

# Conductivities and Seebeck coefficients of boron carbides: Softening bipolaron hopping

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The electrical conductivities and Seebeck coefficients of boron carbides  $B_{12+x}C_{3-x}$  with  $0.06 \leq x \leq 1.7$  have been measured from 8 K to as high as 1750 K. At high temperature, the temperature dependence of the conductivities is Arrhenius and the activation energy,  $\approx 0.16$  eV, is independent of the carbon concentration. The preexponential factors of the conductivity exhibit a nonmonotonic dependence on  $x$ , peaking near  $x=1$ . These results are consistent with a previously proposed model based on holes forming singlet bipolarons on the boron carbide  $B_{11}C$  icosahedra. At low temperature, the boron carbide conductivities are non-Arrhenius with a temperature dependence that is a strong function of the composition  $x$ . This strong sensitivity to composition indicates that percolation effects, arising from boron carbides having carbon atoms in inequivalent locations, influence the conductivity at low temperature. With  $x$  holes per unit cell, boron carbides have very large Seebeck coefficients that depend only weakly on  $x$ . The magnitudes and temperature dependences of the Seebeck coefficients are consistent with large contributions from carrier-induced softening of local vibrations. Softening effects can be exceptionally large when singlet bipolarons are stabilized among degenerate electronic energy levels by their softening of symmetry-breaking vibrations: “softening bipolarons.” The boron carbide transport properties are generally consistent with those expected of softening bipolarons. Finally, two high-temperature effects are observed in the boron carbide conductivities. The conductivities of samples having high carrier densities,  $x \approx 1$ , are suppressed above 700 K. This suppression can arise when the rapid hopping of nearby carriers disrupts the energy coincidence required for a carrier’s hop. At even higher temperatures, a sharp increase in the boron carbide conductivities ( $\sigma \propto T^4$ ) suggests a radiation-induced excitation of mobile charge carriers.

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## I. INTRODUCTION

Icosahedral borides are distinctively bonded solids with structures based on 12-atom icosahedral clusters.<sup>1</sup> Boron carbides  $B_{12+x}C_{3-x}$  are icosahedral borides that exist as a single phase when  $0.06 \leq x \leq 1.7$ . As shown in Fig. 1, the boron carbide icosahedra are centered at the vertices of rhombohedral unit cells, and three-atom intericosahedral chains lie along the extended body diagonals of the cells. A simple chemical picture suggests that boron carbides would be insulating at  $x=0$ .<sup>1</sup> In particular, each [CBC] chain donates its nonbonding electron,  $\rightarrow[CBC]^+$ , to complete the filling of the internal bonding orbitals of a  $(B_{11}C)$  icosahedron,  $\rightarrow(B_{11}C)^-$ . Consistent with this chemical picture, calculations of the boron carbide electronic structure find a filled valence band at this idealized composition.<sup>2</sup>

In realizable boron carbides,  $x \geq 0.06$ , the replacement of C atoms with B atoms removes bonding electrons to produce a significant density,  $\approx 10^{21}/\text{cm}^3$ , of holelike charge carriers. Measurements of low, thermally activated electrical conductivities and Hall mobilities in boron carbides indicate localized carriers that move by polaronic hopping.<sup>3</sup>

However, the large paramagnetic susceptibility expected of a high density of nearly localized spins is not found. Magnetic susceptibility and electron spin resonance measurements of powder, ceramic, and single-crystal boron carbides always detect about  $10^{19}$  spins/ $\text{cm}^3$ , two orders of magnitude less than the carrier densities.<sup>4,5</sup> In addition, recent low-temperature measurements of the boron carbide Seebeck coefficients<sup>6</sup> do not manifest the magnetic-field dependence

associated with orienting localized spins.

Taken together, these experiments indicate that charge carriers in boron carbides pair and move by polaronic hopping. That is, carriers form singlet bipolarons.

The pairing of holes on  $B_{11}C$  icosahedra may be viewed as a disproportionation:  $2(B_{11}C)^0 \rightarrow (B_{11}C)^- + (B_{11}C)^+$ . After contributing 12 electrons toward forming two-center bonds with each of its 12 neighbors, the  $(B_{11}C)^-$  icosahedron has  $26 (= 3 \times 11 + 4 + 1 - 12)$  second-shell electrons available for its internal bonding. These 26 electrons fill an icosahedron’s 13 internal bonding orbitals.<sup>1</sup> By contrast, a  $(B_{11}C)^+$  icosahedron lacks two electrons from its filled-shell  $(B_{11}C)^-$  state. A  $(B_{11}C)^+$  icosahedron thus represents a bipolaronic hole.

