CONDUCTIVITIES AND SEEBECK COEFFICIENTS OF BORON CARBIDES:

"SOFTENING-BIPOLARON" HOPPING

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Abstract

The electrical conductivities and Seebeck coefficients of boron carbides, $B_{12+x}C_{3-x}$ with $0.06 \lesssim x \lesssim 1.7$, 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, ≈ 0.16 eV, is independent of carbon concentration. The pre-exponential factors of the conductivity exhibit a non-monotonic dependence on x, peaking near $x = 1$. These results are consistent with a previously proposed model based on holes forming singlet bipolarons on boron carbides' $B_{11}C$ icosahedra. Singlet bipolarons are most directly indicated by the absence of significant paramagnetism despite having high concentrations of localized carriers. At low temperature, boron carbides' 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 temperature dependence at low temperature. Above 300 K, percolation does not have a notable effect on the conductivity. Boron carbides' Seebeck coefficients are very large with only a weak dependence on x. The magnitudes and temperature dependencies 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

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electronic energy levels by their softening of symmetry-breaking vibrations: "softening bipolarons". Boron carbides' transport properties are generally consistent with those expected of softening bipolarons. Finally, two novel high-temperature effects are observed in boron carbides' 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 boron carbides' conductivities ($\sigma \propto T^4$) suggests the radiation induced excitation of mobile charge carriers.

1. Introduction

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

In realizable boron carbides, $x \gtrsim 0.06$, the replacement of C atoms with B atoms removes bonding electrons to produce a significant density, $\approx 10^{21}/cm^3$, of hole-like charge carriers. Measurements of low, thermally activated electrical conductivities and Hall mobilities in boron carbides indicate localized carriers that move by polaronic hopping.[3] However, the large paramagnetic susceptibility expected of a high density of nearly localized spins is not found.[4] In addition, recent measurements of boron carbides' Seebeck coefficients[5] do not manifest the magnetic-field dependence associated with orienting localized spins. Taken together, these experiments indicate that charge carriers in boron carbides pair to 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 twelve neighbors, the $(B_{11}C)^-$ icosahedron has 26 (= 3 × 11 + 4 + 1 −12) second-shell electrons available for its internal bonding. These 26 electrons fill an icosahedron's 13 internal

bonding orbitals.[1] A $(B_{11}C)^+$ icosahedron, lacking two electrons from its filled-shell $(B_{11}C)^-$ state, signifies a bipolaronic hole.

Free energy considerations[6] and structural and vibrational measurements[7] all suggest that boron atoms primarily replace carbon atoms within chains, CBC → CBB, as x increases from zero to unity. Since CBB chains are isoelectronic to $[CBC]^+$ chains, they do not donate electrons to icosahedra. This substitution then leaves some of the highest-energy bonding orbitals of 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 being CBB, the fraction of all $B_{11}C$ sites occupied by a bipolaron $n_{(B_{11}C)^+}/n_{B_{11}C}$ equals ½.

Reducing carbon concentration beyond $x = 1$ requires boron atoms replacing carbon atoms either within $(B_{11}C)$ icosahedra, → (B_{12}), or within CBB chains, → BBB. Forming (B_{12}) icosahedra would decrease the bipolaron concentration, $n_{(B_{11}C)^+}$, since the density of sites $n_{B_{11}C}$, decreases while disproportionation keeps $n_{(B_{11}C)^+}/n_{B_{11}C}$ constant at ½. Forming BBB chains may also decrease the concentration of bipolarons. In particular, if these chains' two end-chain boron atoms each bond to atoms of the three adjacent icosahedra and the chain's central atoms exist as interstitial B^+ ions, their electrons donated to icosahedra would decrease the density of $(B_{11}C)^+$ icosahedra. Progressively replacing CBB chains by electron-donating $[BB^+B]$ chains thus decreases $n_{(B_{11}C)^+}$ while $n_{B_{11}C}$ remains constant. In either model the conductivity, proportional to the density of bipolarons, $n_{(B_{11}C)^+}$, would reach a maximum at $x = 1$. The Seebeck coefficient, however, depends on the fraction of occupied electrically active sites, $n_{(B_{11}C)^+}/n_{B_{11}C}$. The Seebeck coefficient for x > 1 would be independent of x in the first model but would rise with x

in the second model. We find that the composition dependence of boron carbides' Seebeck coefficients is consistent with BB^+B chains replacing CBB chains as x increases beyond one.

Boron carbides' singlet bipolarons are attributed to holes in the uppermost filled internal bonding states of icosahedra. The highest lying internal bonding states of an ideal icosahedron are a set of four-fold degenerate levels.[8] Emin[9] shows 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[9] by 1) their modest hopping activation energies, 2) the absence of the usual polaronic absorption, and, most dramatically, 3) by a distinctive contribution to the Seebeck coefficient that is 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. Boron carbides' carrier densities, controlled simply by varying the B to C ratio, are sufficiently large, $\approx 10^{21}/cm^3$, to overwhelm intrinsic defect levels. Carriers hop between well-defined sites, $B_{11}C$ icosahedra, arranged on a slightly distorted cubic lattice. The exceptional stability of boron carbides permits transport measurements over an unusually wide range of temperatures, from below 10K to above 1700K.

