

## Structure and single-phase regime of boron carbides

David Emin

*Sandia National Laboratories, Albuquerque, New Mexico 87185*

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The boron carbides are composed of twelve-atom icosahedral clusters which are linked by direct covalent bonds and through three-atom intericosahedral chains. The boron carbides are known to exist as a single phase with carbon concentrations from about 8 to about 20 at. %. This range of carbon concentrations is made possible by the substitution of boron and carbon atoms for one another within both the icosahedra and intericosahedral chains. The most widely accepted structural model for  $B_4C$  (the boron carbide with nominally 20% carbon) has  $B_{11}C$  icosahedra with C—B—C intericosahedral chains. Here, the free energy of the boron carbides is studied as a function of carbon concentration by considering the effects of replacing carbon atoms within  $B_4C$  with boron atoms. It is concluded that entropic and energetic considerations both favor the replacement of carbon atoms with boron atoms within the intericosahedral chains, C—B—C→C—B—B. Once the carbon concentration is so low that the vast majority of the chains are C—B—B chains, near  $B_{13}C_2$ , subsequent substitutions of carbon atoms with boron atoms occur within the icosahedra,  $B_{11}C$ → $B_{12}$ . Maxima of the free energy occur at the most ordered compositions:  $B_4C, B_{13}C_2, B_{14}C$ . This structural model, determined by studying the free energy, agrees with that previously suggested by analysis of electronic and thermal transport data. These considerations also provide an explanation for the wide single-phase regime found for boron carbides. The significant entropies associated with compositional disorder within the boron carbides, the high temperatures at which boron carbides are formed (> 2000 K), and the relatively modest energies associated with replacing carbon atoms with boron atoms enable the material's entropy to be usually important in determining its composition. As a result, boron carbides are able to exist in a wide range of compositions.

### I. INTRODUCTION

It has been realized for some time that the bonding of boron-rich molecules and solids differ markedly from that of other elements.<sup>1-3</sup> This distinction arises from the confluence of the boron atom's small size, its strong tendency to form *s-p* hybrids and its electron deficiency (the number of second-shell electrons, three, is less than the number of second-shell orbitals, four). In particular, the bonding of boron-rich structures may be characterized by the prevalence of "three-center" bonding.<sup>1-4</sup> As a result, boron-rich solids form unusual structures. In particular, the icosahedral boron-rich solids are composed of arrays of twelve-atom boron-rich icosahedral clusters of atoms.

The boron carbides are well known icosahedral boron-rich solids. The extraordinary hardness of these materials has led to their widespread use in armor. The anomalously large Seebeck coefficients and surprisingly low thermal conductivities of these refractory materials suggest a potential use as very-high-temperature thermoelectric materials.<sup>5</sup>

Despite the extensive use of boron carbides, fundamental questions concerning their composition remain. It is well established that boron carbides consist of twelve-atom icosahedral units connected with direct bonds and through three-atom intericosahedral chains in the manner illustrated in Fig. 1.<sup>6</sup> Nonetheless, while bo-

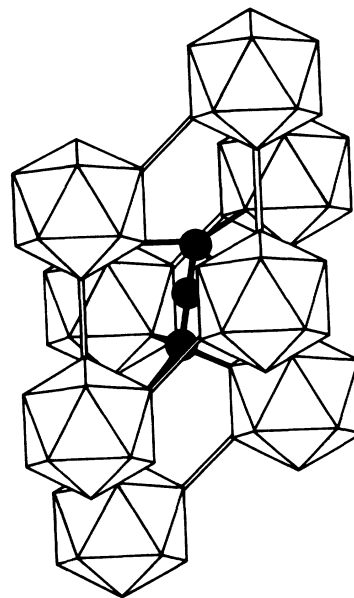


FIG. 1. Crystal structure of boron carbides. Here a twelve-atom boron-rich icosahedron resides at the corners of a rhombohedron. Each icosahedron is bonded to six other icosahedra via direct bonds. In addition, three-atom intericosahedral chains reside between icosahedra. Each chain links six different icosahedra since the end atoms of each chain are bonded to three different icosahedra.

ron carbide has often been assigned the chemical formula  $B_4C$ ,<sup>7</sup> single-phase boron carbides with the same rhombohedral crystal structure are readily produced by hot-pressing with carbon concentrations ranging from about 8.8 at. % to about 20 at. % carbon.<sup>8,9</sup> Furthermore, even for a given carbon concentration, the carbon location is not unambiguously known. For example, the composition  $B_4C$  (20% carbon) has been described both as  $B_{12}$  icosahedral clusters with C—C—C intericosahedral chains<sup>3</sup> and as  $B_{11}C$  icosahedral clusters with C—B—C intericosahedral chains.<sup>9–11</sup> Similarly, the composition  $B_{13}C_2$  (13.3% carbon) has been described as  $B_{12}$  icosahedra with C—B—C chains<sup>12</sup> and as  $B_{11}C$  icosahedra with C—B—B chains.<sup>10,13</sup> The uncertainty in carbon composition and location persists because of the difficulty of distinguishing between boron and carbon, adjacent elements in the Periodic Table. In addition, NMR analyses have yielded conflicting conclusions about the carbon location in boron carbides.<sup>14–16</sup>

The electronic transport properties of the boron carbides provide indirect information concerning the structure of boron carbides. In particular, analysis of electrical-conductivity, Seebeck-coefficient, Hall-mobility, and magnetic-susceptibility measurements on boron carbides with between 10% and 20% carbon implies a specific model of carbon location as a function of carbon concentration.<sup>9,17,18</sup> Succinctly stated, the combination of electronic and magnetic measurements indicates that the charge carriers are *p*-type singlet bipolarons, bound pairs of holes, which move via thermally activated hopping between similar sites throughout the entire composition range studied.<sup>10,13,17–21</sup> Because the pairing of electrons to form bipolarons is opposed by the Coulomb repulsion between like-signed charges, the exceptionally large twelve-atom icosahedral clusters are the natural centers for bipolaron formation.<sup>10,13,20</sup> The persistence of *p*-type conduction among similar sites (manifested by mobility and conductivity activation energies that are independent of carbon concentration) throughout the entire range of carbon concentrations investigated is consistent with only one of the proposed structural models.<sup>10,13,19,21</sup> Namely, the transport data imply that (1) the hopping sites are  $B_{11}C$  icosahedra, (2)  $B_4C$  is primarily composed of  $B_{11}C$  icosahedra linked by C—B—C chains, and (3) with decreasing carbon concentration boron preferentially substitutes for carbon in the intericosahedral chains to convert C—B—C chains to C—B—B chains. Analyses of the dependencies of the thermal conductivity,<sup>22</sup> Raman spectra,<sup>23</sup> and electron-spin resonance<sup>24,25</sup> of boron carbides on carbon concentration are also consistent with this structural model.

Despite its successes, some question remains concerning the analysis of the electronic transport data in terms of the structural model described above. In particular, consideration of the electronic structure finds  $B_4C$  (with either of the previously described arrangements) to be an insulator having filled bonding orbitals separated by an energy gap from higher-lying states.<sup>3,11,26</sup> However, electronic transport measurements on boron-carbide crystals or hot-pressed polycrystalline samples with the nominal composition  $B_4C$  generally find a high density ( $\approx 10^{21}$

$cm^{-3}$ ) of charge carriers.<sup>9</sup> This finding may mean that the boron carbide samples are not really  $B_4C$ . This circumstance can arise because there has been no accurate determination of the carbon concentration of the small solution-grown boron-carbide single crystals. Furthermore, while the average composition of polycrystalline hot-pressed samples is known to be close to  $B_4C$ , the general observation of carbon inclusions in such samples indicates that the carbon concentration in the actual boron carbide crystals may be somewhat less than the 20% that characterizes  $B_4C$ .<sup>27</sup> This suggestion is consistent with the observation that, while the carrier densities in hot-pressed samples with nominal compositions of  $B_4C$  are not insulating, their (*p*-type) carrier densities are less than those found at lower carbon concentrations.<sup>9</sup>

Thus, fundamental questions concerning the structure of the boron carbides remain. Is the structural model implied by the electronic transport experiments correct? Are there, and should there be,  $B_4C$  boron-carbide crystals? Why is the range of carbon concentrations in the single-phase regime for boron carbides so wide (between about 8% and about 20% carbon)?

To shed additional light on these questions, the free energy of the boron carbides is herein studied. Explicitly, it is presumed that an ideal crystal of  $B_4C$  would consist of  $B_{11}C$  icosahedra and C—B—C chains. Then, the effects of replacing some carbon atoms with boron atoms are determined. In particular, two possible substitutions are considered. A carbon atom may be replaced by a boron atom within either a  $B_{11}C$  icosahedron,  $B_{11}C \rightarrow B_{12}$ , or within a C—B—C chain,  $C—B—C \rightarrow C—B—B$ . The lowest carbon concentration possible in this scheme is  $B_{14}C$ , corresponding to each unit cell containing a  $B_{12}$  icosahedron and a C—B—B chain. With the replacement of a carbon atom by a boron atom, an electron is removed from the system. The resulting charge carriers are presumed to either pair as bipolarons on  $B_{11}C$  icosahedra or remain unpaired on  $B_{12}$  icosahedra. The free energy of a boron carbide of a given carbon concentration,  $B_{12+n}C_{3-n}$  with  $0 \leq n \leq 2$ , is then minimized with respect to the two parameters which determine (1) the distribution of the sites of the carbon substitutions between icosahedra and chains, and (2) the respective densities of carriers on  $B_{12}$  icosahedra and on  $B_{11}C$  icosahedra. This procedure determines (1) where carbon substitutions occur, and (2) the densities of both types of carriers as a function of the carbon concentration.

It is found that entropic considerations alone strongly favor the substitution of boron atoms for carbon atoms occurring within the intericosahedral chains rather than within the icosahedra. An estimate of the relative magnitudes of the model's energetic parameters also favors this picture. Thus, one may describe the structure as  $(B_{11}C)(C—B—C)_{1-n}(C—B—B)_n$  for  $0 \leq n \leq 1$  and as  $(B_{11}C)_{2-n}(B_{12})_{n-1}(C—B—B)$  for  $1 \leq n \leq 2$ . This model is in accord with the model determined from analysis of the electronic transport data.

This calculation also yields an expression for the change in the free energy per unit cell as carbon is replaced by boron,  $\Delta f(n)$ . It is found that the carbon con-

centrations corresponding to  $B_4C$ ,  $B_{13}C_2$ , and  $B_{14}C$  all correspond to local *maxima* of the free energy. This feature may explain the absence of clear evidence for boron carbides at these compositions. Beyond this result, the free energy depends strongly on two energetic parameters,  $\epsilon_1$  and  $\epsilon_2$ , and weakly on a third,  $\epsilon_3$ . The experimentally determined width of the single-phase region and the energy of dissociating  $B_4C$  into  $\beta$ -rhombohedral boron and graphite provides limits on the acceptable values of these energies. The *a priori* estimates of these energies are found to be consistent with the values inferred from experiment.

