

Spin susceptibility of boron carbides: Dissociation of singlet small bipolarons

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Using ESR, the spin susceptibilities of a crystal and ceramics of boron carbides have been measured between 4 and 1200 K. A thermally generated contribution to the spin susceptibility, which may be discerned emerging above 100 K, becomes unmistakable above 300 K. The g values of these spins differ from those of the temperature-independent background spins that dominate low-temperature ESR measurements. Thus, ESR measurements at temperatures well above those of previous works unearth thermally generated spins in boron carbides. We suggest that these thermally induced spins arise from thermal dissociation of boron carbides' singlet small bipolarons. The energy with which a small bipolaron is bound with respect to dissociating into two small polarons is estimated to be about 0.2 eV. [S0163-1829(96)07121-4]

I. INTRODUCTION

Boron carbides, $B_{1-x}C_x$, are refractory solids that exist as a single phase with carbon concentrations between about 9 and 19 at. %.¹ Within this single-phase regime, boron carbides' structure can be represented as comprising 12-atom icosahedra and three-atom chains. As illustrated in Fig. 1, the

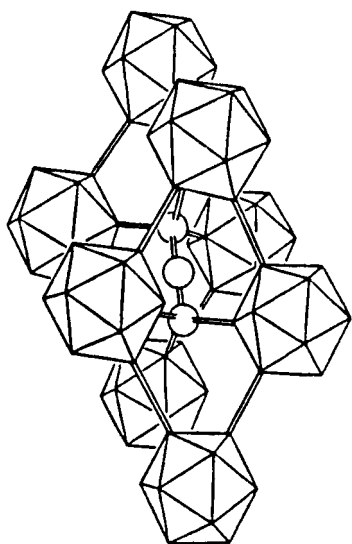


FIG. 1. Boron carbides' structure consists of 12-atom icosahedral units at the corners of a rhombohedron with a three-atom chain lying along the longest diagonal of the rhombohedral cell.

icosahedra reside at the vertices of a rhombohedral unit cell with the three-atom chains lying along the longest diagonal of the rhombohedral cell.

At the *idealized* upper limit of the single-phase region, 20 at. % carbon, boron carbides consist of icosahedra composed of 11 boron atoms and a solitary carbon atom, $B_{11}C$ icosahedra.² Each three-atom chain is then composed of a boron atom that lies between two carbon atoms, a CBC chain. Each carbon atom at an end of a chain is covalently bonded to an atom of each of three adjacent icosahedra.

In actuality, there are two reasons why boron carbides always form with less than 20 at. % carbon. First, as a result of carbon atoms being distributed among different sites the entropies of boron carbides increase and their free energies decrease as their carbon concentration is reduced from its idealized upper limit, 20 at. %.³ Second, carbon atoms tend to form a second phase, graphite, rather than being incorporated within boron carbides since the free energy of graphite is much lower than that of boron carbides.⁴ In fact, boron carbides can form with as little as 9 at. % carbon because boron carbides' free energy is much lower than that of β -rhombohedral boron, the form of elemental boron that is stable at the temperature of boron carbides' synthesis.⁴ These "nonideal" boron carbides form as boron atoms replace carbon at some of their sites in the idealized structure.

Boron carbides are therefore disordered for two reasons. First, boron replaces carbon at only some of the geometrically equivalent "carbon sites." Second, carbon atoms located within different $B_{11}C$ icosahedra do not generally occupy geometrically equivalent sites.

While idealized boron carbide is an insulator, replacement of a significant fraction of carbon atoms with boron atoms introduces large densities of holes, $\approx 10^{21} \text{ cm}^{-3}$, into boron carbides. Measurements of the electronic transport of boron carbides as functions of carbon concentration and temperature always reveal p -type thermally assisted conduction.⁵ The activation energy of the conductivities from 400 to 800 K are nearly independent of carbon concentration and about 0.17 eV. Furthermore, Hall mobilities are low, $< 1 \text{ cm}^2/\text{V sec}$, and thermally activated, indicating the hopping of small-polaronic carriers.⁵

However, measurements of the magnetic susceptibility and ESR of boron carbides below room temperature yield spin densities, $\approx 10^{19} \text{ cm}^{-3}$, that are orders of magnitude below the densities of holes introduced as the carbon concentration is lowered below 20 at. %.^{6,7} These observations imply that most holes produced in boron carbides are paired as singlets. That is, the carriers form small bipolarons. By contrast, in common hopping-type semiconductors, where carriers do not pair to form bipolarons, the densities of localized spins at least equal the densities of hopping-type carriers.