Unfortunately, a detailed picture of electrical conduction in boron carbides has been obscured by significant inconsistencies in transport measurements.[3,10-20] Sources of irreproducibility in prior measurements include the presence of free-carbon inclusions within some samples and uncertainties of or inhomogeneities in samples' carbon concentrations. In this paper,

measurements of the conductivity and Seebeck coefficients of well-characterized boron carbide samples having compositions spanning the single-phase region are shown to be consistent with the properties expected of softening-stabilized singlet pairs, softening bipolarons. A brief description of some of these results has been published.[21]

2. 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 1900 C under high vacuum prior to its use in order to remove volatile oxygen and carbon impurities, as described previously.[22] The electrical properties of samples were not sensitive to the boron source.

Samples were prepared by hot-pressing these mixtures for 15 to 30 minutes at 2150 C in graphite dies lined with high-purity BN. Details of the hot-pressing procedure are given elsewhere.[19] The densities of all samples produced by this procedure exceeded 95% of 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 Raman peaks near 1375 and 1580 cm^{-1} in any sample confirms the absence of major inclusions of either crystalline or amorphous carbon.

Rectangular specimens of approximately 2 × 6 × 8 mm were cut from hot-pressed cylinders using electric spark cutting or a diamond-impregnated saw. Four-point electrical

conductivities were measured on these rectangular samples from below 10 K to 1775 K using several apparatus. Sputtered Cr/Au electrical contacts were used for low-temperature measurements while graphite and/or Ta contacts were used at high temperature. Measurements of the high-temperature conductivities of several as-hot-pressed cylinders were nearly identical to those on the slabs cut from them. All high-temperature measurements were made under an atmosphere of flowing gettered Ar to inhibit sample oxidation. Despite this precaution, post-measurement Raman analysis of some samples revealed a thin amorphous carbon layer. The presence of this layer is consistent with the preferential oxidation of a small amount of boron at the surface.

Several apparatus were also used to measure Seebeck coefficients between 10 and 900 K. Samples were clamped between Cu or graphite blocks. The temperatures of the blocks were independently controlled and monitored with resistance thermometers or K- or S-type thermocouples. Induced emf's were recorded while either steady-state or slowly swept temperature differentials up to ±3K were imposed across the sample while holding the mean temperature constant. Over one hundred individual measurements were used to determine the emf vs. ΔT slope at each temperature. These slopes were then corrected by the Seebeck coefficients of the Cu or Pt leads to yield the Seebeck coefficients of the sample. All high-temperature Seebeck measurements were performed under an atmosphere of slowly flowing gettered Ar.

3. Results and Discussion

3.1 Electrical Conductivity

Two figures plot the conductivities of representative boron carbide samples whose compositions span the single-phase region, $0.06 \lesssim x \lesssim 1.7$. Figure 1 depicts the dc conductivities

as functions of the inverse temperature from 8 to 300 K. Figure 2 shows representative conductivities against 1000/T at higher temperatures; 300 to 1775 K. Boron carbides' conductivities peak at an intermediate carbon concentration, near $x = 1$, at every temperature. This non-monotonic dependence of carrier density on carbon concentration is consistent with the model described in the Introduction in which the bipolaron density peaks at $x = 1$. In further accord with the model, at high temperatures where the conductivities are Arrhenius, the conductivity prefactors are just proportional to the bipolaron densities. Details of the high-temperature conductivity, Fig. 2, are discussed below.

Below 300K, Fig. 1, boron carbides' conductivities have a non-Arrhenius temperature dependence. Non-Arrhenius conduction is a consequence of the progressive freezing out of multi-phonon contributions to phonon-assisted jump rates with decreasing temperature.[23] 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.[23,24] This percolative aspect of low-temperature hopping is evident in the strong sensitivity of the temperature dependence of boron carbides' low-temperature conductivities to carbon concentration.

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

As x is decreased 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. Repulsive interactions between a bipolaronic hole, $(B_{11}C)^+$, and positively charged chains introduced near it produce energetic disorder. Energetically favorable icosahedral sites, associated with 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, boron carbides' conductivities garner the additional temperature dependence arising from percolation among energetically inequivalent icosahedral sites. This percolative effect is washed out when the thermal energy, k_BT, exceeds the characteristic disorder energy. The data of Fig. 1 shows the dispersion in the temperature dependence of boron carbides' conductivities being washed out above about 150 K. The characteristic disorder energy is thus of the order of 0.01 eV.

At sufficiently high temperatures, typically above about 1/3 of the relevant phonon temperature, the atomic vibrations involved in phonon-assisted hopping may be treated classically and conduction becomes Arrhenius.[25,26] In this semi-classical, high-temperature limit, the conductivity due to bipolaron hopping may be expressed as:

$$\sigma = \frac{Nc(1-c)q^2a^2v}{k_BT}\exp(\frac{-E_A}{k_BT})P(T) \tag{1}$$

when percolative effects are ignorable. Here N is the concentration of sites between which hops occur, c the fraction of these sites occupied by a bipolaron, $q = 2e$ is the electronic charge of a bipolaronic carrier, a is the length of an average hop, and v is a characteristic vibrational frequency. With hopping of bipolarons $(B_{11}C)^+$ between boron carbides' $B_{11}C$ icosahedra, N = $n_{B_{11}C}$ and $c = n_{(B_{11}C)^+}/n_{B_{11}C}$. The activation energy, E_A, is the minimum energy required to bring the electronic energies of the initial and final sites of a hop into coincidence with one another. The last factor in Eqn. (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.

