PHYSICAL REVIEW B VOLUME 29, NUMBER 8 15 APRIL 1984

Conduction mechanism in boron carbide

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(Received 12 September 1983)

Electrical conductivity, Seebeck-coefficient, and Hall-effect measurements have been made on single-phase boron carbides, $B_{1-x}C_x$, in the compositional range $0.1 \leq x \leq 0.2$ between room temperature and 1273 K. The results indicate that the predominant conduction mechanism is small-polaron hopping between carbon atoms at geometrically inequivalent sites.

INTRODUCTION

Boron carbides have been utilized extensively in reactor technology for the absorption of thermal neutrons. More recently the high-temperature stability of these and similar semiconducting materials (e.g., the boron-rich borides) has sparked interest in their use as high-temperature semiconductors. Here we report the measurement and analysis of the steady-state electrical transport properties of a variety of boron carbides, $B_{1-x}C_x$, in the composition range $0.1 \leq x \leq 0.2$ from 300 to 1273 K.

Over the compositional range $0.088 \leq x \leq 0.200$ boron carbides are usually viewed as crystallizing in a rhombohedral structure $D_{3d}^5-R\bar{3}m$ with deformed icosahedra shared at the corners of the unit cell and a three-atom chain, containing one or more carbon atoms, along the cell diagonal connecting the icosahedra (Fig. 1).[1,2] The unit cell shrinks slightly with increasing carbon content.[3] The melting points of compositions lying within the single-phase region are in the neighborhood of 2600 K.

Our analysis of the dc conductivities, Hall mobilities, and Seebeck coefficients views the charge carriers as forming small polarons and moving through the material by phonon-assisted hopping. Furthermore, the composition dependences of these transport coefficients lead us to suggest that the charge carriers, namely the holes, hop between inequivalently located carbon atoms. Such hops might be between carbon atoms located in the three-membered chains and those in the icosahedra of the hypothesized boron-carbide structure. Electrical transport data on other boron-rich borides suggest similar behavior although there the hopping sites are, of course, different.

EXPERIMENTAL PROCEDURE

In this study boron-carbide specimens, $B_{1-x}C_x$, in the single-phase regime, $0.088 \leq x \leq 0.200$, were prepared by vacuum (10^{-6} to 10^{-5} Torr) hot pressing (2400 K) at 6000 psi for 15 min using high-purity ($B \sim 30$ ppm, $C \sim 10$ ppm maximum impurities) powders (-325 mesh) in boron-nitride-lined graphite dies. Similar samples, examined by x-ray diffraction, were found to be single phase with lattice constants varying with composition essentially in the manner reported by Bouchacourt and Thevenot.[3] In the hot-pressing procedure graphite end caps were bonded to the boron-carbide cylinders (approximately 1 cm diameter) which facilitated attachment of thermocouple and electrical leads for Seebeck and electrical conductivity measurements. A four-probe method was employed to measure the electrical conductivity. For accurate Seebeck-coefficient measurements it was found to be essential to determine Seebeck voltage as a function of temperature gradient in order to avoid such problems as spurious voltages and thermocouple errors. Hall-effect measurements were made up to 1273 K on 1-mm-thick slices cut perpendicular to the cylinder axis using the dc van der Pauw technique.[4] The use of symmetrical samples allowed the measurement to be permuted with respect to the electrodes and thus improved signal averaging. However, at 10 000 G the Hall-voltage signal-to-noise ratio was still very low, yielding the error bars of Fig. 4.

EXPERIMENTAL RESULTS

The electrical conductivities and Seebeck coefficients of various boron carbides $B_{1-x}C_x$ with compositions ($0.1 \leq x \leq 0.2$) lying within the single-phase regime are plotted against reciprocal temperature and temperature, respectively, in Figs. 2 and 3. All Seebeck coefficients are *p* type. A noteworthy aspect of these results is the contrast of the "metalliclike" behavior of the Seebeck coefficients (they increase with increasing temperature) with the semiconducting behavior of the electrical conductivities (they increase with increasing temperature).