The calculation also yields the densities of bipolaronic holes on  $B_{11}C$  icosahedra,  $p_2$ , and of electrons on  $B_{12}$  icosahedra,  $2p_2'$ . The densities of bipolaronic holes are in accord with those determined from numerous electronic transport measurements.<sup>9,10,13</sup> The relatively small density of electrons on  $B_{12}$  icosahedra should only lead to an observable *n*-type conduction at very (perhaps, unattainably) low carbon concentrations. The relatively high (100  $\text{cm}^2/\text{V s}$ ) mobilities reported in  $\alpha$ -rhombohedral boron,<sup>28</sup> a material with the structure of boron carbide but devoid of carbon and of intericosahedral chains, leads to the suspicion that an *n*-type boron carbide (if it can be made) would have high-mobility nonpolaronic carriers.

This paper is arranged in the following manner. Section II contains the derivation of a general expression for the system's free energy. In Sec. III this free-energy expression is minimized with respect to (1) the distribution of carbon substitutions between chains and icosahedra, as well as (2) the distribution of charge carriers between  $B_{11}C$  and  $B_{12}$  icosahedra. Section III concludes with the resulting (minimized) free energy being presented as a function of the carbon concentration. In Sec. IV the origin of the wide single-phase regime of the boron carbides is considered. It is shown that the structural model of this paper, with acceptable values of the relevant energies, is compatible with the wide single-phase regime that is observed. The paper's final section, Sec. V, contains a summary of this work.

## II. THE FREE ENERGY

At the maximum carbon concentration,  $B_4C$ , each of the  $N$ -unit cells of our model consists of a  $(C-B-C)^+$  chain and a  $(B_{11}C)^-$  icosahedron. With the replacement of  $N_i$  of the  $(B_{11}C)^-$  icosahedra with  $B_{12}^{2-}$  icosahedra, the Helmholtz free energy is altered by

$$\Delta F_i = N_i E_i - k_B T \ln[N!/N_i!(N-N_i)!] + k_B T N_i \ln(\alpha), \quad (1)$$

where  $E_i$  is the energy difference associated with replacing a  $(B_{11}C)^-$  icosahedron with a  $B_{12}^{2-}$  icosahedron. The first entropy term is just that associated with randomly mixing  $N_i$  of the  $B_{12}^{2-}$  icosahedra with  $N-N_i$  of the  $(B_{11}C)^-$  icosahedra. Replacing a  $B_{11}C$  icosahedron with a  $B_{12}$  icosahedron eliminates the entropy-related lowering of the free energy associated with having the unbiased distribution of the carbon atom of a  $B_{11}C$  icosahedra among each of  $\alpha$  locations within an icosahedron. This effect is described by the final term of Eq. (1). If all of the icosahedron's sites may be equivalently occupied by a carbon atom,  $\alpha$  is 12. However, if, in accord with the symmetry of an icosahedron within a boron carbide,<sup>6</sup> only one of the two sets of six equivalent icosahedral locations may be occupied by a carbon atom,  $\alpha$  is 6.

Replacing  $N_c$  of the  $(C-B-C)^+$  chains by  $C-B-B$  chains changes the Helmholtz free energy by

$$\Delta F_c = N_c E_c - k_B T \ln[N!/N_c!(N-N_c)!] - k_B T N_c \ln(2), \quad (2)$$

where  $E_c$  is the energy difference associated with replacing a  $(C-B-C)^+$  chain by a  $C-B-B$  chain. The first entropy term arises from the random mixing of  $N_c$  chains of the  $C-B-B$  type and  $N-N_c$  chains of the  $(C-B-C)^+$  type. The second entropy term arises from the orientational disorder of  $C-B-B$  chains since the chains may equivalently be aligned as  $C-B-B$  chains or  $B-B-C$  chains.

To maintain overall charge neutrality, replacing a carbon atom by a boron atom must remove an electron from the boron carbide. This effect is now taken into account by assuming that the electrons which are removed by the system with the substitution of boron atoms for carbon atoms produce holes which either pair together to form bipolaronic holes on the  $(B_{11}C)^-$  icosahedra or remain unpaired on the  $B_{12}^{2-}$  icosahedra. In particular, the substitution of  $N_c + N_i$  carbon atoms with boron atoms produces  $N_c + N_i$  (paired and unpaired) holes on icosahedra. The number of bipolaronic holes on the  $N-N_i$  carbon-containing icosahedra is denoted  $p_2 N$ , where  $p_2$  is the average number of bipolarons per unit cell on  $B_{11}C$  icosahedra. The number of holes on the  $N_i$  boron icosahedra is  $N_c + N_i - 2p_2 N$ . Thus, the Helmholtz free energy associated with the distribution of holes among the icosahedra is

$$\Delta F_h = p_2 N E_b + (N_c + N_i - 2p_2 N) E_h - k_B T \ln[(N-N_i)!/(p_2 N)!(N-N_i-p_2 N)!] \\ - k_B T \ln\{(2N_i)!/[(N_i+N_c)-2p_2 N]![2N_i-(N_i+N_c)+2p_2 N]!\}, \quad (3)$$

where  $E_b$  is the energy to produce a bipolaronic hole on a  $(B_{11}C)^-$  icosahedron and  $E_h$  is the energy to produce a hole on a  $B_{12}^{2-}$  icosahedron. The entropy terms arise from the random distribution of  $p_2 N$  singlet bipolaronic holes on the  $N-N_i$  carbon-containing icosahedra and the random distribution of  $N_i + N_c - 2p_2 N$  holes among the  $2N_i$  states of the  $N_i$  all-boron icosahedra. Because of spin degeneracy, the number of states for a hole on the  $N_i$   $B_{12}^{2-}$  icosahedra is twice the number of sites,  $2N_i$ .

Considering an arbitrarily large solid,  $N \rightarrow \infty$ , the entropy terms of the above equations can be rewritten by noting

the general relation

$$\lim_{N \rightarrow \infty} \ln[N_i! / N_j! (N_i - N_j)!] / N \rightarrow -[n_j \ln(n_j) + (n_i - n_j) \ln(n_i - n_j) - n_i \ln n_i], \quad (4)$$

where  $n_i = N_i / N$  and  $n_j = N_j / N$ . In particular, the total change in the Helmholtz free energy per unit cell as  $N \rightarrow \infty$  is found by combining the three contributions given in Eqs. (1)–(3) and using Eq. (4) and analogous relationships:

$$\begin{aligned} \Delta f = (\Delta F_c + \Delta F_i + \Delta F_h) / N = & n_c [E_c + E_h - k_B T \ln(2)] + n_i [E_i + E_h + k_B T \ln(\alpha)] + p_2 (E_b - 2E_h) \\ & + k_B T \{ [n_i \ln(n_i)] + [n_c \ln(n_c) + (1 - n_c) \ln(1 - n_c)] \\ & + [(n_i + n_c - 2p_2) \ln(n_i + n_c - 2p_2) + (2p_2 + n_i - n_c) \ln(2p_2 + n_i - n_c) - 2n_i \ln(2n_i)] \\ & + [p_2 \ln(p_2) + (1 - n_i - p_2) \ln(1 - n_i - p_2)] \}. \end{aligned} \quad (5)$$

In Eq. (5) the four square-bracketed entropy terms successively arise from (1) carbon replacement within icosahedra, (2) carbon replacement within chains, (3) carriers on all-boron icosahedra, and (4) bipolaronic holes on carbon-containing icosahedra.

The chemical formula of the boron carbides is conveniently written as  $B_{12+n}C_{3-n}$  for  $0 \leq n \leq 2$ , where  $n$  is the total number of carbon atoms per unit cell removed from  $B_4C$  to produce a boron carbide of a given composition,  $n = n_c + n_i$ . Therefore, it is useful to reexpress  $\Delta f$  in terms of  $n$ . In making this change of variable, the second composition parameter in  $\Delta f$  may be kept as  $n_i$ , the number of carbon atoms per unit cell extracted from icosahedra. Thus, the Helmholtz free energy is reexpressed in terms of (1)  $n$ , the number of carbon atoms replaced by boron atoms per unit cell of a boron carbide, (2)  $n_i$ , the number of the replaced carbon atoms per unit cell which are associated with icosahedra, and (3)  $p_2$ , the number of bipolaronic holes per unit cell on  $(B_{11}C)^-$  icosahedra:

$$\begin{aligned} \Delta f = & n [E_c + E_h - k_B T \ln(2)] + n_i [E_i - E_c + k_B T \ln(2\alpha)] + p_2 (E_b - 2E_h) \\ & + k_B T \{ [n_i \ln(n_i)] + [(n - n_i) \ln(n - n_i) + (1 - n + n_i) \ln(1 - n + n_i)] \\ & + [(n - 2p_2) \ln(n - 2p_2) + (2n_i - n + 2p_2) \ln(2n_i - n + 2p_2) - 2n_i \ln(2n_i)] \\ & + [p_2 \ln(p_2) + (1 - n_i - p_2) \ln(1 - n_i - p_2)] \}. \end{aligned} \quad (6)$$

Equation (6) describes the change in the Helmholtz free energy which results when (1)  $n$  carbon atoms per unit cell of  $B_4C$  are replaced with boron atoms in different icosahedra or intericosahedral chains, (2)  $n_i$  of these substitutions (per unit cell) occur within icosahedra, (3)  $n - 2p_2$  holes per unit cell are distributed among  $n_i$  all-boron icosahedra per unit cell, and (4)  $p_2$  bipolaronic holes per unit cell are distributed among  $n - n_i$  carbon-containing  $(B_{11}C)^-$  icosahedra per unit cell.

### III. COMPOSITION DEPENDENCE OF THE FREE ENERGY

To examine the dependence of the free energy on carbon content, the free energy is now minimized with respect to  $n_i$  and  $p_2$ . This procedure yields  $n_i$  and  $p_2$  as functions of  $n$ . Inserting these two functions into the expression of Eq. (6) then yields the free energy as a function solely of  $n$ :  $\Delta f(n, n_1(n), p_2(n))$ .