Boron carbides with the highest carbon concentrations have the lowest carrier densities. As shown in Fig. 2 for $x = 0.06$ and $x = 0.27$, the conductivities of such boron carbides follow a linear dependence of $\log(\sigma T)$ vs. $1/T$ over a wide range of temperatures, 300-1400 K. This behavior is consistent with the adiabatic hopping ($P(T) \approx 1$) of a temperature-independent concentration of bipolarons. Most significantly, the measured values of the pre-exponential factors are close to those predicted by Eq. (1). The density of hopping sites $n_{B_{11}C}$ may be determined from unit cell dimensions,[22] and the model gives bipolaron occupancy fractions of $c \approx 0.03$ and $c \approx 0.13$ for $x = 0.06$ and $x = 0.27$, respectively. Taking 1) the length of an average hop to be $\approx 10\text{Å}$ and 2) the characteristic vibrational frequency to be $\approx 10^{13}/\text{sec}$, the conductivity prefactors for adiabatic hopping range from 2×10^5 to 8×10^5 K-Ω^{-1}-cm^{-1}. The best-fit prefactors from Fig. 2, 1.8×10^5 K-Ω^{-1}-cm^{-1} ($x = 0.03$) and 4.5×10^5 K-Ω^{-1}-cm^{-1} ($x = 0.27$), are in reasonable agreement with these estimates. It is finally noted that the activation energies, about 0.16 eV, while typical of small-polaron hopping, are smaller than what might be expected for conventional bipolaron motion. However, the activation energies for the hopping of softening bipolarons are significantly smaller than those for the hopping of conventional bipolarons.[9]

The activation energies of the conductivities of boron carbides with higher carrier densities, $0.38 \leq x \leq 1.65$ in Fig. 2, also approach 0.16 eV above 400 K. However, the temperature dependencies of the conductivities diminish above 700 K. This decrease of the temperature dependence of the conductivity at high temperatures is most pronounced when the carrier density

is highest, near $x = 1$. These observations also occur in many others of our samples (not shown in Fig. 2), and in others' measurements.[14-16] Thus, boron carbides' hopping conduction is progressively suppressed as both the temperature and the carrier density become quite large.

Emin[27] describes a correlation mechanism by which the rapid hopping of some carriers interferes with the jumps of others. As a result, the hopping conductivity tends to saturate when the temperature and the carrier density are both high. His argument begins by noting that a phonon-assisted hop only occurs when, amidst atoms' motions, the electronic energies of initial and final sites achieve a "coincidence" with one another. The coincidence persists for a time interval Δt_c during which the difference in the electronic energies of the two sites is less than ΔE_c, where $\Delta E_c \Delta t_c \approx h$. The coincidence will be destroyed, and the hop thereby suppressed, if jumps of other carriers are close enough in both space and time to significantly perturb the coincidence, $\Delta E > \Delta E_c$, during its duration Δt_c. The condition that sufficient carriers hop fast enough to produce a significant suppression is:[27]

$$c \left[\frac{\left(q^2 / \varepsilon_0 a \right)}{(h\nu)^{1/6} (E_A k_B T)^{5/12}} \right]^{3/2} \exp\left(\frac{-E_A}{k_B T} \right) \approx 1, \tag{2}$$

where ε_0 is the static dielectric constant. Eqn. (2) is only satisfied by boron carbides with relatively high carrier densities, $c \approx 0.5$, when the temperature is sufficiently high, $T \geq 700K$. Thus, this collective effect provides a plausible explanation of the suppression of the conductivities of boron carbides having high carrier densities above 700K.[28]

Finally, we note that the conductivities of boron carbides of all compositions shown in Fig. 2 rise sharply above 1400 K. This behavior is also found in others' measurements of boron carbides.[10,14,15] 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 inter-band transitions below 2 eV.[19] Thus, the 0.6 eV activation energy cannot be attributed to thermal generation of the high-mobility carriers required to significantly enhance the conductivity. We observe that the conductivities between 1400 and 1800 K show a power-law behavior of $\sigma \propto T^4$, see Fig. 3. This behavior suggests that high-mobility charge carriers are being generated by intense thermal radiation.