Free-energy considerations<sup>7</sup> and structural and vibrational measurements<sup>8</sup> all suggest that boron atoms primarily replace carbon atoms within chains,  $CBC \rightarrow CBB \rightarrow BBB$ , as  $x$  increases,  $0 \rightarrow 1.0 \rightarrow 1.7$ . Since CBB chains are isoelectronic to  $[CBC]^+$  chains, they do not donate electrons to icosahedra. Thus, substituting CBB for  $[CBC]^+$  chains leaves the highest-energy bonding orbitals of some icosahedra unfilled. As a result, the concentration of bipolarons,  $n_{(B_{11}C)^+}$ , increases as  $x$  increases from 0 toward 1. At  $x=1$ , with all chains ideally being CBB, the fraction of  $B_{11}C$  sites occupied by a bipolaron,  $c = n_{(B_{11}C)^+} / n_{B_{11}C}$ , equals  $\frac{1}{2}$ . Because each chain-end B atom of  $BB^+B$  chains is bonded to atoms of the three adjacent icosahedra, the chain’s central atoms are viewed as interstitial  $B^+$  ions. Electrons are donated to icosahedra from these  $B^+$  ions. As a consequence, the density of

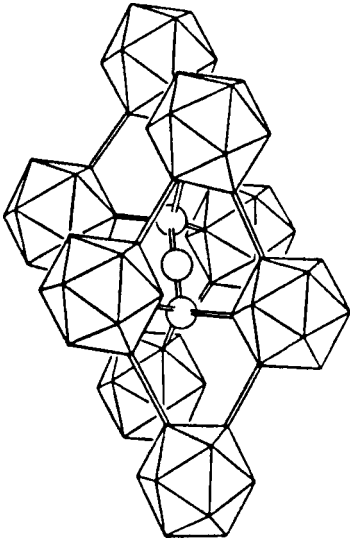


FIG. 1. Twelve-atom icosahedra are centered at the vertices of the boron carbide rhombohedral unit cell. Three-atom intericosahedral chains lie along the long cell diagonal.

$(B_{11}C)^+$  icosahedra decreases as  $x$  increases beyond unity. All told, the progressive replacement of carbon atoms by boron atoms,  $CBC \rightarrow CBB \rightarrow BBB$ , causes the density of bipolarons,  $n_{(B_{11}C)^+}$ , to peak at  $x=1$ .

The boron carbide singlet bipolarons are attributed to holes in the uppermost internal bonding states of icosahedra. The highest-lying internal bonding states of an ideal icosahedron are a set of fourfold degenerate levels.<sup>9</sup> Emin<sup>10</sup> showed that carriers that occupy degenerate orbitals can be induced to pair as singlets by their softening of local symmetry-breaking deformations. Here the primary contribution to the stabilization of the self-trapped pair comes from their reduction of the vibrational free energy, rather than from their inducing large atomic displacements. Pairs stabilized by their reductions of local vibrational frequencies are termed “softening bipolarons.” Softening bipolarons may be identified<sup>10</sup> by (1) their modest hopping activation energies, (2) the absence of the usual polaronic absorption, and, most dramatically, (3) by distinctive contributions to the Seebeck coefficient that are independent of the carrier density.

Boron carbides offer an excellent model system to study bipolaronic-hopping conduction and to search for distinguishing features of softening bipolaron transport. In particular, the boron carbide carrier densities, controlled simply by varying the B to C ratio, are sufficiently large,  $\approx 10^{21}/\text{cm}^3$ , that they overwhelm intrinsic defect levels. Furthermore, carriers hop between well-defined sites,  $B_{11}C$  icosahedra, arranged on a slightly distorted cubic lattice. Finally, the exceptional stability of boron carbides permits transport measurements over an unusually wide range of temperatures, from below 10 K to above 1700 K.

Unfortunately, a detailed picture of electrical conduction in boron carbides has been obscured by significant inconsistencies in prior transport measurements, often made on commercial samples.<sup>3,11–22</sup> Sources of irreproducibility in these measurements include the presence of free-carbon inclusions within some samples and uncertainties of or inhomogeneities

in the sample carbon concentrations. In this paper, we report measurements of the conductivity and Seebeck coefficients of homogeneous, well-characterized boron carbide samples having compositions spanning the single-phase region. These measurements are consistent with a model of small bipolaron hopping among  $B_{11}C$  icosahedra. In particular, we find these transport properties to agree with those expected of softening-stabilized singlet pairs, softening bipolarons. In addition, our very-high-temperature conductivity measurements reveal two features for which we offer explanations.

## II. EXPERIMENTAL DETAILS

Boron carbide samples were prepared from mixtures of graphite powder (Ultra-Carbon Corporation, 99.9999% purity) with either crystalline boron powder (Eagle-Picher Industries, whose major impurities are several hundred ppm C and Si) or amorphous boron powder (Callery Chemical Company, whose major impurities are about 0.1% C and O). Amorphous boron was heated to  $\sim 2200$  K under high vacuum prior to its use in order to remove volatile oxygen and carbon impurities, as described previously.<sup>23</sup> Electrical properties did not depend on the source of boron.