Differentiating  $\Delta f$  of Eq. (6) with respect to  $n_i$  and  $p_2$ , respectively yields

$$\frac{\partial \Delta f}{\partial n_i} = E_i - E_c + k_B T \ln(2\alpha) + k_B T \ln \left[ \frac{(1 - n + n_i)(2n_i - n + 2p_2)^2}{(4n_i)(n - n_i)(1 - n_i - p_2)} \right] \quad (7)$$

and

$$\frac{\partial \Delta f}{\partial p_2} = (E_b - 2E_h) + k_B T \ln \left[ \frac{p_2(2n_i - n + 2p_2)^2}{(1 - n_i - p_2)(n - 2p_2)^2} \right]. \quad (8)$$

To minimize  $\Delta f$  with respect to  $n_i$  and  $p_2$ , these two partial derivatives are equated to zero, resulting in the relations

$$(1 - n + n_i)(2n_i - n + 2p_2)^2 / (4n_i)(n - n_i)(1 - n_i - p_2) = (2\alpha)^{-1} \exp[-(E_i - E_c) / k_B T] \quad (9)$$

and

$$\begin{aligned} & [p_2(2n_i - n + 2p_2)^2 / (1 - n_i - p_2)(n - 2p_2)^2] \\ & = \exp[-(E_b - 2E_h) / k_B T]. \end{aligned} \quad (10)$$

At this point it is useful to estimate the relative magni-

tudes of the energies which enter into Eqs. (9) and (10). In considering Eq. (9), the relevant energies are  $E_c$ ,  $E_i$ , and  $k_B T$ . It is first observed that the energy associated with the isoelectronic replacement of a carbon nucleus with a boron nucleus within a  $(C-B-C)^+$  chain,  $E_c$ , is just the energy of removing a proton from a positively

charged unit. However, the energy associated with the isoelectronic replacement of a carbon nucleus with a boron nucleus in a  $(B_{11}C)^-$  icosahedra,  $E_i$ , is roughly the energy of removing a proton from a negatively charged unit. From this point of view, it is expected that  $E_i \gg E_c$ . Furthermore, the Coulombic energy associated with removing a proton from a structure which is charged  $-|e|$ , even with screening, is expected to be at least comparable to  $k_B T$  at the temperatures at which boron carbides are produced,  $k_B T \approx 0.2$  eV. It is therefore assumed that  $E_i > E_c, k_B T$ . In addition, the factor  $1/2\alpha$  is much less than unity since  $\alpha$  is 6 for an icosahedron in the boron carbides. As a result, regardless of the magnitude of the energetic factor within the exponential, the right-hand side of Eq. (9) is very much less than unity.

A similar analysis may be applied to the energies of Eq. (10). Namely,  $E_b$  is the energy associated with removing a pair of electrons from a  $(B_{11}C)^-$  icosahedron. This energy should be at least of the magnitude of that associated with removing an electron from a neutral entity: without screening, several eV.<sup>29</sup> Furthermore, as noted in the preceding paragraph, even with screening, such a Coulomb energy is generally greater than  $k_B T$  at the temperatures that are relevant in the formation of boron carbides. The remaining energy in Eq. (10) is  $E_h$ , the energy associated with removing only one electron from a structure which is charged doubly negative, a  $B_{12}^{2-}$  icosahedron. Thus, it is expected that  $E_b > E_h, k_B T$ . With the energies on the right-hand side of Eq. (10) obeying these inequalities, the right-hand side of Eq. (10) is generally less than unity.

Solutions of Eqs. (9) and (10) for  $0 \leq n \leq 2$  may be obtained by exploiting the smallness of the right-hand sides of these equations. In particular, setting the right-hand side of Eq. (9) to zero leads to two solutions of Eq. (9):  $n_i = n - 1$  and  $n_i = n/2 - p_2$ . The first of these mathematical solutions is physically unacceptable for  $0 \leq n < 1$ , since  $n_i$ , the number of icosahedra per unit cell in which a carbon atom is replaced by a boron atom, must always be a positive number. Thus, for  $n < 1$  the solution of Eq. (9) is  $n_i = n/2 - p_2$ . Inserting this solution into Eq. (10) results in the vanishing of the numerator of the left-hand side of Eq. (10). However, the right-hand side of Eq. (10) generally does not vanish since it depends on parameters which are independent of the parameters of Eq. (9). Thus, the only acceptable simultaneous solutions of Eqs. (9) and (10) must have the denominator of Eq. (10) vanish in such a way as to cancel the vanishing of the numerator of Eq. (10). Such a situation can only be accomplished if  $n = 2p_2$ . Thus, the solution of Eqs. (9) and (10) for  $n \leq 1$  in the limit of the right-hand side of Eq. (9) vanishing is  $p_2 = n/2$  and  $n_i = 0$ . The values of  $p_2$  and  $n_i$  obtained from solving Eqs. (9) and (10) with  $n \leq 1$  in the limit that the right-hand side of Eq. (9) vanishes are plotted against  $n$  in Figs. 2(a) and 2(b), respectively.

For  $n > 1$ , however,  $p_2 = n/2$  and  $n_i = 0$  is not a physically acceptable solution of Eqs. (9) and (10) because the number of icosahedra per unit cell in which a carbon atom is replaced by a boron atom,  $n_i$ , must exceed zero when the number of carbon atoms replaced by boron

atoms,  $nN$ , exceeds the total number of chains,  $N$ . In other words, once all of the C—B—C chains are replaced by C—B—B chains, a further reduction of the carbon content must come from replacing  $B_{11}C$  icosahedra by  $B_{12}$  icosahedra. Thus, for  $n \geq 1$  the only physically acceptable solution of Eq. (9) when its right-hand side is set equal to zero is  $n_i = n - 1$ . With the condition  $n_i = n - 1$ , Eq. (10) becomes

$$\begin{aligned} & [p_2(n-2+2p_2)^2 / (2-n-p_2)(n-2p_2)^2] \\ & = \exp[-(E_b - 2E_h) / k_B T]. \quad (11) \end{aligned}$$

Recalling that the right-hand side of Eq. (11) is presumed to be small compared with unity, first consider the solutions of Eq. (11) when its right-hand side vanishes. Two mathematical solutions are possible:  $p_2 = 0$  and  $n - 2 + 2p_2 = 0$ . However, the continuity of the  $n \leq 1$  and  $n \geq 1$  solutions at  $n = 1$  imposes the requirement that  $p_2 = \frac{1}{2}$  at  $n = 1$ . Thus, the solution of Eqs. (9) and (10) for  $2 \geq n \geq 1$  is  $n_i = n - 1$  and  $p_2 = 1 - n/2$  in the limit that the right-hand sides of Eqs. (9) and (10) both vanish. The values of  $p_2$  and  $n_i$  obtained from solving Eqs. (9) and (10) with  $1 \leq n \leq 2$  in the limit that the right-hand sides of Eqs. (9) and (10) both vanish are plotted against  $n$  in Figs. 2(a) and 2(b), respectively.

The physical content of these solutions of Eqs. (9) and (10) may be described in words. First, as the carbon content of  $B_4C$  is reduced by the replacement of carbon atoms by boron atoms, carbon is first removed from the C—B—C chains: for  $n \leq 1$  one has  $n_i = 0$ . Then, when all chains are C—B—B chains, subsequent removal of

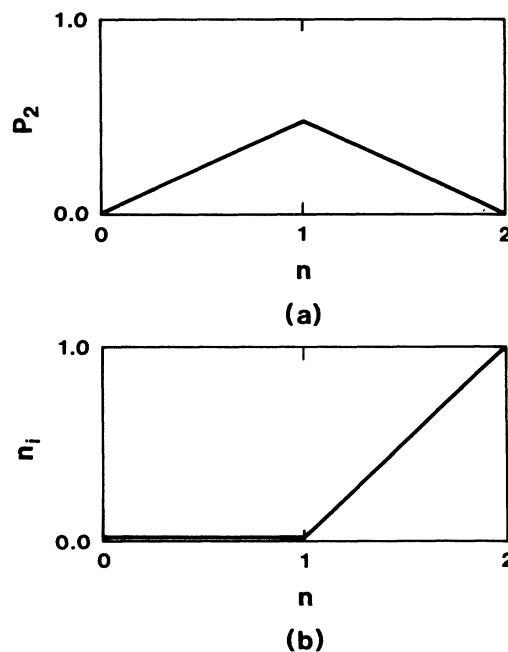


FIG. 2. Values of  $p_2$  and  $n_i$  obtained from solving Eqs. (9) and (10) in the limit that the activated terms of these equations vanish are plotted against  $n$  in (a) and (b), respectively. For clarity, the  $n_i = 0$  line in (b) is displayed slightly from zero.

carbon from the boron carbide occurs with the replacement of  $B_{11}C$  icosahedra by  $B_{12}$  icosahedra: for  $1 \leq n \leq 2$ , one has  $n_i = n - 1$ . Second, since the replacement of a carbon atom in a chain by a boron atom removes an electron from the system, each such replacement introduces a hole. When  $n \leq 1$ , there are only  $B_{11}C$  icosahedra. Thus,  $n$  such holes per unit cell must form  $p_2 = n/2$  bipolaronic holes per unit cell on  $B_{11}C$  icosahedra. When  $1 \leq n \leq 2$ , all chains are C—B—B chains and the icosahedra are either  $B_{12}$  or  $B_{11}C$  icosahedra. With the presumed vanishing of the right-hand side of Eq. (10), the  $B_{12}$  icosahedra are constrained to remain neutral. Then, bipolaronic holes only arise when the unpaired electrons that would be on the  $2-n$  neutral  $B_{11}C$  icosahedra per unit cell pair ( $2B_{11}C \rightarrow B_{11}C^+ + B_{11}C^-$ ) to produce  $(2-n)/2 = 1 - n/2$  bipolaronic holes per unit cell on  $B_{11}C$  icosahedra. These statements describe the physical origin of the curves of Fig. 2.

The curves of Fig. 2 would change somewhat if the right-hand side of Eq. (9) were not taken to vanish, but simply to remain small,  $\ll 1$ . In particular, in such a situation, the discontinuity of the curves of Fig. 2 at  $n = 1$  would be eliminated. This circumstance corresponds to some boron atoms replacing carbon atoms within icosahedra prior to all of the C—B—C chains being replaced by C—B—B chains.