3.2 Seebeck Coefficient

A solid's Seebeck coefficient measures the open-circuit emf produced by a temperature differential divided by the temperature difference. Physically, the Seebeck coefficient equals the entropy transported with a charge carrier divided by the carrier's charge.[30] The Seebeck coefficient may be expressed as the sum of two contributions: $\alpha_{presence}$, the change in entropy produced by the presence of a charge carrier divided by its charge, and $\alpha_{transport}$, the net energy E_T transported with a charge carrier divided by qT.[31] Simple treatments of the Seebeck coefficient ignore $\alpha_{transport}$. In addition, elementary treatments of $\alpha_{presence}$ neglect interactions of a carrier with its environment. Then $q\alpha_{presence}$ is just the change in the entropy of mixing, $q\alpha_{mix}$, produced by adding a charge carrier. Simple expressions for α_{mix} result in the limit that the temperature is sufficient that all sites are accessible.[32] In particular, for our model of singlet bipolarons that only singly occupy $B_{11}C$-icosahedra sites:

$$\alpha_{mix} = \frac{k_B}{q} \ell n \left(\frac{1-c}{c} \right), \tag{3}$$

where $k_B/q = 43 \mu V/K$ when $q = 2e$ and $c = n_{(B_{11}C)^{\bullet}} / n_{B_{11}C}$, the fraction of $B_{11}C$ sites occupied by bipolarons.

The Seebeck coefficients of boron carbides at a high temperature, 773K, are plotted as a function of their carbon concentration in Fig. 4. Eqn. (3) predicts that the Seebeck coefficient will fall from about 150 to 0 μV/K when the carbon concentration is reduced from $x \approx 0.06$ to $x = 1.0$. Indeed, Fig. 4 shows a fall of about 100 μV/K between $x \approx 0.06$ and $x = 1.0$. The small, consistent increase in the Seebeck coefficient as x rises above 1 suggests a decrease in c. As described in the Introduction, this decrease in $n_{(B_{11}C)^*} / n_{B_{11}C}$ is consistent with electron-donating BB^+B chains replacing CBB chains. Unfortunately, phase separation precludes making meaningful measurements for $x \geq 1.7$. All told, Eqn. (3) provides a rough representation of the *composition dependence* of boron carbides' Seebeck coefficients.

Significantly, boron carbides' high-temperature Seebeck coefficients are much greater than expected from the entropy-of-mixing contribution alone. For example, the measured value of α at T > 100 K is ≈ 200 μV/K while $\alpha_{mix} = 0$ at $x = 1$ where $c = \frac{1}{2}$. Indeed, Seebeck coefficients of conventional solids are generally small, < 100 μV/K, when carrier concentrations are as high as those in boron carbides. Moreover, measurements of boron carbides' conductivities and Hall mobilities confirm the high carrier densities given by our model: $c = x/2$ for $0.06 < x < 1$ and $c = (2 - x)/2$ for $1 < x < 1.7$. Thus, there is a large contribution to boron carbides' Seebeck coefficients in addition to α_{mix}. Furthermore, since α_{mix} alone describes the dependence of boron carbides' Seebeck coefficients on carrier concentration, this additional contribution to the Seebeck coefficient has little dependence on the carrier concentration.

It is also noteworthy that the Seebeck coefficients of boron carbides of all carbon concentrations manifest a distinctive temperature dependence. Figure. 5 shows that boron carbides' Seebeck coefficients first rise to a peak as the temperature is increased from near zero and then approach a large constant value at sufficiently high temperatures.[20]

Such a contribution to the Seebeck coefficient can be obtained when localized (hopping-type) carriers reduce the inter-atomic stiffness constants of the atoms with which they interact.[33,34] Carrier-induced softening results from a localized carrier's electronic wave function changing in response to atomic motion. Indeed, carrier-induced softening is sometimes simply proportional to a localized carrier's electronic polarizability.[35] Furthermore, the softening effect can be especially large when carriers that occupy degenerate states combine as singlet bipolarons.[9]

The augmentation of the Seebeck coefficient from "carrier-induced softening" is the sum of two types of contribution.[33,34] A contribution to $\alpha_{presence}$ occurs because the addition of a carrier reduces atoms' vibrational frequencies thereby producing a carrier-induced increase of vibrational entropy. This contribution has the form

$$\alpha_{vibrations} = \left(\frac{-\Delta v}{v}\right)\left(\frac{k_B}{q}\right)\left[\frac{(h v / 2 k_B T)}{\sinh(h v / 2 k_B T)}\right]^2 D_g, \tag{4}$$

where Δv is the carrier-induced reduction of the frequency of the typical vibration to which the carrier is coupled, v, and D_g is the enhancement for singlet bipolarons formed from carriers occupying g-fold degenerate orbitals: $D_g \sim g(g+1)/2$.[9] This contribution to the Seebeck coefficient rises monotonically with increasing temperature from zero to a plateau of $(k_B/q)(-\Delta v/v)\, g(g+1)/2$ when $k_B T > h v$. Boron carbides' bipolarons are formed of four-fold degenerate orbitals, $g = 4$.[8]

A second contribution arises from carrier-induced softening because heat is transported along with a carrier as it hops from a softened region to an unsoftened region:[32-33]

$$\alpha_{transport} = \left(\frac{-\Delta v}{v}\right)\left(\frac{E_A(T)}{qT}\right), \tag{5}$$

where $E_A(T)$ is the "differential activation energy" defined as the derivative of the logarithm of the phonon-assisted jump-rate with respect to $1/k_BT$. At low temperatures phonon-assisted hopping rates are non-Arrhenius.[23] Then the super-linear rise of $E_A(T)$ with T causes $\alpha_{transport}$ to rise with increasing temperature. However, at sufficiently high temperatures, multi-phonon hopping becomes Arrhenius with $E_A(T)$ being the temperature-independent activation energy. In this high-temperature regime $\alpha_{transport}$ falls with increasing temperature in proportion to $1/T$. Thus, $\alpha_{transport}$ is a peaked function of temperature.