Samples were prepared by hot pressing these mixtures for 15–30 min at 2423 K in graphite dies lined with high-purity BN. Details of the hot-pressing procedure are given elsewhere.<sup>20</sup> The densities of all samples produced by this procedure exceeded 95% of the theoretical values determined by x-ray diffraction. Analysis of x-ray diffraction, optical and scanning electron microscopy, Raman spectroscopy, electron probe microanalysis, and analytical chemistry data confirmed that samples were single phase with homogeneous compositions near their as-mixed value. Sample compositions  $x$  in  $B_{12+x}C_{3-x}$  are hereafter reported as this batch value. The absence of carbon’s characteristic Raman peaks near 1375 and 1580  $\text{cm}^{-1}$  in any sample confirms the absence of major inclusions of either crystalline or amorphous carbon.

Conductivities were measured by standard four-point techniques from below 10 to 1750 K, using several apparatus. The conductivities of small samples cut from hot-pressed cylinders were the same as those measured on the whole cylinders. Seebeck coefficients were measured between 10 and 900 K, also using several different apparatus. Each Seebeck coefficient was calculated from the slope of over 100 individual emf vs  $\Delta T$  measurements and corrected for the reference leads of Cu or Pt. High-temperature measurements were made under slowly flowing gettered Ar to inhibit sample oxidation.

## III. RESULTS AND DISCUSSION

### A. Low-temperature conductivity: Disorder and percolation

The dc conductivities of boron carbides whose compositions span the single-phase region  $0.06 \leq x \leq 1.7$  are plotted in Fig. 2 as functions of the inverse temperature from 8 to 300 K. Two features of the boron carbide low-temperature conductivities are noteworthy. First, these conductivities all have non-Arrhenius temperature dependences that are very

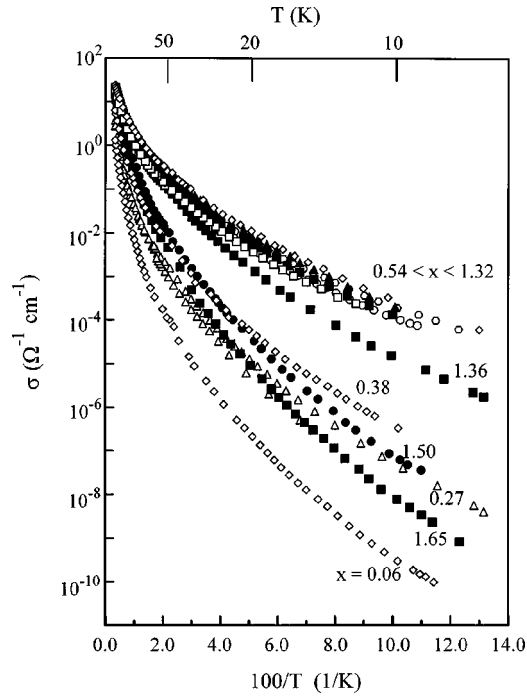


FIG. 2. Conductivities of boron carbides below 300 K are plotted against reciprocal temperature for carbon concentrations spanning the single-phase region. Conductivities are closely clustered within the composition range  $0.54 < x < 1.32$ . Open symbols denote samples with  $0.06 \leq x \leq 1.0$ ; solid symbols denote samples with  $1.0 \leq x \leq 1.7$ .

sensitive to the sample carbon concentrations. Second, the highest conductivities and weakest temperature dependences occur in samples with  $x$  near 1.

Non-Arrhenius conduction is a general consequence of the progressive freezing out of multiphonon contributions to phonon-assisted jump rates with decreasing temperature.<sup>24</sup> The temperature dependence of low-temperature hopping conduction can also be affected by the freezing out of higher-energy conduction paths among energetically disordered sites.<sup>24,25</sup> Evidence of such percolative conduction among disordered sites is found in the strong sensitivity of the temperature dependence of the boron carbide low-temperature conductivities to composition. In particular, the distribution of the boron carbide carbon atoms among inequivalent locations gives rise to composition-dependent disorder.

Boron carbides with compositions near  $x=1$  have both the highest conductivities and the weakest temperature dependences in Fig. 2. Near this composition, bipolaronic holes move among  $B_{11}C$  icosahedra having nearly uniform surroundings of neutral, CBB, chains. Non-Arrhenius conduction under these comparatively uniform circumstances is attributed primarily to the freezing out of multiphonon processes.

Bipolaronic holes,  $(B_{11}C)^+$ , will be repelled from icosahedral sites near positively charged intericosahedral chains. As  $x$  decreases from 1 toward 0.06, neutral, CBB, chains are progressively replaced by positively charged,  $[CBC]^+$ , chains. Similarly, CBB chains are replaced by positively charged,  $[BB^+B]$ , chains as  $x$  increases from 1 toward 1.7.

