{1,4} The present calculations indicate that bipolaron formation on $B_{11}C$ deformed icosahedra is greatly favored energetically over bipolaron formation on B_{12} icosahedra. Thus, we regard the present calculation as providing support for this transport model.

ACKNOWLEDGMENTS

The work of one of us (I.A.H.) was supported by the Jet Propulsion Laboratory under Contract No. 956970 and the U.S. Department of Energy (DOE) under Contract No. DE-FG04-85ER45272. The work of another (C.L.B.) was supported by the Center for High Technology Materials of the University of New Mexico (UNM) and the U.S. DOE under Contract No. DE-FG04-85ER45272. One of us (D.E.) was supported by the U.S. DOE under Contract No. DE-AC04-76-DP00789. We would like to thank J. V. Ortiz of UNM for supplying the PRDDO codes.

¹D. Emin, in *Boron-Rich Solids*, Proceedings of the Conference on Boron-Rich Solids, AIP Conf. Proc. No. 140, edited by D. Emin, T. L. Aselage, C. L. Beckel, I. A. Howard, and C. Wood (AIP, New York, 1986), p. 189.

²L. Longuet-Higgins and M. deV Roberts, Proc. R. Soc. London, Ser. A **230**, 110 (1955).

³C. Wood and D. Emin, Phys. Rev. B **29**, 4582 (1984).

⁴D. Emin, G. A. Samara, L. J. Azevedo, E. L. Venturini, H. H. Madden, G. C. Nelson, J. A. Shelnut, B. Morosin, M. Moss, and C. Wood, *J. Less-Common Metals* **117**, 415 (1986).

⁵I. A. Howard, C. L. Beckel, and D. Emin, Phys. Rev. B **35**, 2929 (1987).

⁶L. J. Azevedo, E. L. Venturini, D. Emin, and C. Wood, Phys. Rev. B **32**, 7970 (1985).

⁷E. L. Venturini, L. J. Azevedo, D. Emin, and C. Wood, in *Boron-Rich Solids*, Proceedings of the Conference on Boron-Rich Solids, AIP Conf. Proc. No. 140, edited by D. Emin, T.

L. Aselage, C. L. Beckel, I. A. Howard, and C. Wood (AIP, New York, 1986), p. 292.

⁸H. Yakel, *Acta Crystallogr. Sect. B* **31**, 1797 (1975).

⁹R. K. Bohn and M. D. Bohn, *Inorg. Chem.* **10**, 350 (1971).

¹⁰T. A. Halgren and W. N. Lipscomb, *J. Chem. Phys.* **58**, 1569 (1973).

¹¹D. A. Dixon, D. A. Kleier, T. A. Halgren, H. H. Hall, and W. N. Lipscomb, *J. Am. Chem. Soc.* **99**, 6226 (1977).

¹²We have considered the effect of our imposition of the overall charge neutrality condition for the tie-off atoms on the energetics of our clusters. We find that this constraint leads to an underestimate of the binding energy of the two added electrons on both the B_{12}^{2-} and $B_{11}C^-$ clusters. This, however, does not alter our conclusion that the energy lowering on the $B_{11}C$ cluster is significantly greater than that on the B_{12} .

¹³T. D. Klimova, L. A. Gribov, and V. I. Stanko, *Opt. Spektrosk. USSR* **36**, 650 (1974).