More generally, additional bipolaronic holes can be produced on  $B_{11}C$  icosahedra by transferring pairs of electrons from  $B_{11}C^-$  icosahedra to  $B_{12}$  icosahedra (e.g.,  $B_{11}C^- + 2B_{12} \rightarrow B_{11}C^+ + 2B_{12}^-$ ). Furthermore, an electron added to a  $B_{12}$  icosahedron functions as a second type of charge carrier when it moves to other  $B_{12}$  icosahedra. To permit electrons to occupy the  $B_{12}$  icosahedra, the solution of Eq. (11) is generalized to permit the non-

vanishing of the right-hand side of Eq. (11) for  $1 \leq n \leq 2$ . In particular, defining  $p'_2$  as the number of bipolaronic holes per unit cell on  $B_{11}C$  icosahedra formed by transferring pairs of electrons to  $B_{12}$  icosahedra, the total number of bipolaronic holes per unit cell on  $B_{11}C$  icosahedra is

$$p_2 = 1 - n/2 + p'_2. \quad (12)$$

Here,  $2p'_2$  is the number of electrons per unit cell on  $B_{12}$  icosahedra. Then, inserting Eq. (12) into Eq. (11) yields an equation for  $p'_2$ ,

$$(1 - n/2 + p'_2)(p'_2)^2 / (1 - n/2 - p'_2)(n - 1 - p'_2)^2 = \exp[-(E_b - 2E_h)/k_B T]. \quad (13)$$

Assuming that the right-hand side of Eq. (13) is small, Eq. (13) is solved for  $p'_2$  to lowest order in  $p'_2$ ,  $p'_2 \ll n - 1$ ,  $1 - n/2$ , yielding

$$p'_2 = (n - 1) \exp[-(E_b/2 - E_h)/k_B T]. \quad (14)$$

Thus, the number of electrons per unit cell that are free to move between  $B_{12}$  icosahedra,  $2p'_2$ , is thermally activated. The activation energy is the difference between half the energy of removing a pair of electrons from a  $(B_{11}C)^-$  icosahedron,  $E_b/2$ , and the energy of removing an electron from a  $B_{12}^{2-}$  icosahedron,  $E_h$ . The prefactor of the electron density on the  $B_{12}$  icosahedra,  $2p'_2$ , is  $2(n - 1) = 2n_i$ , the number of electronic states per unit cell associated with the  $B_{12}$  icosahedra.

The free energy of the system with  $n_i$  and  $p_2$  given by the solutions of the minimization conditions may now be displayed. In particular, since, for  $n < 1$ ,  $p_2 = n/2$  and  $n_i = 0$ , Eq. (6) becomes

$$\Delta f = n[E_c + E_b/2 - k_B T \ln(2)] + k_B T \{ [n \ln(n) + (1 - n) \ln(1 - n)] + [(n/2) \ln(n/2) + (1 - n/2) \ln(1 - n/2)] \}. \quad (15)$$

The physical interpretation of Eq. (15) is straightforward. The replacement of a carbon atom in an intericosahedral chain with a boron atom and the concomitant production of half of a bipolaron on a  $B_{11}C$  icosahedron is associated with the energy  $E_c + E_b/2$ . The entropy associated with the two possible alignments of the resulting C—B—B chain, C—B—B or B—B—C, gives rise to the entropy-related factor  $-k_B T \ln(2)$  for each substitution of a C—B—B chain for a C—B—C chain. The first square-bracketed term in the remaining entropy-related contribution is associated with the mixing of C—B—B and C—B—C chains. The final square-bracketed term in the entropy-related contribution arises from the mixing of  $(B_{11}C)^+$  and  $(B_{11}C)^-$  icosahedra.

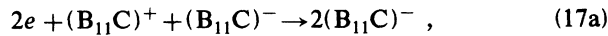
For  $n > 1$  it is convenient to express the free energy in terms of  $p'_2$ . Thus, the conditions  $n_i = n - 1$  and Eq. (12) are inserted into Eq. (6) to obtain

$$\begin{aligned} \Delta f = & [E_c + E_b/2 - k_B T \ln(2)] + (n - 1)[E_i - E_b/2 + 2E_h + k_B T \ln(\alpha)] + p'_2(E_b - 2E_h) \\ & + k_B T \{ [2(n - 1 - p'_2) \ln(n - 1 - p'_2) + 2p'_2 \ln(p'_2) - (n - 1) \ln(n - 1)] \\ & + [(1 - n/2 + p'_2) \ln(1 - n/2 + p'_2) + (1 - n/2 - p'_2) \ln(1 - n/2 - p'_2)] \}. \end{aligned} \quad (16)$$

The first square-bracketed term of Eq. (16) is just the value of  $\Delta f$  at  $n = 1$ , when each C—B—C chain has been replaced by a randomly oriented C—B—B chain. The second term in Eq. (16) indicates that when  $n > 1$ ,  $n - 1$  carbon atoms per unit cell are replaced by boron atoms in  $B_{11}C$  icosahedra. Because the electrons on  $B_{11}C$  icosahedra

are paired, it is convenient to think of the energetics described by this term of Eq. (16) in terms of two carbon atoms being replaced by two boron atoms in two oppositely charged  $B_{11}C$  icosahedra. In particular, one can understand the energetics of this process by envisioning a sequence of three events. First, a pair of electrons is add-

ed to a  $(B_{11}C)^+$  icosahedron,



altering the electronic energy by  $-E_b$ . Second, the carbon nucleus is replaced by a boron nucleus in each of the two  $(B_{11}C)^-$  icosahedra,

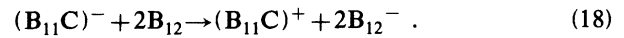


altering the system's energy by  $2E_i$ . Third, two electrons are removed from each of two resulting  $B_{12}^{2-}$  icosahedra,



altering the electronic energy by  $4E_h$ . The fourth contribution to the free energy of the second term describes the reduced entropy of a  $B_{11}C$  icosahedron accompanying the replacement of the carbon nucleus with a boron nucleus. With this substitution the icosahedron loses the free-energy reduction associated with the distribution of the carbon atom among  $\alpha$  equivalent sites. The third contri-

bution to the  $\Delta f$  in Eq. (16) is the energy of removing  $p'_2$  electron pairs per unit cell from  $(B_{11}C)^-$  icosahedra,  $p'_2 E_b$ , and placing  $2p'_2$  electrons per unit cell on  $B_{12}$  icosahedra,  $-2p'_2 E_h$ ,



Both of the square-bracketed terms within the curly brackets of Eq. (16) are associated with entropic contributions to the free energy per unit cell,  $\Delta f$ . The first such square-bracketed term arises from  $2p'_2$  electrons per unit cell being randomly distributed among  $n - 1$   $B_{12}$  icosahedra per unit cell which, in turn, are randomly mixed with  $2 - n$   $B_{11}C$  icosahedra per unit cell. The second square-bracketed term within the curly brackets is associated with  $1 - n/2 + p'_2$  bipolaronic holes per unit cell randomly distributed among  $2 - n$   $B_{11}C$  icosahedra per unit cell.

With  $p'_2$  being sufficiently small compared with  $n - 1$  and  $1 - n/2$ , the right-hand side of Eq. (16) may be expanded to lowest order in  $p'_2$ , yielding

$$\Delta f = [E_c + E_b/2 - k_B T \ln(2)] + (n - 1)[E_i - E_b/2 + 2E_h + k_B T \ln(\alpha)] + k_B T [(n - 1)\ln(n - 1) + 2(1 - n/2)\ln(1 - n/2)] + p'_2 \{ (E_b - 2E_h) + 2k_B T \{ \ln[p'_2/(n - 1)] - 1 \} \}. \quad (19)$$

Inserting Eq. (14), the expression for  $p'_2$  obtained when  $p'_2$  is sufficiently small, into Eq. (19) yields an expression for  $\Delta f$  as a function of  $n$  in the regime when  $1 \leq n \leq 2$ :

$$\begin{aligned} \Delta f &= [E_c + E_b/2 - k_B T \ln(2)] + (n - 1)[E_i - E_b/2 + 2E_h + k_B T \ln(\alpha)] \\ &\quad + k_B T [(n - 1)\ln(n - 1) + 2(1 - n/2)\ln(1 - n/2)] - 2p'_2 k_B T \\ &= [E_c + E_b/2 - k_B T \ln(2)] + (n - 1)\{E_i - E_b/2 + 2E_h + k_B T \ln(\alpha) - 2k_B T \exp[-(E_b/2 - E_h)/k_B T]\} \\ &\quad + k_B T [(n - 1)\ln(n - 1) + 2(1 - n/2)\ln(1 - n/2)]. \end{aligned} \quad (20)$$

The two terms within the last set of square brackets of Eq. (20) arise, respectively, from the mixing of  $B_{11}C$  and  $B_{12}$  icosahedra and the distribution of electron pairs on the  $B_{11}C$  icosahedra. Thus, the first of these terms vanishes when the icosahedra are either all  $B_{11}C$  icosahedra,  $n = 1$ , or all  $B_{12}$  icosahedra,  $n = 2$ . Furthermore, the second of these terms vanishes when there are no  $B_{11}C$  icosahedra,  $n = 2$ .

Thus, the Helmholtz free energy of the boron carbides,  $B_{12+n}C_{3-n}$ , has been obtained over the entire range of carbon concentrations permitted by the model presented in Sec. II,  $0 \leq n \leq 2$ . Equation (15) gives  $\Delta f$  as a function of  $n$  in the range  $0 \leq n \leq 1$ . Equation (20) gives  $\Delta f$  as a function of  $n$  in the range  $1 \leq n \leq 2$ . Beyond the thermal energy,  $k_B T$ , three energies are involved in these formulas. These three energies are now reexpressed as

$$\epsilon_1 = E_c + E_b/2, \quad (21a)$$

$$\epsilon_2 = E_i - E_b/2 + 2E_h, \quad (21b)$$

and

$$\epsilon_3 = E_b/2 - E_h. \quad (21c)$$

$\epsilon_1$  is the energy associated with replacing a carbon atom within a C—B—C chain with a boron atom. As described through Eqs. (17a)–(17c),  $\epsilon_2$  is the energy associated with replacing a carbon atom within an icosahedron with a boron atom.  $\epsilon_3$  is the energy associated with promoting an electron from a carbon-containing icosahedron to a  $B_{12}$  icosahedron. In terms of these energies, the expressions for the free energy, Eqs. (15) and (20), become

$$\Delta f = n\epsilon_1 + k_B T [(1 - n)\ln(1 - n) + (3n/2)\ln(n/2) + (1 - n/2)\ln(1 - n/2)] \quad (22)$$

for  $0 \leq n \leq 1$ , and

$$\begin{aligned} \Delta f &= \epsilon_1 + (n - 1)[\epsilon_2 - 2k_B T \exp(-\epsilon_3/k_B T)] \\ &\quad + k_B T \{ -\ln(2) + (n - 1)\ln[\alpha(n - 1)] + 2(1 - n/2)\ln(1 - n/2) \} \end{aligned} \quad (23)$$

for  $1 \leq n \leq 2$ .