All compositions were prepared under similar conditions by using similar starting materials. Samples prepared under different conditions and from materials of different purities have shown a range of values for the electrical conductivity and Seebeck coefficient. However, general features, such as the increase of the conductivity and Seebeck coefficient with increasing temperature, are always observed. Furthermore, the conductivity and Seebeck coefficient of virgin samples are altered somewhat with thermal cycling. In particular, with repeated cycling the Seebeck coefficient tends toward higher values by as much as 10% and the conductivity curves shift toward

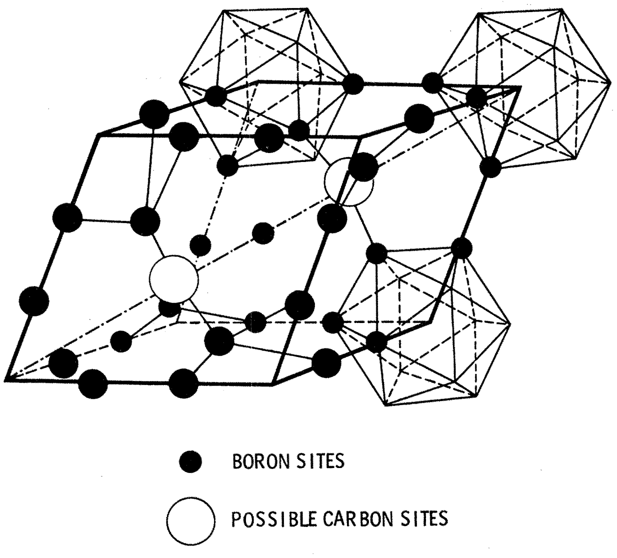

FIG. 1. Hypothesized crystal structure for boron carbide; carbon atoms are distributed among open circles and within icosahedra.

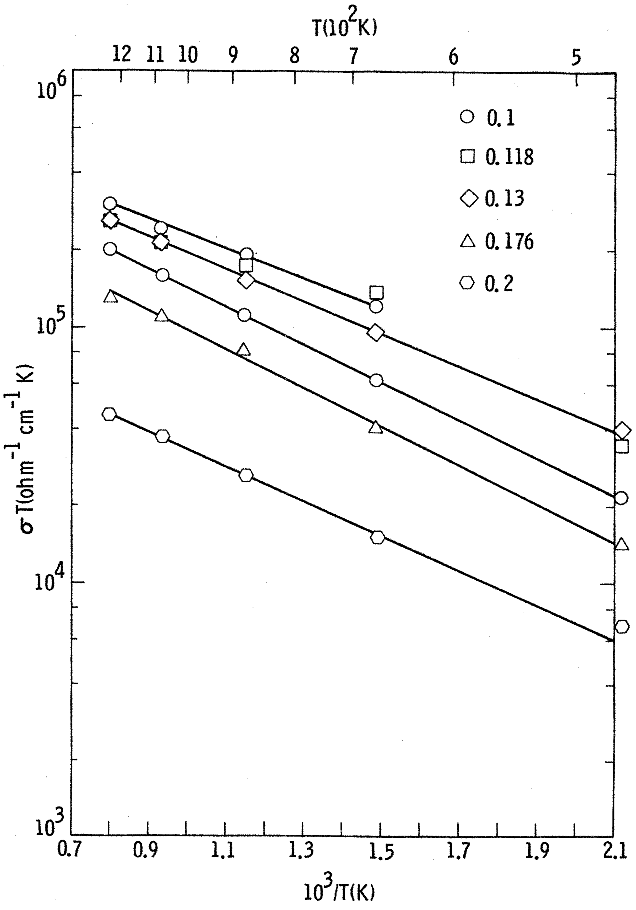

FIG. 2. Plots of $\ln(\sigma T)$ vs reciprocal temperature for $B_{1-x}C_x$ compositions from $x=0.1$ to 0.2, i.e., from B_9C to B_4C.