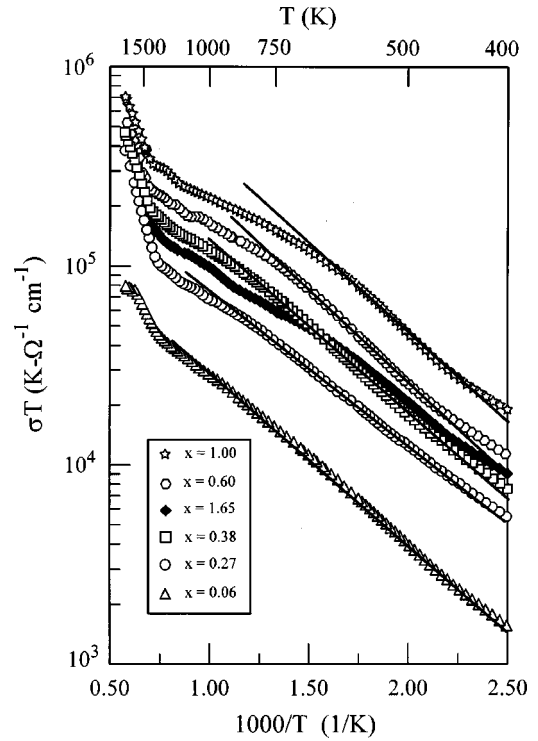


FIG. 3. Conductivities of representative boron carbides are plotted against reciprocal temperature between 400 and 1750 K for  $0.06 \leq x \leq 1.7$  (open symbols) and for  $x=1.65$  (solid symbol).

Energetically favorable icosahedral sites near to neutral CBB chains thus become increasingly disconnected and small in number as the carbon concentration moves from  $x=1$  toward either of its extremes,  $x \approx 0.06$  and  $x \approx 1.7$ . Concomitantly, the boron carbide conductivities garner an additional temperature dependence arising from percolation among energetically inequivalent icosahedral sites. This percolative effect is washed out when the thermal energy  $k_B T$  exceeds the characteristic disorder energy. The data of Fig. 2 show the dispersion in the temperature dependence of the boron carbide conductivities being washed out above about 150 K. The characteristic disorder energy is thus small:  $\approx 0.01$  eV.

### B. High-temperature conductivity: Adiabatic bipolaron hopping

The temperature dependence of the boron carbide conductivities goes smoothly from non-Arrhenius at low temperatures, Fig. 2, to Arrhenius as the temperature rises above about 400 K. Figure 3 shows the conductivities of six representative boron carbide samples versus  $1000/T$  between 400 and 1750 K. Data from measurements on many ( $\approx 15$ ) additional samples are similar, but are not plotted in Fig. 3 in the interest of clarity. Figure 3 indicates nearly Arrhenius temperature dependences from 400 K to between 700 and 1000 K, depending on the sample composition. At still higher temperatures, the temperature dependences of the conductivities change dramatically. This very-high-temperature regime is discussed in Sec. III C.

The temperature dependence of (bi)polaron hopping becomes Arrhenius when the temperature rises above that of

the highest-energy phonons with which carriers interact. Then the atomic vibrations involved in phonon-assisted hopping may be treated classically.<sup>26,27</sup> In this semiclassical limit, the conductivity due to bipolaron hopping is expressed as

$$\sigma T = \frac{Nc(1-c)q^2a^2v}{k_B} \exp\left(\frac{-E_A}{k_B T}\right) P(T), \quad (1)$$

where  $N = n_{B_{11}C}$  is the concentration of icosahedral sites between which hops occur,  $c = n_{(B_{11}C)^+} / n_{B_{11}C}$  is the fraction of these sites occupied by a bipolaron,  $q = 2|e|$  is the electronic charge of a bipolaronic hole,  $a$  is the length of an average hop, and  $v$  is the frequency characterizing the vibrations to which carriers are coupled. With percolation effects negligible, the activation energy  $E_A$  is the minimum energy required to bring the electronic energies of a carrier at the initial and final sites of a hop into coincidence with one another. The last factor in Eq. (1),  $P(T)$ , represents the probability that a carrier will jump from its initial to final site when such a momentary coincidence of electronic energy levels occurs. Typically, electronic motion is sufficiently rapid so that carriers readily follow atomic motions. Then  $P(T) \approx 1$  and the hopping is termed adiabatic.

In the Arrhenius regime, the activation energies of the boron carbide conductivities, about 0.16 eV, are nearly independent of carbon concentration. This insensitivity to composition is consistent with carriers hopping among similar sites,  $B_{11}C$  icosahedra, over the entire single-phase region. Activation energies of 0.16 eV, while typical of small-polaron hopping, are much smaller than expected for moving conventional small bipolarons, in which pairing is attributed to an especially strong electron-lattice interaction. However, a small activation energy for joint hopping of singlet pairs is a distinguishing characteristic of softening bipolarons.<sup>10</sup>

Figure 3 shows that the boron carbide conductivities peak near  $x=1$ , in agreement with the model described in the Introduction. The magnitudes of the preexponential factors are also consistent with this model. For example, Eq. (1) gives a prefactor of  $2 \times 10^5 \text{ K } \Omega^{-1} \text{ cm}^{-1}$  when  $c=0.03$ , and assuming  $a^2v \approx 0.1 \text{ cm}^2/\text{sec}$  and  $P(T) \approx 1$ . The experimental prefactor of the corresponding sample,  $x=0.06$  ( $x=2c$ ), is  $1.8 \times 10^5 \text{ K } \Omega^{-1} \text{ cm}^{-1}$ . Furthermore, the tenfold increase in the prefactor expected upon increasing  $c$  from 0.03 to 0.5, assuming all other factors are constant, is evident in Fig. 3 as the sample composition  $x$  increases from 0.06 to 1.