A model was introduced to describe how the density of singlet-bipolaron holes evolves with boron carbides' carbon concentration.^{3,8} This model recognizes that boron icosahedra B_{12} have no net electronic spin and possess a strong bielectron affinity, $2e + B_{12} \rightarrow B_{12}^{2-}$. Furthermore, this bielectron affinity is greatly enhanced when a boron nucleus ($Z=5$) is replaced by a carbon nucleus ($Z=6$), $B_{12}^{2-} \rightarrow (B_{11}C)^-$ because of the carbon nucleus' additional positive charge.

The model envisions the idealized boron carbide (an insulator) to comprise CBC chains that each donate an electron to $B_{11}C$ icosahedra: $(CBC)^+(B_{11}C)^-$. As the carbon concentration is reduced from its idealized upper limit, chains that donate electrons to icosahedra, CBC chains, are replaced by chains that do not donate electrons to icosahedra, CBB chains. For each CBC that is replaced by a CBB chain, one electron is removed from a $(B_{11}C)^-$ icosahedra: $(B_{11}C)^- \rightarrow (B_{11}C)^0$. However, since holes in boron carbides are not associated with unpaired spins, the holes presumably find it energetically favorable to pair as nonmagnetic bipolarons. This process can be represented by the chemical formula: $2(B_{11}C)^0 \rightarrow (B_{11}C)^- + (B_{11}C)^+$. Thus, for every *two* CBB chains that are introduced, one $(B_{11}C)^-$ icosahedron is replaced by a $(B_{11}C)^+$ icosahedron. A $(B_{11}C)^+$ icosahedron is a chemical representation of a singlet bipolaronic hole in boron carbides.

The model predicted that the density of these bipolarons will cease to increase with decreasing carbon content once all CBC chains are replaced by CBB chains, at 13 1/3 at. % carbon, $(CBB) [(B_{11}C)_{0.5}^-(B_{11}C)_{0.5}^+]$. With further reduction of the carbon concentration, the model has boron atoms replacing carbon atoms within icosahedra. The resulting B_{12} icosahedra remain neutral since their electron affinity is much less than that of $B_{11}C$ icosahedra. Thus, the concentration of $(B_{11}C)^+$ icosahedra *falls* with decreasing carbon once the carbon concentration falls below 13 1/3 at. %. That is, the model predicts that the concentration of singlet bipolarons will peak near 13 at. % carbon.

Consistent with this model, the preexponential factor of the conductivity is found to have a maximum near 13 at. %

carbon.⁹ Furthermore, replacement of some chains of boron carbides of near 19 at. % carbon with phosphorus-containing complexes that are believed to donate several electrons led to the expected reduction of the density of hole-type carriers.¹⁰

One means of further testing this model is to search for the thermal dissociation of singlet bipolarons. Each of the polarons produced by dissociating a bipolaron has a spin that could contribute to the system's magnetic susceptibility. Indeed, ESR has proved able to observe the spins of small-polaronic carriers.¹¹

Here we report the results of ESR measurements on boron carbides with carbon concentrations between 10 and 19 at. %. The experiments have been carried out from 4 up to 1200 K. In agreement with prior works,^{7,12-14} we find that the low-temperature ESR signal is dominated by a low density ($\approx 10^{19} \text{ cm}^{-3}$) of localized spins that are presumably related to defects. However, as measurements are extended to higher temperatures than those of prior studies, a large (up to $\approx 10^{20} \text{ cm}^{-3}$) density of additional spins with a different g value becomes apparent. We ascribe these spins to localized polarons produced by breaking up singlet bipolarons.

II. EXPERIMENTAL

Boron carbide samples were prepared by two methods. A single crystal of boron carbide with a composition near the carbon-rich homogeneity limit (above 19 at. %) was precipitated from a metallic copper solvent by slowing cooling from 2000 to 1300 K.⁴ Five other samples with carbon concentrations between ≈ 19 and 9 at. % (10, 13.3, 16, 18.2, and 19.2) were prepared by uniaxial reactive hot pressing (2450 K) of high purity powders of boron and carbon.

Powders for ESR measurements were produced by grinding the hot-pressed samples and inserting them in a suprasil tube. The tubes were then sealed with a small helium admixture to facilitate heat transfer.

ESR measurements were performed at 9.4 GHz with different gas-flow cryostats being used for the two different temperature ranges (4–300 K) and (300–1200 K). The susceptibilities were determined by integrating the ESR signal after taking account of the temperature dependence of the cavity's Q . Measurement of the room-temperature ESR after gentle heating and pumping on the sample-containing tubes did not suggest that either air or water influences the ESR.

Four-probe conductivity measurements were made on polished thin platlets that were cut from the hot-pressed samples. Hall-effect measurements used a six-probe contact configuration. The linearity of the Hall voltage with magnetic field was checked up to our maximum field of 12 T. The reversibility of the Hall voltage with field was checked by rotating the sample by 180° at least three times at each temperature.