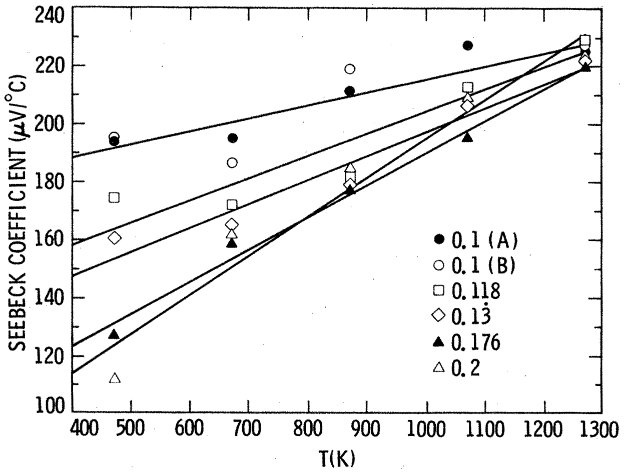

FIG. 3. Seebeck coefficient vs temperature for $B_{1-x}C_x$ compositions from $x=0.1$ to 0.2, i.e., from B_9C to B_4C.

lower values by as much as 30%. The extent of these changes decreases progressively with successive temperature cycling, ultimately yielding results which are strictly reproducible.

Hall-constant (R_H), $\ln\sigma T$, and Hall-mobility (μ_H) data for $B_{0.8}C_{0.2}$ are shown in Fig. 4. This Hall mobility is typical of all compositions $B_{1-x}C_x$, $0.1 \leq x \leq 0.2$. Thus the Hall mobilities (1) are low, (2) increase with temperature to a maximum and then decrease as the temperature

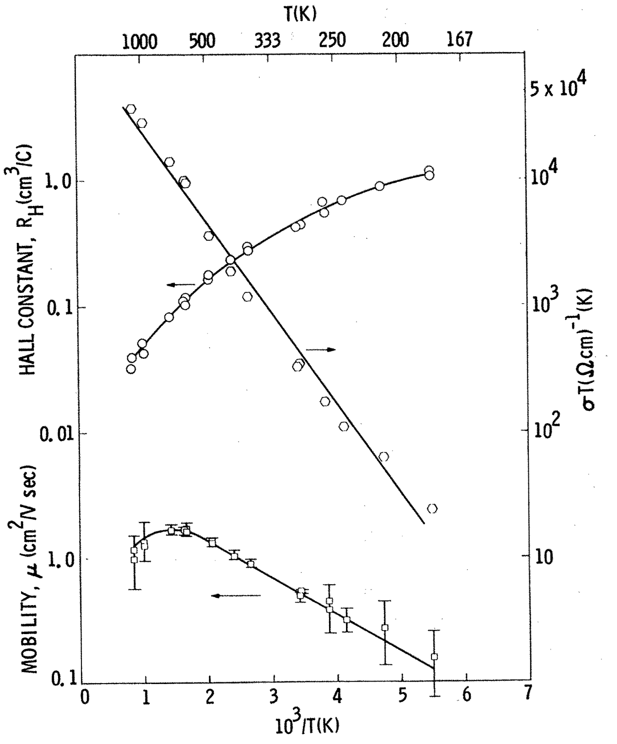

FIG. 4. Logarithm of the Hall constant R_H, the electrical conductivity temperature product σT, and the hole mobility μ vs reciprocal temperature for $B_{1-x}C_x$ with $x=0.2$, i.e., B_4C.

is raised further, and (3) have a negligible dependence on carbon content. Finally, although all compositions produced p-type Seebeck coefficients, at low carbon concentrations, i.e., for $B_{0.9}C_{0.1}$ and $B_{0.96}C_{0.04}$ (a two-phase material) "anomalously" signed (n-type) Hall mobilities were observed.