### C. Very-high-temperature conductivity: Hopping suppression and photo excitation

At sufficiently high temperatures, the temperature dependences of the boron carbide hopping conductivities diminish, Fig. 3. This saturation is observed reproducibly at the lowest temperature, about 700 K, in samples having the highest carrier densities,  $x$  close to 1. By contrast, samples with  $|1-x| \geq 0.6$  have nearly Arrhenius conductivities to 1000 K or higher.

The Appendix describes a correlation mechanism through which the rapid hopping of some carriers interferes with the

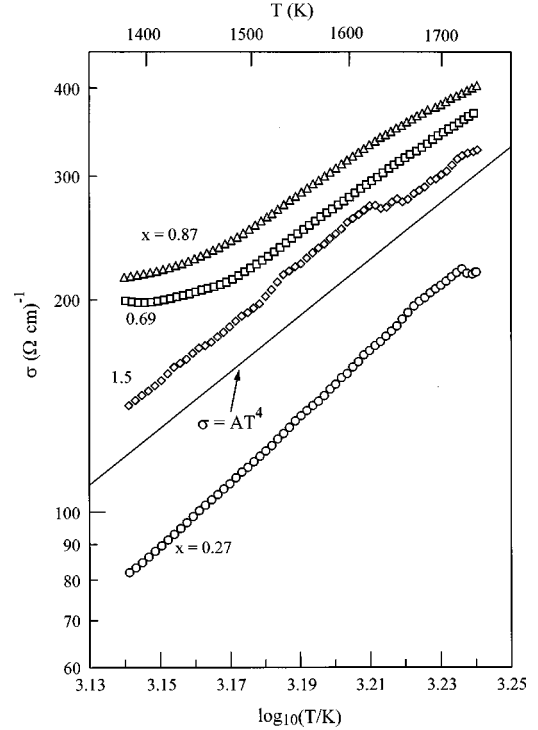


FIG. 4. The logarithm of conductivities of several representative boron carbides are plotted against the logarithm of the temperature for  $T > 1400$  K. The very-high-temperature conductivities of boron carbides approximate a power law dependence of  $\sigma = AT^4$ .

jumps of others. As a result of this interference, hopping conductivities tend to saturate when both the temperature and carrier density are high. Equation (A8) expresses the condition that the carrier density and temperature are sufficiently high to induce a saturation of the hopping conductivity. Equation (A8) is satisfied by boron carbides of the highest carrier densities  $c \approx 0.5$  only when the temperature is sufficiently high,  $T \gtrsim 700$  K. In further agreement with our observations, progressively higher temperatures are required to satisfy Eq. (A8) as  $c$  is reduced from 0.5. Thus this collective interference effect provides a plausible explanation of the high-temperature saturation of the boron carbide conductivities.<sup>28</sup>

At even higher temperatures, above 1400 K, the conductivities of all boron carbides increase sharply. Fitting this sharp rise as an activated process yields an activation energy of about 0.6 eV. However, optical measurements of boron carbides do not detect any absorption indicative of interband transitions below 2 eV.<sup>20</sup> Thus the 0.6 eV activation energy cannot be attributed to thermal generation of the high-mobility carriers that would be required to significantly enhance the conductivity. Figure 4 demonstrates that between 1400 and 1750 K the conductivities obey a power law  $\sigma \propto T^4$ . This parallel between the conductivity and intensity of blackbody radiation suggests that high-mobility charge carriers are generated by photoexcitation at these very high temperatures. Such photoinduced conductivity would become apparent when enough high-mobility carriers are generated to predominate over the hopping conduction.