The limitations on the validity of Eqs. (22) and (23) arise from the restrictions on the solutions of Eqs. (9) and (10). Expressed in terms of  $\epsilon_1$ ,  $\epsilon_2$ , and  $\epsilon_3$ , these restrictions are

$$\exp[-(\epsilon_2 - \epsilon_1 - 2\epsilon_3)/k_B T] \ll 2\alpha \quad (24)$$

and

$$\exp(-2\epsilon_3/k_B T) < 1. \quad (25)$$

The free energy  $\Delta f$  as given by Eqs. (22) and (23) contains terms that depend on the energies  $\epsilon_1$ ,  $\epsilon_2$ , and  $\epsilon_3$  as well as entropy-related terms that are independent of these energies. The terms that are dependent of these energies produce a linear dependence of  $\Delta f$  on  $n$  that is proportional to  $\epsilon_1$  for  $n < 1$  and to  $\epsilon_2 - 2k_B T \exp(-\epsilon_3/k_B T)$  for  $n > 1$ . The sum of the entropy-related terms that are independent of the energies  $\epsilon_1$ ,  $\epsilon_2$ , and  $\epsilon_3$  is displayed in Fig. 3, where  $\Delta f/k_B T$  is plotted against  $n$  for  $\epsilon_1 = \epsilon_2 = 0$  and  $\epsilon_3 \rightarrow \infty$ . It is evident that this curve possesses minima at two compositions. One of these minima is between  $n = 0$  and 1, between  $B_4C$  and  $B_{13}C_2$ , and the other is between  $n = 1$  and 2, between  $B_{13}C_2$  and  $B_{14}C$ . In addition, this curve has maxima with slopes of infinite magnitudes

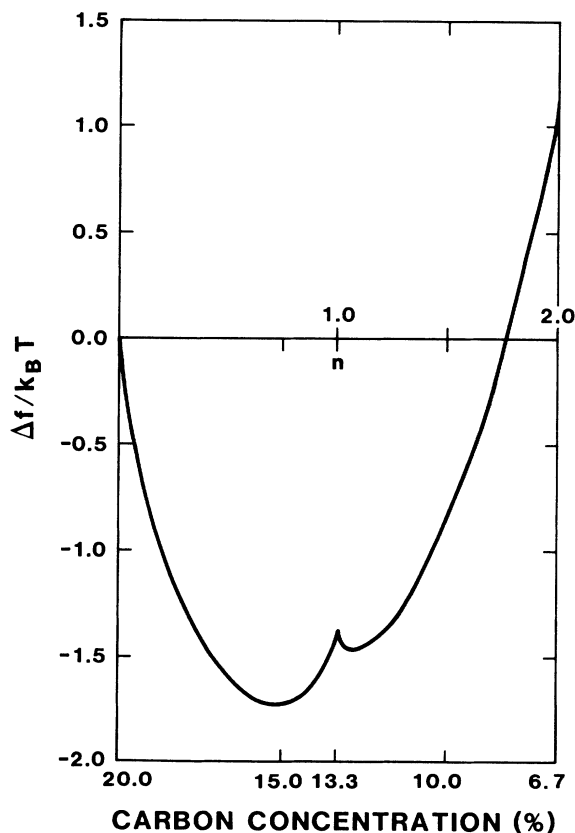


FIG. 3.  $\Delta f/k_B T$  for  $B_{12+n}C_{3-n}$ , obtained from Eqs. (22) and (23), plotted against  $n$  when  $\alpha = 6$ ,  $\epsilon_1 = \epsilon_2 = 0$ , and  $\epsilon_3 \rightarrow \infty$ . This plot depicts the entropy-related contributions to  $\Delta f/k_B T$  when excitation of electrons from  $(B_{11}C)^-$  icosahedra to  $B_{12}$  icosahedra is precluded by an arbitrarily large value of the excitation energy,  $\epsilon_3$ .

at  $n = 0, 1$ , and 2. Thus, none of the compositions which correspond to these maxima,  $B_4C$ ,  $B_{13}C_2$ , and  $B_{14}C$ , can be minima of the total free energy,  $\Delta f$ , at any finite temperature.

The asymmetry of the curve of Fig. 3 about  $n = 1$  reflects the asymmetric effects of replacing carbon atoms with boron atoms within C—B—C chains and  $B_{11}C$  icosahedra. In particular, an increase in  $n$  for  $n \leq 1$  corresponds to the substitution of a boron atom for a carbon atom within an increasing fraction of C—B—C chains. Because of the orientational degeneracy of each C—B—B chain, each such substitution contributes the term  $-n \ln(2)$  to  $\Delta f/k_B T$ . However, an increase in  $n$  for  $n \geq 1$  corresponds to the substitution of a boron atom for a carbon atom within an increasing fraction of  $B_{11}C$  icosahedra. The energy contribution to  $\Delta f$  arising from the degeneracy of the carbon location within each  $B_{11}C$  icosahedron,  $nk_B T \ln(\alpha)$ , is lost with each such substitution. Thus, the increase of  $n$  beyond  $n = 1$  contributes the term  $(n - 1)\ln(\alpha)$  to  $\Delta f/k_B T$ . These two entropic effects respectively contribute a negative component to the slope of  $\Delta f/k_B T$  versus  $n$  for  $n \leq 1$  and a positive component to the slope of  $\Delta f/k_B T$  versus  $n$  for  $n \geq 1$ . Indeed, the nonzero value of the entropic contribution to  $\Delta f/k_B T$  at  $n = 2$  is caused by these entropic effects. At  $n = 0$  the boron carbide,  $B_4C$ , is composed of C—B—C chains and  $B_{11}C$  icosahedra. At  $n = 2$  the boron carbide,  $B_{14}C$ , is composed of C—B—B chains and  $B_{12}$  icosahedra. The total entropic contribution to  $\Delta f/k_B T$ , the reduced free energy relative to  $B_4C$ , at  $n = 2$  is thus  $\ln(\alpha) - \ln(2) = \ln(\alpha/2)$ . With  $\alpha = 6$ , the entropic contribution to  $\Delta f/k_B T$  at  $n = 2$  is just  $\ln(3)$ , as shown in Fig. 3.

#### IV. WIDTH OF THE SINGLE-PHASE REGION OF BORON CARBIDES

The change of the system's free energy,  $\Delta f$ , as the carbon concentration is reduced from that of  $B_4C$  to  $B_{12+n}C_{3-n}$ , is given by Eqs. (22) and (23), where  $\Delta f$  is given as a function of  $n$ . The purely entropic contribution of  $\Delta f$  is presented as a function of  $n$  in Fig. 3. However, determination of the total change in the free energy,  $\Delta f$ , requires knowledge of the three energies which enter into Eqs. (22) and (23):  $\epsilon_1$ ,  $\epsilon_2$ , and  $\epsilon_3$ . Here, crude estimates of the relative sizes of these energies are first described. Then, the limits imposed on the magnitudes of these energies by the observed width of the single-phase regime are estimated. These two estimates of the energetic parameters of the free energy are then compared and are found to be consistent with one another. The small values of the bond-energy and Coulomb-energy parameters which result can be understood (or rationalized) in terms of known physical features of the boron carbides.

##### A. The free energy

To provide a very rough estimate of the relative magnitudes of  $\epsilon_1$ ,  $\epsilon_2$ , and  $\epsilon_3$ , first consider the energies from which these energies were constituted:  $E_b$ ,  $E_h$ ,  $E_i$ , and  $E_c$  [cf. Eqs. (21a)–(21c)]. The energy to remove a pair of



electrons from a bonding orbital associated with a  $(B_{11}C)^-$  icosahedron in a boron carbide,  $E_b$ , is roughly  $2E_{\text{bond}} + U$ , where  $E_{\text{bond}}$  is the energy associated with the orbital that is being depleted and  $U$  is an energy of Coulombic origin. The first contribution,  $2E_{\text{bond}}$ , arises because two electrons are being removed from a bonding-type state. The second contribution,  $U$ , may be considered the result of separately taking two electrons from the negatively charged icosahedron to infinity. Considered sequentially, the first electron is taken from the negatively charged icosahedron and then the second electron is removed from the residual neutral icosahedron. This sequence is defined as yielding only a single Coulomb energy, since only the second event requires breaking a Coulombic attraction.

Reckoned similarly, the energy of removing a pair of electrons from a  $B_{12}^{2-}$  icosahedron,  $2E_h$ , is  $2E_{\text{bond}} - U$ . Here the first contribution,  $2E_{\text{bond}}$ , accounts for two electrons being removed from a bonding orbital. The second contribution is the sum of the two Coulombic energies associated with sequentially removing an electron from a center that is charged doubly negative,  $-U$ , and removing an electron from the remaining center that is charged singly negative, 0. Since the  $(B_{11}C)^-$  and  $B_{12}^{2-}$  icosahedra only differ by the presence of a positive nuclear charge, the difference in the double ionization energies for these two icosahedra,  $E_b - 2E_h$ , must be  $2U$ , as it is.

The energy associated with the transformation of a  $(B_{11}C)^-$  icosahedron to a  $B_{12}^{2-}$  icosahedron by the removal of a positive nuclear charge,  $E_i$ , is similarly estimated as the Coulomb energy  $2U$ . This Coulombic energy is essentially that of a proton attracted to two electrons. Fi-

nally, this reasoning scheme also yields a vanishing energy for that associated with transforming a  $(C-B-C)^+$  intericosahedral chain into a  $C-B-B$  intericosahedral chain by removing a positive nuclear charge:  $E_c \approx 0$ .

The results of these rough considerations may be succinctly summarized by

$$E_b \approx 2E_{\text{bond}} + U, \quad (26a)$$

$$E_h \approx 2E_{\text{bond}} - U/2, \quad (26b)$$

$$E_i \approx 2U, \quad (26c)$$

and

$$E_c \approx 0. \quad (26d)$$

Inserting these very crudely estimated energies into Eqs. (21a)–(21c) yields

$$\epsilon_1 \approx E_{\text{bond}} + U/2, \quad (27a)$$

$$\epsilon_2 \approx E_{\text{bond}} + U/2, \quad (27b)$$

and

$$\epsilon_3 \approx 2U. \quad (27c)$$

The effect of the energy terms on the free energy is now addressed. To facilitate the discussion, it is useful, but not essential, to take  $\epsilon_1$  and  $\epsilon_2$  to equal a common value,  $\epsilon$ . Beyond easing the presentation without qualitatively affecting the discussion, this simplification is consistent with the very crude estimates of Eq. (27a) and (27b). With this simplification, the expressions for  $\Delta f/k_B T$ , obtained from Eqs. (22) and (23), become

$$\Delta f/k_B T = n\epsilon/k_B T + [(1-n)\ln(1-n) + (3n/2)\ln(n/2) + (1-n/2)\ln(1-n/2)] \quad (28)$$

for  $0 \leq n \leq 1$ , and

$$\Delta f/k_B T = \epsilon/k_B T + (n-1)[\epsilon/k_B T - 2\exp(-\epsilon_3/k_B T)] + \{-\ln(2) + (n-1)\ln[\alpha(n-1)] + 2(1-n/2)\ln(1-n/2)\} \quad (29)$$

for  $1 \leq n \leq 2$ .