DISCUSSION

The previously described observations are all consistent with the hopping motion of a large ($\sim 10^{20}$ cm^{-3}) temperature-independent density of small-polaron holes. Then the temperature dependence of the conductivity is that of the mobility. At temperatures above some fraction ($\sim \frac{1}{3}$) of the characteristic phonon temperature small-polaron hopping generates a thermally activated mobility with a temperature-dependent prefactor.[5] In particular, when the transfer energy characterizing the hopping is sufficiently large (as the Hall-mobility and Seebeck-coefficient results suggest is the case) the charge adiabatically follows the atomic motion resulting in a mobility that varies with temperature as[5]

$$\mu \propto T^{-1}\exp(-E_A/kT) , \tag{1}$$

here E_A is the mobility activation energy. The data of Fig. 2 is in good agreement with this temperature dependence. It is noteworthy that, because of the modest value of the activation energy (0.14 ± 0.01 eV) and the high temperatures involved, the temperature dependence of the conductivity prefactor significantly affects the net temperature dependence of the conductivity. As a result, we see that the temperature dependences of the conductivity prefactor characterizing conventional broad-band (high-mobility) semiconductors (varying from temperature independence to a $T^{3/2}$ dependence) are not consistent with our data.

The magnitude of the electrical conductivity varies somewhat with preparative conditions and material purity. Nonetheless, it is generally found that increases of the carbon concentration decrease the magnitude of the conductivity prefactor. However, the temperature dependence of the conductivity is independent of carbon concentration.

Thus the salient features of the conductivity data on $B_{1-x}C_x$ are as follows: (1) its temperature dependence is essentially independent of carbon concentration, (2) the magnitude of the conductivity prefactor falls with increasing carbon content, and (3) the temperature dependence of the conductivity agrees well with that of adiabatic small-polaron hopping but not that of conventional broad-band semiconductor transport. We interpret these results as indicating that the current is carried by small-polaronic carriers whose density falls with increasing carbon content.

The measured Seebeck coefficients shown in Fig. 3 can be empirically described by the equation

$$\alpha = A + BT , \tag{2}$$

where A decreases and B increases with carbon concentration. We emphasize that the Seebeck coefficients are increasing functions of temperature yet are much larger than those characteristic of degenerate conduction. We interpret this behavior as manifesting a distinctive feature of hopping conduction. Namely, for hopping conduction, the Seebeck coefficient is the sum of two terms.[6] The first, the standard term, is proportional to the average change of the entropy, ΔS, of the material when a charge carrier is injected into it. The second is proportional to the average vibrational energy transported with a carrier as it hops, E_T. Explicitly,

$$\alpha = (T\Delta S + E_T)/qT , \tag{3}$$

where q is the carrier's charge. In terms of the average energy associated with the insertion of a carrier E and the chemical potential η, this expression is simply

$$\alpha = |E - \eta|/qT + E_T/qT . \tag{4}$$

In conventional transport (ignoring low-temperature phonon drag) and, with a few exceptions,[6,7] in discussions of hopping transport only the first term is considered. However, for the hopping of charge carriers between states which differ both in their energy and in their coupling to the atomic vibrations, the second term generally contributes. In particular, the vibrational energy transferred in a hop from an "initial" state i to a "final" state f is given by[6]

$$E_T^{i,f} = \tfrac{1}{2}(E_f - E_i)(\Gamma_i - \Gamma_f)/(\Gamma_i + \Gamma_f) , \tag{5}$$

where E_i and E_f refer to the energies of the system when sites i and f are occupied and Γ_i and Γ_f denote the electron-lattice coupling strengths associated with the occupation of the two respective sites. This term only vanishes for hopping between sites that are equivalent in either energy ($E_i = E_f$) or in electron-lattice coupling strength ($\Gamma_i = \Gamma_f$). Furthermore, the electron-lattice coupling strength of a localized state generally increases with the severity of its localization, which, in turn, depends upon the state's energy. Thus, for sufficiently small energy differences one has that $(\Gamma_i - \Gamma_f) \propto (E_f - E_i)$. Then the vibrational energy transferred in a hop varies as the square of the energy difference between the sites