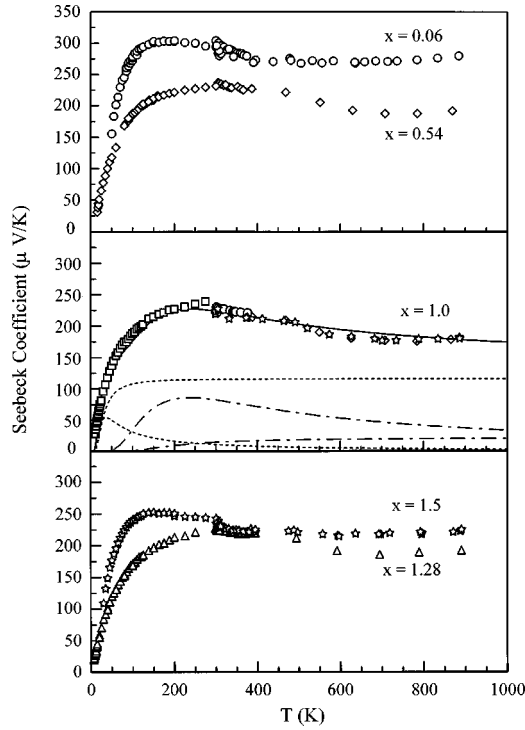


FIG. 5. The Seebeck coefficients of boron carbides with representative carbon concentrations are plotted against temperature between 10 and 900 K. All data for an individual sample are represented by a single symbol in the upper and lower panels. In the middle panel, different symbols represent data obtained with different apparatus. The middle panel also illustrates a fit (solid line) of the data to contributions from carrier-induced softening (Ref. 21). In this fit, bipolarons interact with phonon bands of energy 0.01 eV (short dashed line) and 0.06 eV (dot-dashed line). Two contributions to the net Seebeck coefficient, described by Eqs. (3) and (4), result from the bipolaron interactions with each phonon band.

#### D. Seebeck coefficient: Softening-bipolaron enhancements

The Seebeck coefficients of representative boron carbides with  $0.06 \leq x \leq 1.5$  measured between 10 and 900 K are plotted in Fig. 5. Measurements of many additional samples between 300 and 900 K agree with those shown in Fig. 5.

Above about 600 K, the Seebeck coefficients of our boron carbides become nearly independent of temperature. The composition dependence of these high-temperature (773 K) Seebeck coefficients is depicted in Fig. 6. Distinctively, the Seebeck coefficients have a minimum near  $x = 1$ .

To explain this minimum, we first recall that the Seebeck coefficient is the entropy transported with a charge carrier divided by the carrier's charge,  $q$ .<sup>30</sup> At sufficiently high temperatures the ratio of the carrier density to the density of potential hopping sites,  $c$ , becomes temperature independent. Then the contribution to the Seebeck coefficient associated with the carrier-induced change of the entropy of mixing becomes<sup>31</sup>

$$\alpha_{\text{mix}} = \frac{k_B}{q} \ln\left(\frac{1-c}{c}\right). \quad (2)$$

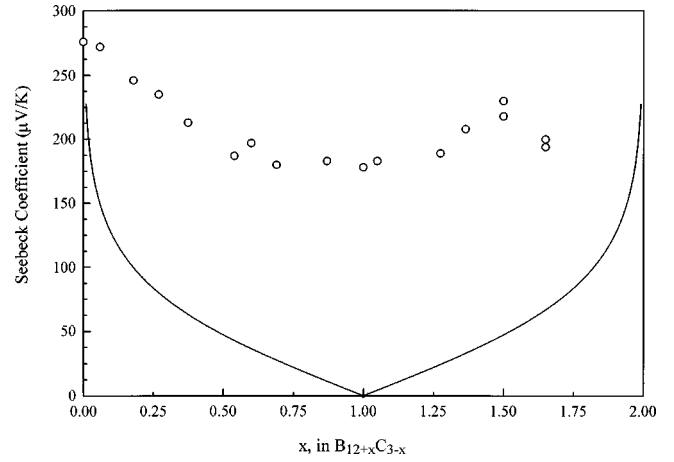


FIG. 6. The Seebeck coefficients of boron carbides at 773 K are plotted against  $x$ . The solid line is a plot of the high-temperature limit of the entropy-of-mixing contribution to the Seebeck coefficient, Eq. (2).

To determine how  $\alpha_{\text{mix}}$  varies with  $x$  requires knowing how  $c$  depends on  $x$ . We adopt the idealized model presented in the Introduction:  $c = x/2$  for  $0.06 < x < 1$  and  $c = (2-x)/2$  for  $1 < x < 1.7$ . As noted in Sec. III B, these relations between  $c$  and  $x$  are consistent with the magnitudes of our conductivity preexponential factors. A plot of  $\alpha_{\text{mix}}$  against  $x$  is presented in Fig. 6, where it can be compared with the high-temperature Seebeck coefficients that have been measured for our boron carbides. It is evident that our calculation of  $\alpha_{\text{mix}}$  approximates only the *composition dependence* of the Seebeck coefficients of our boron carbides (within the uncertainties in the measured values of the Seebeck coefficient and  $x$ ). In particular, the smallest Seebeck coefficient occurs at the composition for which the carrier concentration is largest,  $x = 1$ . A large, carrier-density-insensitive contribution must be added to  $\alpha_{\text{mix}}$  to reproduce the *magnitudes* of the boron carbide high-temperature Seebeck coefficients.