The net contribution to the Seebeck effect from softening bipolarons is obtained by summing Eqs. (4) and (5). This contribution is independent of carrier density and possesses a similar temperature dependence to what we measure for boron carbides' bipolarons. This summing of the temperature dependencies of $\alpha_{vibrations}$ and $\alpha_{transport}$ is illustrated in the center panel of Fig. 5 for carriers' coupled to two phonon bands whose energies are 0.01 and 0.06 eV.[20] Summing $\alpha_{vibrations}$ and $\alpha_{transport}$ for these two bands yields a softening contribution to the Seebeck coefficient whose temperature dependence mirrors the $x = 1$ data of Fig. 5. The net contribution rises to a peak and then gradually falls to a plateau. The carrier-density-dependent term, α_{mix}, also contributes when $x \neq 1.0$. The net Seebeck coefficient obtained in this manner describes the composition dependence and the magnitudes of boron carbides' high-temperature Seebeck coefficients. This model also describes the low-temperature Seebeck coefficients of boron

carbides. Here the increase of $E_A(T)$ as x approaches 0.06 and 1.7 (Fig. 1) contributes significantly to the x-dependence of α.

Finally, we note that the composition and temperature dependencies of boron carbides' Seebeck coefficients shown in Figs. 4 and 5 differ from those of some earlier measurements.[3,10,14,16,18] In particular, some other measurements found that with x near to or even less than zero, the Seebeck coefficients of samples were small, 10 to 120 μV/K at 300K, and grew with increasing temperature. However, the high-temperature Seebeck coefficients of samples with lower carbon concentrations were similar to Fig. 5. This discrepancy is attributed to the presence of conducting free carbon inclusions whenever x is smaller than the carbon-rich limit, $x \lesssim 0.06$. These inclusions increasingly dominate the conductivities and Seebeck coefficients of boron carbides as the temperature is lowered.[17] In particular, the Seebeck coefficient of a composite is the conductivity-weighted average of the individual phases of the composite. Carbon's small Seebeck coefficient is most heavily weighted at low temperatures because of its relatively large conductivity. As boron carbides' conductivity grows with increasing temperature, the Seebeck coefficient of the composite approaches that of boron carbides.

Conclusions

The most conspicuous feature of boron carbides' electronic transport properties is their having both high carrier densities and large Seebeck coefficients. The magnitudes and temperature dependencies of the Seebeck coefficients are consistent with large contributions from "softening bipolarons": singlet bipolarons whose stabilization is significantly affected by their softening of local vibrations. Boron carbides' high carrier densities, small activation energies for hopping (≈ 0.16 eV), and "anomalously" large Seebeck coefficients combine with

their low, glass-like thermal conductivities to make them unexpectedly efficient high-temperature thermoelectrics.[3,10,12]

Acknowledgments

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28. Boron carbides' high-temperature conductivities could be suppressed if the concentrations of mobile bipolarons were diminished by their thermal dissociation.[29] This "pair-breaking" would only suppress the conductivity if bipolarons were more mobile than separated polarons. This is possible for softening bipolarons.[9] However, the conductivity suppression from dissociation would be greatest when c is small.[29] By contrast, suppression is observed

only when c is large, ≈ 0.5. Thus, a model of conductivity suppression through bipolaron dissociation is inconsistent with the experimental results.

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Figure Captions

Fig. 1. Conductivities of boron carbides below 300 K are plotted against reciprocal temperature for carbon concentrations spanning the single-phase region. Open symbols denote samples with $0.06 \le x \le 1.0$, shaded symbols denote samples with $1.0 \le x \le 1.7$. The strong sensitivity of the temperature dependence of the conductivities to carbon concentration suggests percolation among energetically disordered sites.

Fig. 2. Conductivities of representative boron carbides are plotted against reciprocal temperature between 300 and 1750 K for $0.06 \le x \le 1.7$.

Fig. 3. The logarithm of conductivities of several representative boron carbides are plotted against the logarithm of the temperature for $T > 1400K$. The very-high-temperature conductivities of boron carbides approximate a power law dependence of $\sigma = AT^4$.

Fig. 4. 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, Eqn. 3.

Fig. 5. The Seebeck coefficients of boron carbides with representative carbon concentrations are plotted against temperature between 10 and 900 K. Each sample exhibits a similar unconventional temperature dependence. The Seebeck coefficients rise to a low-temperature maximum, then fall to a large, temperature-independent plateau. The middle panel illustrates a fit (solid line) of the observed the temperature dependence for a bipolaron that interacts with

phonon bands of energy 0.01 (short dash) and 0.06 eV (dot-dash). Two contributions to the net