$$E_T^{i,f} = C(E_f - E_i)^2 . \tag{6}$$

In particular, for small-polaron hopping the constant is given[8] by $C = zJ^2/16E_b^3$, where z is the number of nearest neighbors, J is the intersite transfer energy, and E_b is the small-polaron binding energy characterizing an average site in the material. The dependence of $E_T^{i,f}$ on the *square* of the energy difference illustrates that vibrational energy is transported with the carrier regardless of whether the lower-energy, relatively strong-coupled, state is the initial state (at which energy is absorbed) or the final state (at which vibrational energy is emitted). With a broad distribution of energies ($> kT$), averaging of this term yields a contribution to the Seebeck coefficient which increases linearly with temperature: $(k/q)(8CkT)$. In contrast, the entropy contribution for a weakly degenerate semiconductor (as we envision the boron carbides) varies relatively weakly with temperature. For example, with the chemical potential just inside a rectangular energy band (by less than $\sim kT$) the entropy contribution to the Seebeck coefficient is $(k/q)|2 - \eta/kT|$, where η is measured from the band edge and $\eta \lesssim kT$. Thus for weakly degenerate small-polaron hopping among a broad distribution of inequivalent sites the Seebeck coefficient is reasonably close to the observed form, $\alpha = A + BT$.

The origin of the inequivalence of hopping sites and the resulting width of the small-polaron valence band may be understood in terms of hopping between sites associated with carbon atoms. In particular, small-polaron bandwidths arising from transfer between equivalent sites are known to be negligibly small (very much smaller than kT at the temperatures of interest).[5,9] The relatively large width of the band of small-polaron sites involved in hole hopping in the boron carbides must therefore be attributed to the energetic inequivalence of the sites between which the holes move. Such a situation arises naturally for hops between carbon atoms in the boron-carbide crystal structure since carbon atoms in the icosahedra and in the intericosahedral chains have very different topological and compositional environments. This contrasts with the common situation in glasses where the presence of a single type of short-range order results in only modest disorder broadening of the small-polaron band.

The dependences of the two contributions to the Seebeck coefficient on carbon concentration are also consistent with hopping between carbon locations. The decrease of the entropy contribution A with increasing carbon concentration is attributed to the chemical potential moving deeper into the valence band. This occurs with the addition of carbon as the small-polaron-hole band broadens due to an increasing fraction of energetically unfavorable carbon sites being filled. Thus the average energy disparity between carbon sites increases with the addition of carbon. For example, with increasing carbon concentration the fraction of carbon atoms occupying energetically unfavorable sites (e.g., icosahedral sites) increases due to the prior filling of the energetically favorable sites (e.g., on the intericosahedral chains). As an explicit example of the effect of the band broadening on the chemical potential consider a "square" valence band. Then the difference between the chemical potential and the upper edge of the valence band, $\eta = n_h W_v / N_C$, increases as the increase of the inequivalance-produced bandwidth W_v overcomes a decrease of the ratio of the hole concentration n_h to the carbon-atom concentration N_C. Thus, the entropy contribution to the Seebeck coefficient, $A = (k/q) | 2 - \eta/kT)$, decreases with increasing carbon concentration because η increases.

The hopping contribution to the net Seebeck coefficient, the contribution BT, increases with carbon concentration. This behavior is consistent with our treatment of holes hopping between carbon sites. Namely, with increasing carbon concentration the mean separation between carbon atoms decreases. As a result the characteristic transfer energy for the intercarbon hopping J increases. This produces the observed increase of $B[\equiv (k/q)8Ck \equiv (k/q)(zJ^2/2E_b^3)]$ with carbon content. Thus, our measurements of the dc conductivity and the Seebeck coefficient on a variety of boron carbides suggest that charge is transported by the hopping of small-polaron holes between carbon sites.