Previous work suggests that this large contribution results from carrier-induced softening of the vibrations of surrounding atoms.<sup>32,33</sup> In particular, the contribution from carrier-induced softening is the sum of two terms. One term rises with increasing temperature to a peak and then falls toward zero. The second term rises with increasing temperature to a constant  $C$ . As shown in the center panel of Fig. 5, for  $x = 1$  where  $\alpha_{\text{mix}} = 0$ , the observed Seebeck coefficient resembles the sum of these two contributions.<sup>21</sup> Furthermore, the remaining representative data of Fig. 5 illustrate that the Seebeck coefficients of *all* boron carbides have similarly distinctive temperature dependences.

The large temperature-independent contribution to the high-temperature Seebeck coefficient from carrier-induced softening indicates a large value of the constant  $C$ . This constant is proportional to the average of the product of the number of softened modes and their fractional softening.<sup>32,33</sup>

$$C = \frac{k_B}{q} \left\langle N_{\text{vib}} \left( \frac{-\Delta \nu}{\nu} \right) \right\rangle. \quad (3)$$

Since  $k_B/q = k_B/(2|e|) = 43 \mu\text{V/K}$  for bipolarons, the bracketed factor must be about 4 to fully account for the magnitudes of the boron carbide high-temperature Seebeck coefficients.

Carrier-induced softening of atomic vibrations can be driven by several mechanisms. As a result of vibrational anharmonicity, carrier-induced atomic displacements associated with polaron formation can soften the vibrational modes to which a carrier is coupled.<sup>34</sup> Carrier-induced vibrational softening is also a general consequence of carriers adjusting to changes in the positions of surrounding atoms.<sup>35</sup> This electronic relaxation effect can be greatly enhanced when charge carriers occupying  $g$ -fold degenerate orbitals pair to form singlet bipolarons.<sup>10</sup> In this case,  $N_{\text{vib}} \approx 1 + g(g-1)/2$ . Since the orbitals of the boron carbide icosahedra from which holes pair are fourfold degenerate,  $g=4$ ,<sup>9</sup>  $N_{\text{vib}}$  can be especially large,  $N_{\text{vib}} \approx 7$ . Thus the large softening contribution to the boron carbide Seebeck coefficients appears to arise from the high degeneracy of the orbitals involved in bipolaron formation. A bipolaron associated with degenerate orbitals for which effects of carrier-induced softening are prominent is termed a *softening bipolaron*.<sup>10</sup>

Prior Seebeck measurements do not manifest the systematic dependence on carbon concentration we report in Fig. 6.<sup>3,11–13,15–17,19</sup> We control the boron carbide carbon concentration well enough to produce a regular (rational) dependence of the Seebeck coefficient on carbon concentration.

The temperature dependences we show in Fig. 5 often differ from those reported in prior works.<sup>3,11,15,17,19</sup> We attribute these differences to carbon inclusions. These inclusions result from (1) unreacted carbon, (2) oxidation of boron carbides' boron, and (3) high-temperature reaction of boron carbides' boron with most metal contacts. In addition, carbon inclusions tend to form when  $x$  is near to or smaller than the carbon-rich limit of the single-phase region:  $x \lesssim 0.06$ . With carbon inclusions the Seebeck coefficients (a) are relatively small (10–120  $\mu\text{V/K}$ ) at 300 K and (b) increase monotonically with increasing temperature. In particular, because of their high metal-like conductivity, carbon inclusions tend to short conduction through boron carbides. Such shorting increases the net conductivity and decreases the net Seebeck coefficient. These shorting effects become increasingly marked as the temperature is reduced causing the conductivities of carbon inclusions and boron carbide to be increasingly disparate.<sup>18,19</sup>

#### IV. CONCLUSIONS

We have studied the conductivities and Seebeck coefficients of boron carbides  $\text{B}_{12+x}\text{C}_{3-x}$  over their full single-phase regime  $0.06 \leq x \leq 1.7$ . Sample preparation and characterization are good enough to yield the dependences of these transport coefficients on  $x$ . Measurements were performed over wide temperature ranges: 8–1750 K for the conductivity and 8–900 K for the Seebeck coefficients. The distinctive composition and temperature dependences of the transport coefficients permit identification of the electronic transport mechanisms of boron carbides.

The conductivities and Seebeck coefficients of boron car-

bides manifest the distinguishing characteristics of *softening bipolarons*, singlet pairs stabilized by their reductions of atoms' vibrational frequencies. Most conspicuously, the unusual temperature dependence of the large  $x$ -independent contribution to the Seebeck coefficient is consistent with the carriers being softening bipolarons.

The composition dependences of the preexponential factors of the high-temperature ( $>400$  K) Arrhenius conductivities and the Seebeck coefficients agree with a simple chemical model for the carrier density. The model describes how the carrier density depends on the boron carbide carbon concentration. Charge carriers are paired holes that hop between the boron carbide  $\text{B}_{11}\text{C}$  icosahedra. Holes are produced when three-atom intericosahedral chains [(CBC)<sup>+</sup>, CBB, or (BBB)<sup>+</sup>] fail to donate the electrons that are required to fill icosahedral electronic states.