Presently, no realistic theoretical estimates of  $\epsilon$  exists. In fact, there is no definite knowledge of the nature of the orbitals associated with bipolaron formation in the boron carbides. Analysis of electronic transport measurements only associates the bipolaron formation with the carbon-containing icosahedra.<sup>10,13</sup> Beyond this, the results of the application of hydrostatic pressure on the electrical conductivity imply that a bipolaronic hole is associated with a local dilatation of the lattice.<sup>17</sup> These observations have motivated calculations of the bipolaronic expansion of icosahedral molecules resulting from the removal of electrons from its internal bonding orbitals.<sup>29–31</sup> In these molecular studies, the highest-lying icosahedral bonding orbital has an energy of about 1.3 eV.<sup>31</sup> However, the question of the formation of bipolaronic holes within an icosahedral solid, such as a boron carbide, has

not yet been specifically addressed. Nonetheless, it is noted that a solid provides opportunities to reduce the bond energy of the highest-lying filled orbital from that of an icosahedral molecule. In particular, since an icosahedron has atoms surrounding it in a solid which are not present in a molecule, one can conceive of having additional (higher-lying) bonding orbitals centered about an icosahedron in a solid which are not present in a simple molecule [e.g., borane ( $B_{12}H_{12}$ )]. Furthermore, a solid provides additional sources of screening and polarization as well as additional symmetry-breaking-induced level splittings. All these effects can lower  $\epsilon$  in a solid below that of a molecule. Thus, 1 eV is presumed to represent an upper limit for  $\epsilon$ .

The estimate of  $\epsilon_3$  of Eq. (27c),  $\epsilon_3 \approx 2U$ , indicates that  $\epsilon_3$  is of the order of an intraicosahedral Coulomb repulsion energy. In the absence of screening such an energy

will be many electron volts.<sup>29</sup> However, in a solid  $\epsilon_3$  may be reduced considerably by screening. In particular, the large carrier densities,  $> 10^{21} \text{ cm}^{-3}$ , and the presence of large structural elements (icosahedra and three-atom chains) that may be polarized, suggest that the dielectric constants of the boron carbides are extremely large.<sup>31</sup> Measurements of the dielectric constants of boron carbides support this contention.<sup>32</sup>

To illustrate how the magnitudes of  $\epsilon$  and  $\epsilon_3$  affect the free energy,  $\Delta f/k_B T$  of Eqs. (28) and (29) is studied as a function of  $n$  for different values of these energies. The icosahedral degeneracy parameter  $\alpha$  is kept fixed at 6, the value utilized in Fig. 3. Furthermore,  $k_B T$  is taken to be 0.2 eV. This choice is made to model the free energy at the very high temperatures at which boron carbides are frequently made. For example, hot-pressed boron carbides are often made at 2400 K.<sup>9</sup> In accord with the preceding discussion, both large and small values of  $\epsilon$  and  $\epsilon_3$  are considered:  $\epsilon=1.0$  and 0.2 eV as well as both  $\epsilon_3/k_B T \rightarrow \infty$  and 1. Thus, four plots of  $\Delta f/k_B T$  versus  $n$  are presented. Figure 4 is plotted with  $\epsilon=0.2$  eV and  $\epsilon_3/k_B T \rightarrow \infty$ . Figure 5 is plotted with  $\epsilon=0.2$  eV and  $\epsilon_3/k_B T=1$ . Figure 6 is plotted with  $\epsilon=1.0$  eV and  $\epsilon_3/k_B T \rightarrow \infty$ . Figure 7 is plotted with  $\epsilon=1.0$  eV and  $\epsilon_3/k_B T=1$ .

Figures 4–7 have several features in common. All of

these plots have maxima at  $n=0, 1$ , and 2. In addition, one minimum occurs between  $n=0$  and 1 and another minimum occurs between  $n=1$  and 2. As  $\epsilon$  is increased, these minima monotonically move closer to the maxima at  $n=0$  and 1, respectively. It is clear that the general increase of  $\Delta f$  with increasing  $n$  becomes increasingly marked as  $\epsilon$  is increased. In particular, the value of  $\Delta f$  at  $n=2$  is given by

$$\Delta f = 2\epsilon + k_B T [\ln(\alpha/2) - 2 \exp(-\epsilon_3/k_B T)]. \quad (30)$$

Thus, as illustrated by comparing Fig. 4 with Fig. 5 and comparing Fig. 6 with Fig. 7, for a fixed value of  $\epsilon$  an increase of  $\epsilon_3$  increases the variation of  $\Delta f$  between  $n=1$  and 2. Furthermore, when  $\epsilon$  is sufficiently large to dominate the variation of  $\Delta f$  with  $n$ , as in Figs. 6 and 7,  $\Delta f$  has a typical variation of about  $2\epsilon$  as  $n$  rises from 0 to 2. In particular, with a value of  $\epsilon$  of about 1 eV, the range of values of  $\Delta f$  is about 2 eV over the composition range from  $n=0$  to 2.

### B. Phase separation

The single-phase region of boron carbides is defined by the range of carbon concentrations within which carbon and boron atoms exclusively reside with the boron-carbide structure, illustrated in Fig. 1. With a carbon

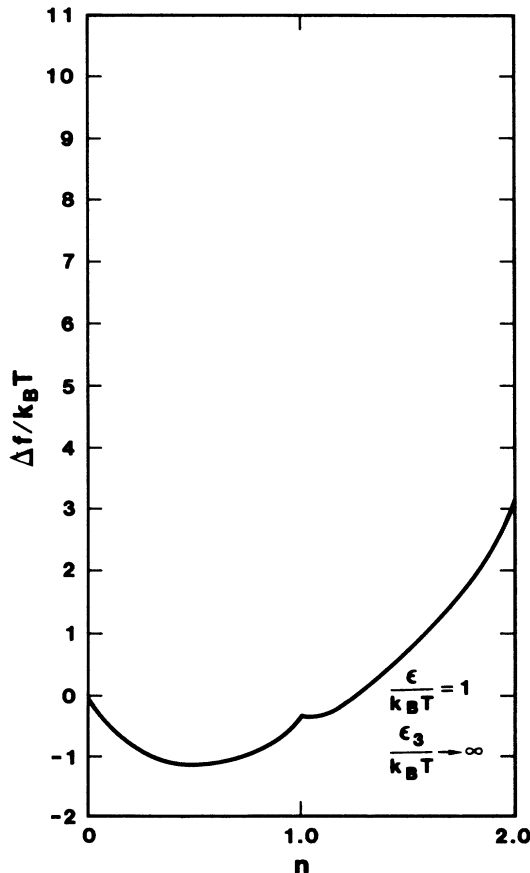


FIG. 4.  $\Delta f/k_B T$  for  $B_{12+n}C_{3-n}$ , obtained from Eqs. (28) and (29), plotted against  $n$  when  $\alpha=6$ ,  $\epsilon/k_B T=1$ , and  $\epsilon_3/k_B T \rightarrow \infty$ .

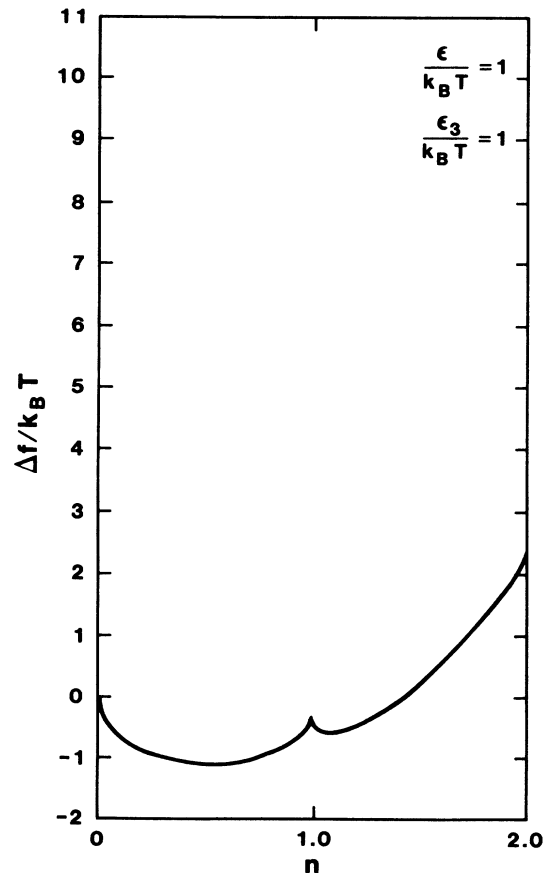
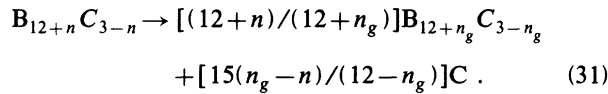


FIG. 5.  $\Delta f/k_B T$  for  $B_{12+n}C_{3-n}$ , obtained from Eqs. (28) and (29), plotted against  $n$  when  $\alpha=6$ ,  $\epsilon/k_B T=1$ , and  $\epsilon_3/k_B T=1$ .

concentration that exceeds the limit of the boron-carbide single-phase regime, graphite regions are formed. With a boron concentration in excess of the limiting boron concentration of the boron-carbide single-phase regime, spatial regions of  $\beta$ -rhombohedral boron are formed.

With boron carbides being represented as  $B_{12+n}C_{3-n}$ , the single-phase region is defined by the allowed range of values for  $n$ . In particular, if  $n$  is less than  $n_g$ , graphite inclusions are formed and if  $n$  exceeds  $n_b$ , inclusions of  $\beta$ -rhombohedral boron are formed. Thus, the single-phase region of boron carbides is defined by  $n_g \leq n \leq n_b$ . Specifically, with  $n \leq n_g$ , inclusions of graphite are formed within a boron carbide whose composition is  $B_{12+n_g}C_{3-n_g}$  with the proportions given by the chemical formula



With  $n \geq n_b$ , inclusions of  $\beta$ -rhombohedral boron are formed within the boron carbide of the composition  $B_{12+n_b}C_{3-n_b}$  with the proportions given by the chemical relation

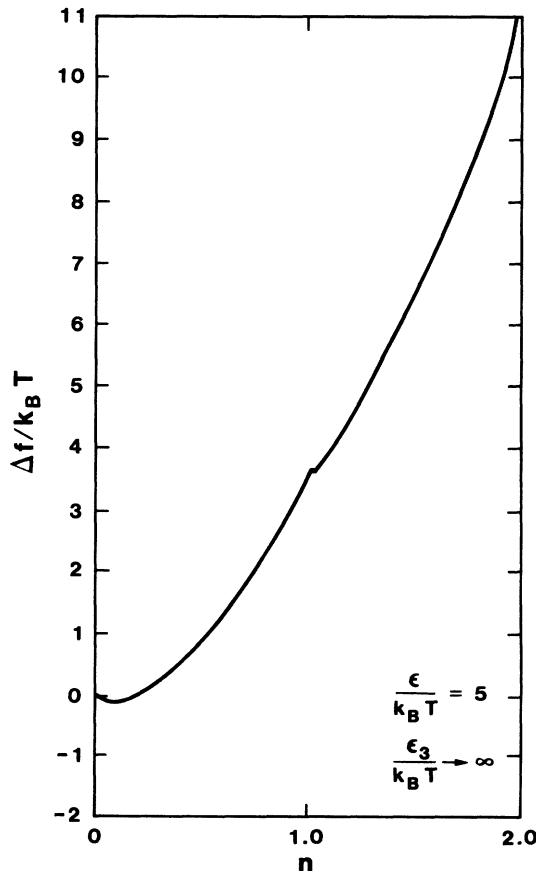
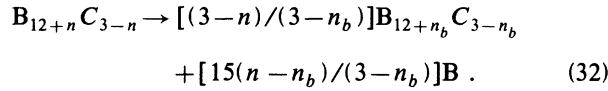


FIG. 6.  $\Delta f/k_B T$  for  $B_{12+n}C_{3-n}$ , obtained from Eqs. (28) and (29), plotted against  $n$  when  $\alpha=6$ ,  $\epsilon/k_B T=5$ , and  $\epsilon_3/k_B T \rightarrow \infty$ .