Seebeck coefficient, described by Eqns. (4) and (5), result from the bipolaron's interaction with
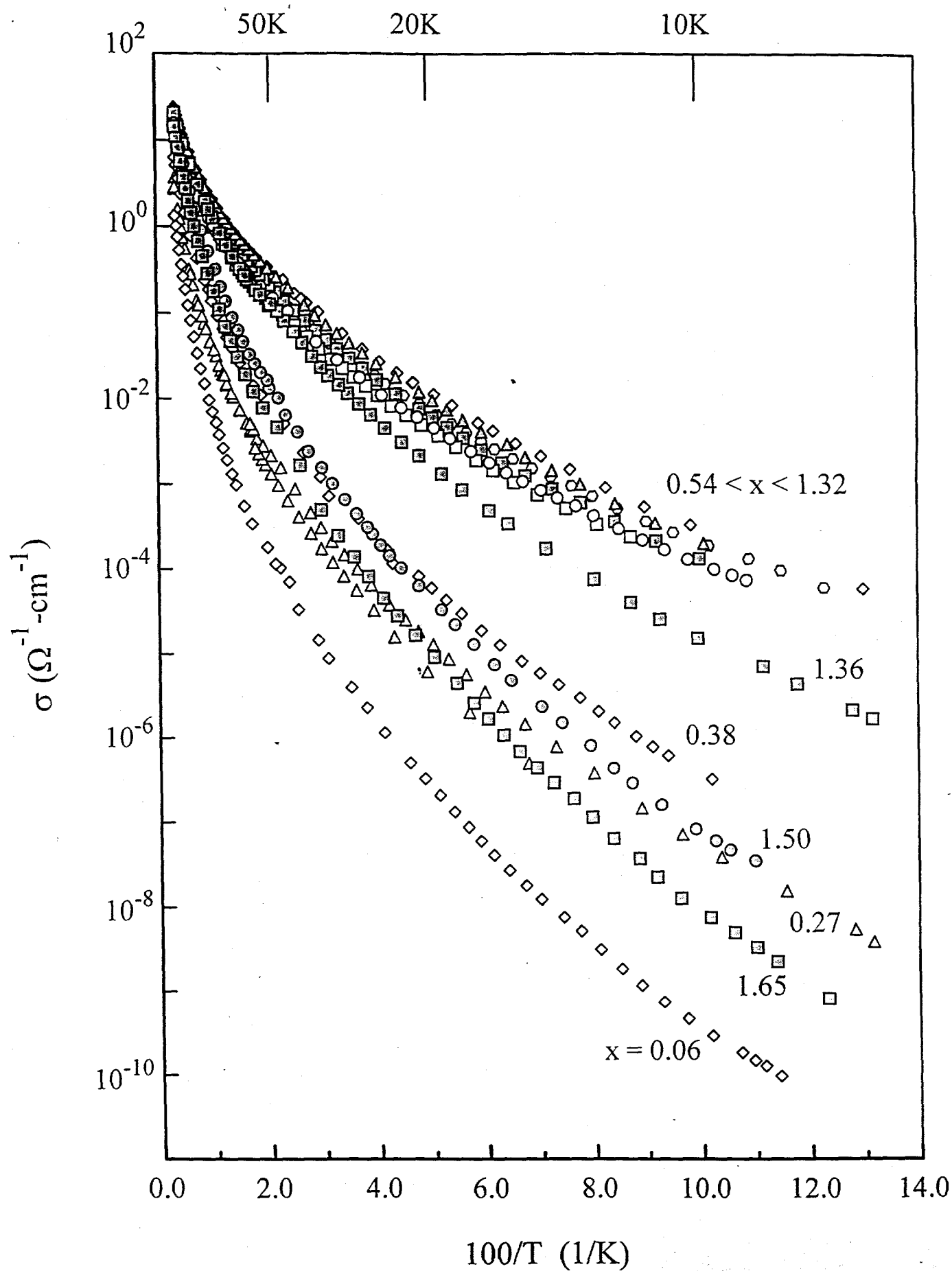