Measurements of the Hall mobility support this view. Namely, the Hall mobility is generally low ($\mu_{\text{Hall}} \lesssim 1$ cm^2/V sec) with a weakly, thermally activated temperature dependence (activation energy 0.05 eV) that is independent of carbon concentration.

Although theory does not give a precise prediction for the magnitude of the Hall mobility,[10] the maximum value of the Hall mobility is of the order of $qd^2/\hbar$, where d is the characteristic hopping distance. For example, a hopping distance of 8 Å gives a value for $qd^2/\hbar$ of 1.76 cm^2/V sec. Thus the observed maximum Hall-mobility value of 1.7 cm^2/V sec is compatible with small-polaron hopping between carbon sites.

In situations in which the charge moves via hopping motion the Hall mobility departs significantly from the drift mobility (the mobility that enters into the dc conductivity).[5] In particular, model calculations of the Hall mobility due to small-polaron hopping yield activation energies for hole motion which are roughly $\frac{1}{3}$ that of the drift mobility.[11-19] Such a relationship is, indeed, frequently observed.[15] In our boron carbides, the Hall-mobility activation energy (0.05 eV) is also essentially $\frac{1}{3}$ that which we ascribed to the drift mobility, i.e., that of the dc conductivity (0.14 eV). With the Hall-mobility activation energy of this magnitude and a Hall-mobility prefactor which varies inversely with temperature (characteristic of most hopping models) the Hall mobility will reach a peak at the temperature corresponding to the activation energy (i.e., at 0.05 eV/k = 600 K). As indicated in Fig. 4, we also observe this feature.

The near independence of the temperature dependence of the Hall mobility on carbon concentration is also consistent with our picture of small-polaron hopping between carbon sites. This is because the temperature dependence of the small-polaron Hall and drift mobilities are both dependent on only the average of local electronic energies associated with the hopping sites. These energies should vary little with carbon concentration x over the concentration range $0.1 \leq x \leq 0.2$. Thus, the independence of the temperature dependences of the Hall and drift mobilities is a natural outgrowth of our model.

Finally, we recall that the *sign* of the Hall mobility for the sample of lowest carbon concentration of the single-phase region, $B_{0.9}C_{0.1}$, is anomalous. That is, here the Hall mobility is measured to be n type while the Seebeck coefficient remains p type. Despite this sign anomaly the temperature dependences of the transport coefficients are similar to those of samples of higher carbon concentration. This is suggestive of small-polaron hopping. Namely, the sign of the Hall effect for hopping motion depends upon the relative orientations of the sites and the local wave functions between which hopping occurs.[15-17] Indeed, Hall-effect sign anomalies are frequently observed in low-mobility transport.[15-17] However, the temperature dependence of the Hall mobility is independent of these considerations. Thus, small-polaron hopping can, in a general sense, account for both the carbon-concentration independence of the temperature dependence of the Hall mobility and the occurrence of a sign anomaly of the Hall effect for low carbon content. The occurrence of Hall-effect sign anomalies is indicative of the carrier's extreme localization (i.e., small-polaron formation): for Hall-effect sign anomalies to occur the spatial extent of the carrier must be less than the intersite separation.[5,17] Nonetheless, we, as yet, do not have sufficient knowledge of the hopping sites or the local wave functions to present a detailed explanation of the Hall-effect sign anomalies. We simply note that the Hall-effect sign anomalies are predicted and observed for small-polaron hopping and that their occurrence depends on the nature and geometrical arrangement of sites between which the carriers hop. Thus, since changes of the carbon concentration alter the number and distribution (and perhaps even the nature) of carbon sites, changes of the Hall-effect *sign* may be encountered for small-polaron hopping at some compositions.