Noting the proportions of the two components of each phase-separated system, the free energies per formula unit of the carbon-rich and boron-rich phase-separated (PS) systems can be written as

$$f_{PS}(n) = \Delta f(n_g) + \left[ \frac{(n_g-n)}{(12-n_g)} \right] \times [15 \Delta f(C) - \Delta f(n_g)] \quad (33)$$

on the carbon-rich side, and as

$$f_{PS}(n) = \Delta f(n_b) + \left[ \frac{(n-n_b)}{(3-n_b)} \right] \times [15 \Delta f(B) - \Delta f(n_b)] \quad (34)$$

on the boron-rich side. Here the free-energy differences  $\Delta f(n)$ ,  $15 \Delta f(B)$ , and  $15 \Delta f(C)$  are all measured from the same fiducial point, the composition  $B_{12}C_3$ . Phase separation occurs when the free energy of the homogeneous system,  $\Delta f(n)$ , exceeds that of the phase-separated system. Expanding the free energy of the homogeneous system about its two limiting values,  $n_g$  and  $n_b$ , yields

$$\Delta f(n) = \Delta f(n_g) + \left. \frac{\partial \Delta f(n)}{\partial n} \right|_{n_g} (n - n_g) \quad (35)$$

and

$$\Delta f(n) = \Delta f(n_b) + \left. \frac{\partial \Delta f(n)}{\partial n} \right|_{n_b} (n - n_b), \quad (36)$$

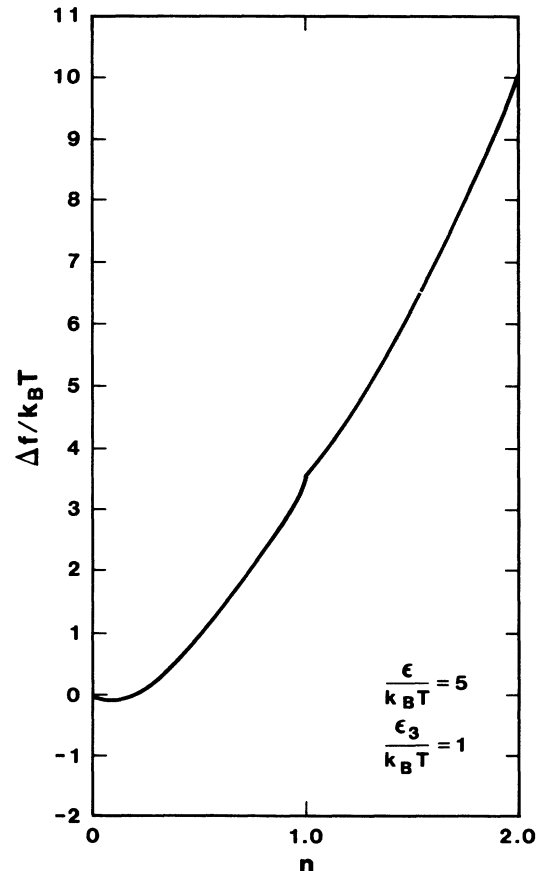


FIG. 7.  $\Delta f/k_B T$  for  $B_{12+n}C_{3-n}$ , obtained from Eqs. (28) and (29), plotted against  $n$  when  $\alpha=6$ ,  $\epsilon/k_B T=5$ , and  $\epsilon_3/k_B T=1$ .

respectively. Using Eqs. (33) and (35), the condition for phase separation on the carbon-rich side,  $f_{\text{PS}}(n) < \Delta f(n)$  for  $n < n_g$ , may, after some algebra, be written as

$$15 \Delta f(\text{C}) < \Delta f(n_g) - \left. \frac{\partial \Delta f(n)}{\partial n} \right|_{n_g} (12 + n_g). \quad (37)$$

On the boron-rich side, the phase-separation condition,

$f_{\text{PS}}(n) < \Delta f(n)$  for  $n > n_b$ , is found from Eqs. (34) and (36) to be

$$15 \Delta f(\text{B}) < \Delta f(n_b) + \left. \frac{\partial \Delta f(n)}{\partial n} \right|_{n_b} (3 - n_b). \quad (38)$$

Anticipating that  $n_g < 1$ , Eq. (28) is used to find that

$$\Delta f(n_g) - \left. \frac{\partial \Delta f(n)}{\partial n} \right|_{n_g} (12 + n_g) = -12\varepsilon + k_B T [13 \ln(1 - n_g) - 18 \ln(n_g/2) + 7 \ln(1 - n_g/2)]. \quad (39)$$

Anticipating that  $n_b > 1$ , Eq. (29) is used to determine that

$$\Delta f(n_b) + \left. \frac{\partial \Delta f(n)}{\partial n} \right|_{n_b} (3 - n_b) = 3\varepsilon + k_B T \{ -4 \exp(-\varepsilon_3/k_B T) + 2 \ln[\alpha(n_b - 1)] - \ln(2 - n_b) \}. \quad (40)$$

Combining Eqs. (37) and (39), one then finds that the limiting value of  $n$  at the carbon-rich side of the single-phase region,  $n_g$ , is given by

$$[5 \Delta f(\text{C}) + 4\varepsilon]/6k_B T = \frac{13}{18} \ln(1 - n_g) - \ln(n_g/2) + \frac{7}{18} \ln(1 - n_g/2). \quad (41)$$

Similarly, taken together, Eqs. (38) and (40) yield an equation for  $n_b$ :

$$[15 \Delta f(\text{B}) - 3\varepsilon]/k_B T + 4 \exp(-\varepsilon_3/k_B T) = 2 \ln[\alpha(n_b - 1)] - \ln(2 - n_b). \quad (42)$$

To sense the physical meaning of Eqs. (41) and (42), consider the limits in which  $n_g \rightarrow 0$  and  $n_b \rightarrow 2$ . Then, the right-hand sides of Eqs. (41) and (42) approach  $-\ln(n_g/2)$  and  $-\ln[(2 - n_b)/\alpha^2]$ , respectively. Then, exponentiating Eqs. (41) and (42) yields equations for the limiting values of  $n$ ,  $n_g$ , and  $n_b$ :

$$n_g = 2 \exp\{ -[5 \Delta f(\text{C}) + 4\varepsilon]/6k_B T \} \quad (43)$$

and

$$n_b = 2 - \alpha^2 \exp\{ -\{ [15 \Delta f(\text{B}) - 3\varepsilon]/k_B T + 4 \exp(-\varepsilon_3/k_B T) \} \}. \quad (44)$$

Equation (43) describes two effects that drive the carbon-rich end of the single-phase region toward  $\text{B}_4\text{C}$  (i.e.,  $n_g$  toward zero). First, as the cost in energy of removing a bonding electron from a boron carbide,  $\varepsilon$ , increases, the system is less willing to depart from the stoichiometry of  $\text{B}_4\text{C}$ , where there is a maximum number of bonding electrons. Second, as  $\Delta f(\text{C})$ , the free energy per carbon atom of graphite, rises, the system is less willing to phase separation and accept the formation of graphite inclusions.

Equation (44) describes four competing effects that affect the boron-rich side of the single-phase regime. First, the larger the value of the degeneracy factor associated with  $\text{B}_{11}\text{C}$  icosahedra,  $\alpha$ , the less willing the system is to pay the entropic price of giving up icosahedral carbon. Second, with an increase of  $\Delta f(\text{B})$ , the free energy per atom of  $\beta$ -rhombohedral boron, the system is less willing to phase separate, forming regions of  $\beta$ -

rhombohedral boron. Third, increasing the energetic cost of removing a bonding electron from a boron carbide,  $\varepsilon$ , drives  $n_b$  down from its maximum value of 2. Finally, decreasing the excitation energy of electrons from  $\text{B}_{11}\text{C}$  icosahedra to  $\text{B}_{12}$  icosahedra,  $\varepsilon_3$ , produces an increase in  $n_b$ . This effect occurs since a reduction of  $\varepsilon_3$  permits a greater variety of configurations of charge carriers, thereby lowering the electronic component of the boron-carbide free energy. Thus, the physical effects described by Eqs. (43) and (44) are qualitatively understood.

To simplify the equations governing the extreme of the boron-carbide single-phase region, Eqs. (41) and (42), two energies are now defined:

$$F = [5 \Delta f(\text{C}) + 4\varepsilon]/6 \quad (45)$$

and

$$F_D = 12 \Delta f(\text{B}) + 3 \Delta f(\text{C}). \quad (46)$$

The free energy  $F$  is the characteristic energy governing the carbon-rich side of the single-phase region. The free energy  $F_D$  is the free energy associated with the decomposition of  $\text{B}_{12}\text{C}_3$  into  $\beta$ -rhombohedral boron and graphite. Equations (41) and (42) are reexpressed in terms of these two free energies as

$$F/k_B T = \frac{13}{18} \ln(1 - n_g) - \ln(n_g/2) + \frac{7}{18} \ln(1 - n_g/2) \quad (47)$$

and

$$(5F_D - 18F)/4k_B T + 4 \exp(-\varepsilon_3/k_B T) = 2 \ln[\alpha(n_b - 1)] - \ln(2 - n_b), \quad (48)$$

respectively.

Equations (47) and (48) give the two limiting values of  $n$ ,  $n_g$  and  $n_b$ , in terms of the energetic parameters  $F_D$ ,  $F$ , and  $\varepsilon_3$ . The value of  $F_D$  may be estimated as being equal to the Gibbs free energy reported for the decomposition

of nominal  $B_{12}C_3$  to  $\beta$ -rhombohedral boron and graphite,  $\approx 1.7$  eV.<sup>33</sup> Since there is no firm knowledge of  $F$  and  $\epsilon_3$ , the limits of the single-phase region cannot be meaningfully predicted. One can, nonetheless, proceed in a converse manner and use the reported limits of the single-phase region of boron carbides to obtain values of  $F$  and  $\epsilon_3$ . These numbers can then be examined for self-consistency and physical cogency. Thus, even without a predictive capacity, this analysis can provide an explanation of the wide single-phase region of the boron carbides.