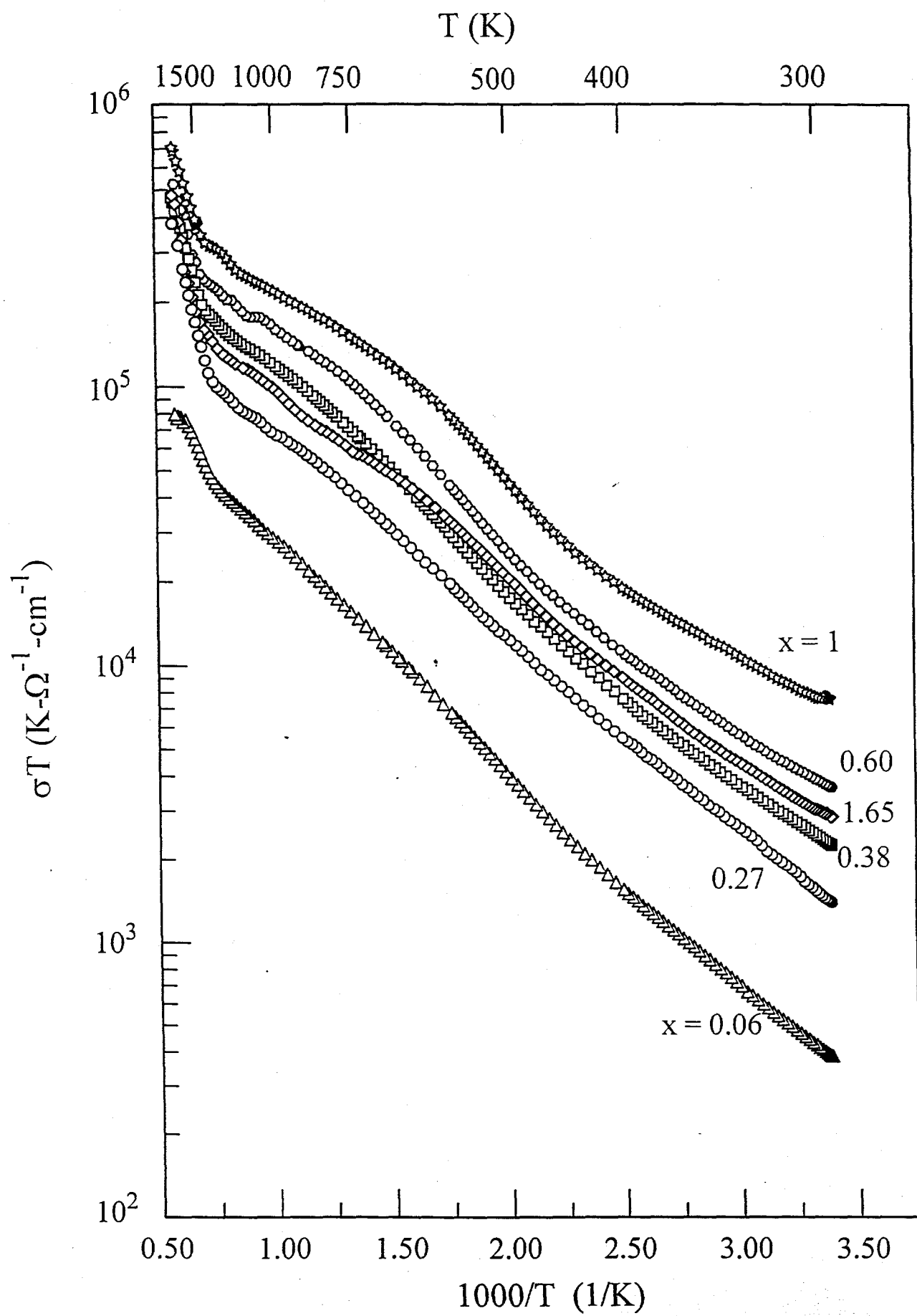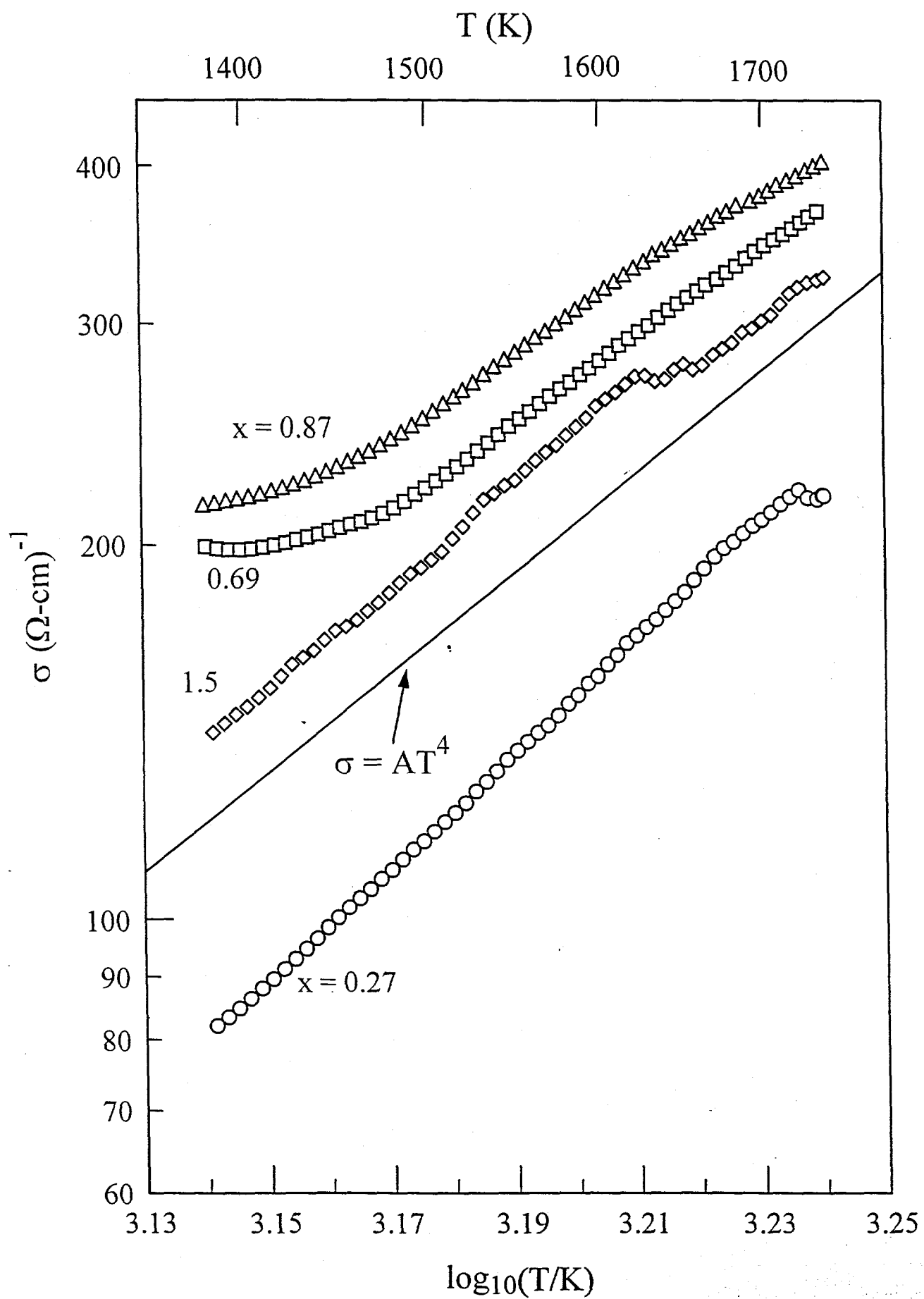
each phonon band.