Thus we see that our electronic transport data on boron carbides can be explained as arising from the hopping of small-polaron holes between carbon atoms distributed among inequivalent sites in $B_{1-x}C_x$. It should be emphasized that the insensitivity of the Hall and drift mobilities to carbon-induced disorder arises because these quantities depend on the *sum* of the electron-lattice coupling strengths at the sites involved in a hop.[10,17] The E_T term of the Seebeck coefficient, however, is very sensitive to carbon-induced disorder since E_T is proportional to the product of the *differences* between the energies and electron-lattice coupling strengths of initial and final sites. While we view the agreement between theory and experiment as very good, it should be cautioned that the model for hopping between inequivalent carbon sites is nonetheless oversimplified. As a result, one should regard the derived values of J and E_b as being of only qualitative significance.

Finally, we note that there have been other attempts to investigate the electronic transport properties of boron carbides.[20-22] In particular, Werheit and deGroot[22] have studied boron carbides produced from much less pure (commercial grade) materials. In some instances their measurements yield results similar to ours. In other cases they differ. Specifically, unlike our studies, Werheit and deGroot report no consistent dependence of the magnitude or temperature dependence of the electrical conductivities of the boron carbides on carbon concentration over the temperature range of their measurements (76 to 700 K). Furthermore, their electrical conductivities (e.g., at room temperature) greatly exceed ours. These facts may indicate that impurity conduction plays a significant role in their measurements. However, in their sample of lowest (room-temperature) conductivity ($x=0.216$) the reported activation energy of the conductivity ($\simeq 0.16$ eV) is comparable to ours (0.14 eV). In this case the Seebeck coefficient is also of comparable magnitude and, as ours, increases almost linearly with temperature. Here, as well, their Hall mobility at room temperature is, as ours, low (<1 cm^2/V sec). Thus, while we suspect that most of their measurements are affected by impurities, their results on their lowest-conductivity material are consistent with our findings.

Werheit and deGroot[22] report non-Arrhenius conductivities in their boron carbides below room temperature. The actual temperature dependences vary irregularly with carbon concentration. We note that the onset of a non-Arrhenius temperature dependence as the temperature is lowered is a general feature of small-polaron hopping.[5,18] It arises as multiphonon jump processes are frozen out. Thus, the observation of a non-Arrhenius ($T^{1/4}$-like) temperature dependence at low temperatures would arise even in the absence of disorder.[18] Disorder effects (e.g., variable-range hopping) are in addition to this freezing out of multiphonon processes. For example, in some amorphous semiconductors the independence of the temperature dependence of the nonactivated conductivity on the density of states involved in hopping suggests that the multiphonon freezeout is the dominant effect.[23]

CONCLUSIONS

The dc conductivities, Hall mobilities, and Seebeck coefficients of polycrystalline boron carbides $B_{1-x}C_x$ have been measured as functions of temperature for samples within the composition range $0.1 \leq x \leq 0.2$. The results are consistent with hopping of small-polaron holes among carbon atoms in inequivalent sites. In particular, the dc conductivity is activated with an activation energy (0.14 eV) typical of small-polaron hopping. Furthermore, the Hall mobilities are each comparable to one another. Their activation energy is about $\frac{1}{3}$ that of the conductivity. As a result the Hall mobility falls at high temperatures where the temperature dependence of the mobility prefactor dominates. At very low carbon content ($x=0.1$) the Hall effect is anomalously signed (n type). Thus we envision an increase of the carbon concentration as decreasing the carrier (hole) concentration but not affecting the basic transport mechanism, viz., thermally activated small-polaron hopping between the vicinities of carbon atoms which are distributed among a variety of sites (e.g., both in chains and in icosahedra). Nonetheless, we do not presently have a detailed microscopic picture of the nature of the hopping sites nor of how the addition of carbon atoms alters the carrier density.

ACKNOWLEDGMENTS

The authors are indebted to N. B. Elsner, G. H. Reynolds, and P. H. Miller for sample preparation and electrical measurements and J. Parker and A. Zoltan for Hall-effect measurements. This research of C.W. was carried out by the Jet Propulsion Laboratory, California Institute of Technology, under contract with the National Aeronautics and Space Administration. The work of D.E. was supported by the U. S. Department of Energy Contract No. DE-AC04-76DP00789.

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