There are several means of determining values of  $n_g$  and  $n_b$ . In particular, an estimate of  $n_g$  of  $\pm 0.2$  is found from studying the microstructure of hot-pressed samples.<sup>8</sup> A compatible estimate of  $n_g = 0.2$  is obtained from electronic transport results.<sup>9</sup> In particular, the transport estimate is based on the observation that the density of holelike bipolarons in the boron carbides with the most carbon (nominally  $B_4C$ ) is about one-fifth that of  $B_{13}C_2$ , where one-half of the unit cells should be occupied by a bipolaron.<sup>9</sup> To have 10% of the unit cells occupied by a bipolaronic hole, one must have 20% of the unit cells having a carbon atom replaced by a boron atom. The remaining carbon in hot-pressed powders of nominal composition  $B_4C$  (about 1.3% of the atoms) is presumed to be associated with carbon inclusions. Indeed, carbon inclusions are observed in Raman spectra of hot-pressed samples which have  $B_4C$  as the nominal composition.<sup>23,27</sup> In addition, an estimate of  $n_b = 1.7$  is reported in a microstructural and chemical study of the width of the single-phase regime of boron carbides.<sup>8</sup>

With  $n_g = 0.2$  and  $n_b = 1.7$ , Eqs. (47) and (48) yield values of  $F$  and  $\epsilon_3$  of 0.42 and 0.05 eV, respectively, when  $F_D = 1.7$  eV,  $\alpha = 6$ , and  $k_B T = 0.2$  eV. This small value of  $\epsilon_3$  is consistent with the previously described notion of a well-screened Coulomb interaction in the boron carbides. To discuss the physical meaning of the value of  $F$ , the value  $F = 0.42$  eV is inserted into Eqs. (45) and (46), yielding  $\Delta f(C) = 0.50$  eV  $- 0.8\epsilon$  and  $\Delta f(B) = 0.016 + 0.2\epsilon$ . Thus,  $\Delta f(C)$  and  $\Delta f(B)$  depend on  $\epsilon$ . In particular, if  $\epsilon$  is large,  $\approx 1$  eV, then  $\Delta f(C) \approx -0.3$  eV and  $\Delta f(B) \approx 0.2$  eV and  $\Delta f(C) \ll \Delta f(B)$ . However, if  $\epsilon$  is small,  $\epsilon \approx 0.2$  eV, the opposite situation prevails:  $\Delta f(C) \gg \Delta f(B)$ . The negative value of  $\Delta f(C)$  and positive value of  $\Delta f(B)$  is consistent with graphite being more stable than  $B_{12}C_3$  and  $\beta$ -rhombohedral boron being less stable than  $B_{12}C_3$ . This feature is compatible with the melting temperature of (nominal)  $B_{12}C_3$  (2743 K) (Ref. 33) exceeding that of  $\beta$ -rhombohedral boron ( $\approx 2600$  K),<sup>7</sup> but being less than that of graphite ( $> 3900$  K).<sup>7</sup> Thus, a value of  $\epsilon$  that is less than but comparable to 1 eV is physically reasonable. As a result, this calculation provides a cogent explanation of the wide single-phase region of the boron carbides.

## V. SUMMARY

Boron carbides exist over a wide range of carbon concentrations as comparably sized and bonded carbon and boron atoms substitute for one another within the chains and icosahedra of the basic rhombohedral structure of Fig. 1. In this paper the free energy of boron carbides has been studied in order to determine the preferred sites

for substitutions as a function of carbon concentration and to understand the origin of the wide single-phase region of the boron carbides.

Two types of twelve-atom icosahedral cluster are considered. The first type of icosahedron contains twelve boron atoms. In the second type of icosahedron a solitary carbon atom is located on one of the geometrically equivalent sites of the deformed icosahedron of a boron carbide. In addition, two types of three-atom intericosahedral chains are considered. The first type, a C—B—C chain, consists of two four-fold-coordinated carbon atoms which are linked by a twofold-coordinated boron atom. The second type of intericosahedral chain, a C—B—B chain, has one of the terminal carbon atoms of the chain replaced by a boron atom.

A neutral boron icosahedron, as a borane molecule ( $B_{12}H_{12}$ ), is two electrons short of filling its internal bonding orbitals. The substitution of a carbon atom for a boron atom contributes an electron to the icosahedron's bonding. To further facilitate the bonding of the solid, the unbonded electron of the central boron atom of the C—B—C chain is presumed to be donated to a bonding orbital of an icosahedron. Thus, at the stoichiometry of  $B_4C$ , with  $B_{11}C$  icosahedra linked by C—B—C chains, there are sufficient electrons to fill all of the system's bonding orbitals.

With a reduction of the carbon content, a boron atom replaces a carbon atom within either a chain or an icosahedron. In forming a C—B—B chain, the unbonded electron of the central boron is donated toward the terminal boron atom to facilitate it satisfying its fourfold bonding requirements.<sup>31</sup> Thus, unlike a C—B—C chain, a C—B—B chain does not have a nonbonding electron to donate to a bonding orbital elsewhere in the solid. Substituting a boron atom for a carbon atom within an icosahedron also removes one electron from the system's bonding orbitals. Motivated by the results of electronic transport studies,<sup>10,13,19,28</sup> the holes that are produced by the replacement of a carbon atom by a boron atom are presumed to either pair to form bipolaronic holes associated with a  $B_{11}C$  icosahedron or to remain as quasifree holes associated with  $B_{12}$  icosahedra.

As complex as this model is, it involves many simplifications. For example, one can conceive of other atomic configurations. In particular, two carbon atoms could reside within an icosahedron or a carbon atom could reside within the central atom of a chain. In addition, one might conceive of holes being centered on chains rather than icosahedra. However, as indicated in the Introduction to this paper, much evidence suggests that the present model is, at least, a good first approximation to the boron carbides.

Here, the free energy of this model has been calculated as a function of (1) the carbon concentration, (2) the proportion of atomic substitutions occurring in chains and icosahedra, and (3) the distribution of electronic carriers between  $B_{11}C$  and  $B_{12}$  icosahedra. This general free-energy expression is then minimized with respect to the sites of the carbon substitution and the location of the electronic carriers. The minimized free-energy expression gives the free energy as a function of carbon concen-

tration. This expression is then utilized to find expressions for the carbon-rich and boron-rich ends of the single-phase regime of boron carbides.

From the minimization procedure it is found that entropy alone provides a strong impetus toward preferentially substituting boron for carbon within the intericosahedral chains. This occurs because replacing a carbon atom by a boron atom in a C—B—C chain introduces an entropic lowering of the free energy of  $k_B T \ln(2)$ , while the replacing of a carbon atom at one of  $\alpha$  equivalent sites in an icosahedron by a boron atom increases the free energy by the entropic factor  $k_B T \ln(\alpha)$ . Thus, after estimating the energetic parameters of the system, it is concluded that boron carbides,  $B_{12+n}C_{3-n}$ , may be represented as  $(B_{11}C)(C—B—C)_{1-n}(C—B—B)_n$  for  $0 < n < 1$  and as  $(B_{11}C)_{2-n}(B_{12})_{1-n}(C—B—B)$  for  $1 < n < 2$ . Furthermore, because this structure is most ordered at  $n=0, 1$ , and  $2$ , these three compositions provide local maxima of the free energy.

The minimization of the free energy also indicates that the density of bipolaronic holes on  $B_{11}C$  icosahedra rises linearly with  $n$  up to a maximum at  $n=1$  and then falls as  $n$  is increased further. The increase of the density of bipolaronic holes as  $n$  is increased reflects a linear increase in the number of unfilled bonding orbitals associated with  $B_{11}C$  icosahedra as  $n$  is increased. The decline of the density of bipolaronic holes as  $n$  is increased past unity arises because the number of  $B_{11}C$  icosahedra decreases linearly with  $n$  when  $n$  exceeds 1 while the fraction of  $B_{11}C$  icosahedra with bipolaronic holes remains at  $\frac{1}{2}$ . Beyond these carrier densities, the thermally induced promotion of electrons from  $B_{11}C$  icosahedra to  $B_{12}$  icosahedra arguments the number of bipolaronic holes on the  $B_{11}C$  icosahedra.

If the carbon concentration becomes too large,  $n < n_g$ , boron carbides phase-separate into the boron carbide  $B_{12+n_g}C_{3-n_g}$  and graphite. Similarly, if the boron concentration becomes too great,  $n > n_b$ , boron carbides phase separate into a boron carbide  $B_{12+n_b}C_{3-n_b}$  and  $\beta$ -rhombohedral boron. By comparing the free energy of the boron carbide with those of phase-separated material, the two limits of the single-phase region are determined in terms of two energetic parameters. The experimentally determined limits of the single-phase region are then utilized to determine these energetic parameters. The values of the energetic parameters determined in this manner are consistent with general expectations. In particular, the promotion energy of an electron from a positive charged center to a neutral center,  $\epsilon_3$ , is found to be

small,  $\approx 0.1$  eV. This value is consistent with the well-screened Coulomb interaction suggested by the large measured dielectric constants.<sup>32</sup> The remaining energetic parameter indicates that graphite is significantly more stable than  $\beta$ -rhombohedral boron. This finding is consistent with graphite having a much higher melting temperature than  $\beta$ -rhombohedral boron.

There are several reasons for the wide single-phase region of boron carbide. First, the similarity in size and in electronic structure of boron and carbon facilitate their substitution for one another. Second, the equivalence of many locations within the structure of boron carbides enhances the role of entropy of the system's free energy. This effect drives the system away from having a well-ordered atomic arrangement. Third, the screening of the boron carbides tends to suppress the energetic factors which compete with entropy within the free energy. Finally, the greater stability of graphite than boron carbides favors phase separation at a lower carbon concentration than 20%. Thus, boron carbides are always found to be highly degenerate semiconductors with carrier densities of  $\approx 10^{21}$  cm<sup>-3</sup> rather than being the insulator expected at a true 20% carbon concentration. At compositions with relatively high concentrations of boron, the fact that  $\beta$ -rhombohedral boron is less stable than nominal  $B_4C$  enables boron carbides to remain stable with respect to phase separation even as their density of bonding electrons is reduced accompanying the replacement of carbon atoms with boron atoms.

In summary, this study provides an explanation for several empirically deduced features of the boron carbides. First, consistent with interpretations of the thermal conductivity and the Raman spectra,<sup>22,23</sup> it is shown that C—B—C intericosahedral chains are preferable to  $B_{11}C$  as sites for the replacement of carbon atoms with boron atoms. Second, this work determined a non-monotonic variation of the density of bipolaronic charge carriers on  $B_{11}C$  icosahedra which agrees with the carrier density determined from analysis of electronic transport experiments.<sup>10,13</sup> Finally, this work provides a cogent explanation of the wide range of atomic concentrations over which boron carbides exist as a single-phase material.

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