Fig. 1.

Fig. 2
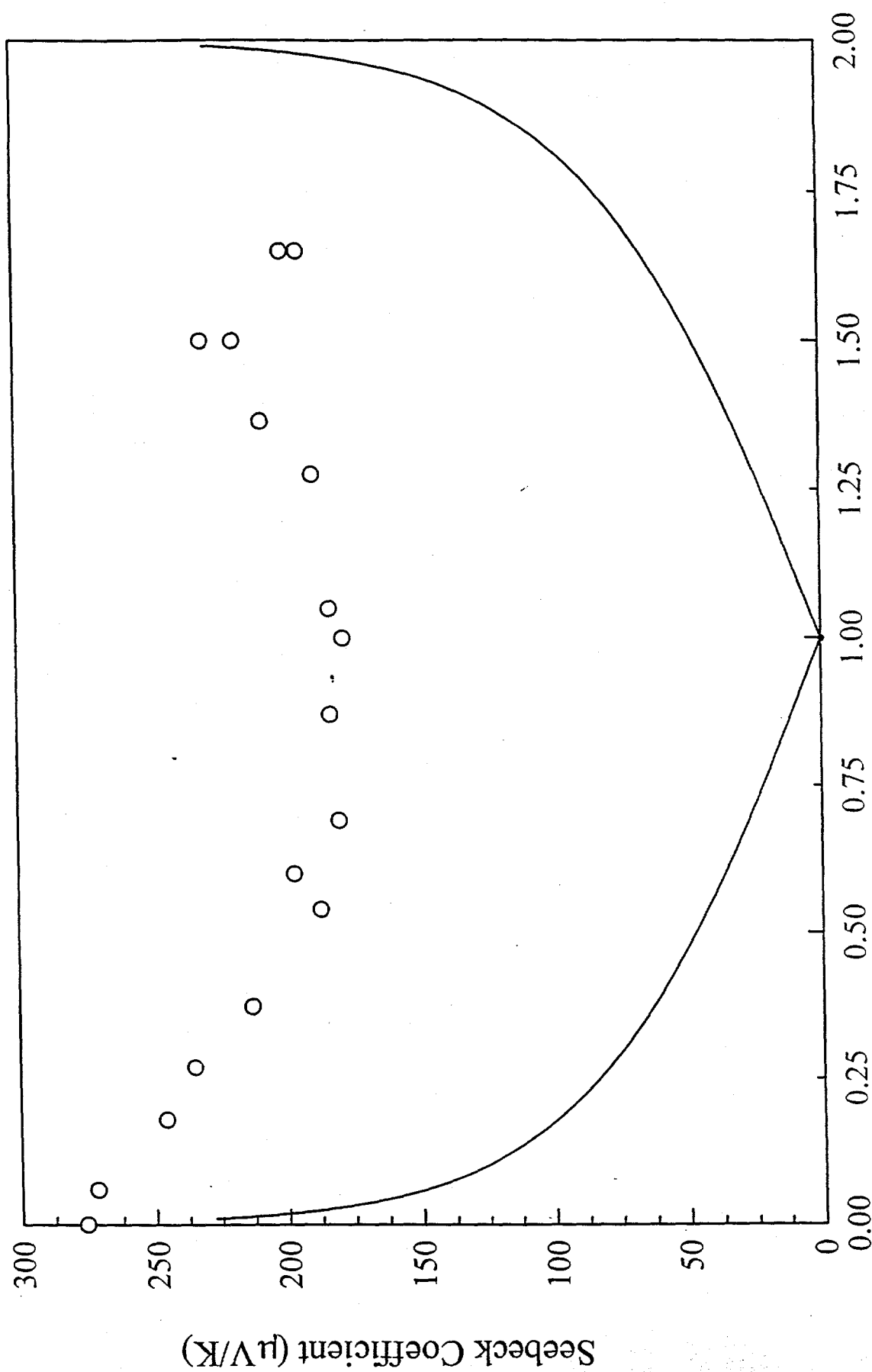
Fig.

Fig. 4

Seebeck Coefficient ($\mu V/K$)

x, in $B_{12+x}C_{3-x}$

Fig. 5