The chemical stability of boron carbides permits conductivity measurements over an exceptionally wide temperature range, 8–1750 K. At low temperatures percolative effects associated with hopping among energetically inequivalent icosahedra are most prominent. This percolation regime is characterized by the temperature dependence of the conductivity changing strongly with the carbon content. This dependence weakens with rising temperature. By 400 K the conductivity displays an Arrhenius behavior with an  $x$ -independent activation energy. This behavior persists in all boron carbides to at least 700 K.

Two features manifest themselves at very high temperatures. Above 700 K, the rise of the conductivities of boron carbides with especially high carrier densities begins to saturate. This feature is consistent with the carrier hops impeding one another when their density and hopping rates are both large enough. In these circumstances, hopping carriers produce changes in the internal electric field that are sufficiently intense and frequent to significantly disrupt the transitory energy coincidences that are required for other carriers to jump. Finally, above 1400 K the conductivities of all boron carbides rise sharply ( $\propto T^4$ ) with increasing temperature. We attribute this effect to photoconduction induced by the materials' own blackbody radiation.

#### ACKNOWLEDGMENTS

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#### APPENDIX

In this appendix we describe a mechanism which increasingly suppresses polarons' hopping as their density and the temperature are raised. We consider high enough temperatures for atoms' vibratory motion to be treated as classical:  $k_B T > \hbar \omega$ , the characteristic phonon energy. In this regime the atom positions may be expressed as explicit functions of time. The energies of electronic states, themselves dependent on the positions of surrounding atoms, are also time depen-

dent. A hop can occur when atoms, amidst their vibrations, pass through a configuration for which the electronic energy of a state occupied by a carrier becomes coincident with that of an unoccupied state.<sup>27</sup>

A coincidence event presents a carrier with a time window  $\Delta t_c$  during which it can move from one site to another. The duration of this window is governed by the uncertainty principle  $\Delta E_c \Delta t_c \approx \hbar$ , where  $\Delta E_c$  is the shift of the relative electronic energies of the initial and final states that occurs during  $\Delta t_c$ .<sup>36</sup> The characteristic values of the duration of the coincidence and the energy difference are<sup>27</sup>

$$\Delta t_c \approx \frac{1}{\omega} \sqrt{\frac{\hbar \omega}{\sqrt{E_b k_B T}}} \quad (\text{A1})$$

and

$$\Delta E_c \approx \sqrt{\hbar \omega \sqrt{E_b k_B T}}, \quad (\text{A2})$$

where  $E_b$  is the small-polaron binding energy.

Time-dependent perturbations that produce large changes of the electronic energy difference,  $\Delta E > \Delta E_c$ , during a coincidence event,  $\Delta t < \Delta t_c$ , destroy its coherence and suppress the associated jump. In particular, hops of other carriers affect the difference between the energies at initial and final sites. The hop of a carrier at a distance of  $r$  from the carrier of interest alters the energy difference between initial and final sites by

$$\Delta E \approx \frac{q^2 a}{\epsilon_0 r^2}, \quad (\text{A3})$$

where  $q$  is the charge of the hopping carrier,  $\epsilon_0$  is the static dielectric constant, and  $a$  is the typical jump distance (mean

separation between sites). Hops that produce large enough energy differences to suppress a jump must be sufficiently close to the sites involved in the hop:

$$r < \sqrt{\frac{(q^2 a / \epsilon_0)}{\Delta E_c}}. \quad (\text{A4})$$

The number of such hops is

$$N \approx f \left[ \frac{(q^2 / \epsilon_0 a)}{\Delta E_c} \right]^{3/2}, \quad (\text{A5})$$

where  $f$  is the fraction of sites occupied by a carrier.

The probability that the hop of a carrier will be suppressed by jumps of nearby carriers is

$$P_s \approx N \left( \frac{\Delta t_c}{\tau} \right), \quad (\text{A6})$$

where  $\tau$  is the mean waiting time between hops of a carrier. When, as in boron carbides, the electronic transfer energy is sufficiently large, electronic carriers adiabatically adjust to atomic motion:<sup>27</sup>

$$\tau \approx \frac{2\pi}{\omega} e^{E_b/2k_B T}. \quad (\text{A7})$$

Combining Eqs. (A1) and (A5)–(A7), we find that suppression of adiabatic hopping occurs when

$$P_s \approx f \left[ \frac{(q^2 / \epsilon_0 a)}{(\hbar \omega)^{1/6} (E_b k_B T)^{5/12}} \right]^{3/2} e^{-E_b/2k_B T} \approx 1. \quad (\text{A8})$$

Thus adiabatic hopping will be suppressed when the temperature and carrier density are sufficiently high. For boron carbides ( $q=2|e|$ ,  $a=0.5$  nm,  $\epsilon_0=8$ ,  $\hbar\omega=0.1$  eV, and  $E_b=0.3$  eV),  $P_s \approx 1$  when  $T > 700$  K and  $f \approx 1/2$ .

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