III. RESULTS

Prior measurements of boron carbides' ESR found narrow Lorentzian lines for samples of the highest carbon content (19 at. %) and broad Lorentzians for carbon concentrations of 13 and 10 at. %.^{7,12,13} Our low-temperature ($T < 100$ K) ESR results are similar to these prior works. In particular, the ESR spectrum for the boron carbide with the largest carbon

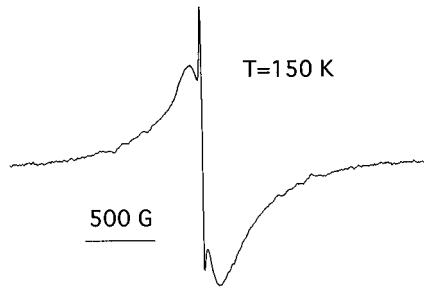


FIG. 2. ESR spectrum of a boron carbide of 18 at. % carbon.

concentration (about 19 at. % carbon) has a linewidth of 1–2 G at 100 K. In addition, our ESR spectra for boron carbides having lower carbon concentrations (18 and 16 as well as 13 and 10 at. % carbon) give much broader Lorentzian lines (up to 100 G at 100 K). In these samples we also observe a narrow line superimposed on the broad Lorentzian. Nonetheless, the integrated intensity of this narrow line is very small. Its integrated intensity is never more than 1/400th that of the main line (found in the sample with 18 at. % carbon). The spectrum of this sample, obtained at 150 K, is shown in Fig. 2.

The low-temperature susceptibilities of most of our samples are shown in Fig. 3(a). The sample with 19 at. % carbon has been deleted from this plot and the magnitude of susceptibility of the boron-carbide single crystal has been reduced by an order of magnitude. In agreement with earlier works, these susceptibilities follow a Curie law below 100 K and are associated with a density of about $10^{19}/\text{cm}^3$ spins with g values of about 2.002. Figure 3(b) shows the (peak to

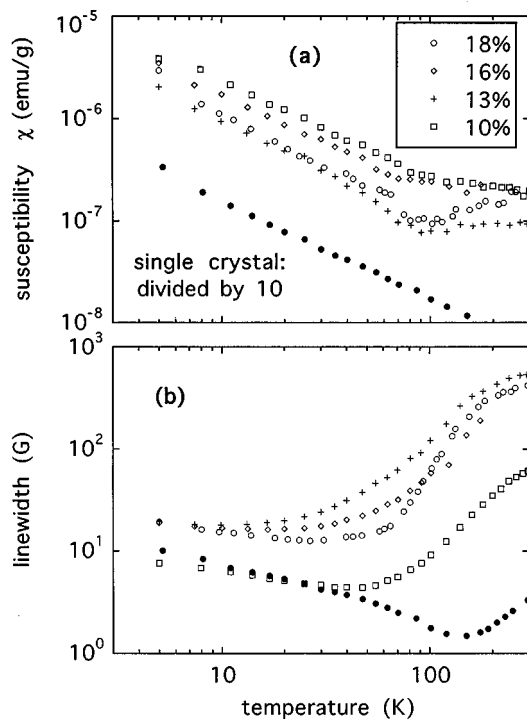


FIG. 3. The magnetic susceptibilities of most of our boron carbides are plotted against temperature in (a). The linewidths of the corresponding ESR spectra are plotted against temperature in (b).

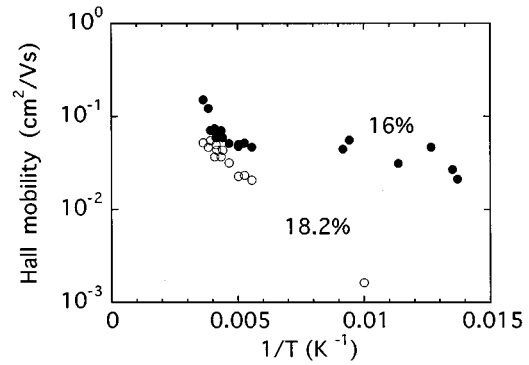


FIG. 4. The Hall mobilities of boron carbides with carbon concentrations of 18 and 16 at. % are plotted against reciprocal temperature.

peak) linewidths of the samples whose susceptibilities are depicted in Fig. 3(a). These linewidths roughly follow the carrier densities. In particular, the linewidths and the carrier density in boron carbides both peak at about 13 at. % carbon.

The density of localized spin centers determined from the low-temperature measurements is two orders of magnitude smaller than the density of carriers, about 10^{21} cm^{-3} , determined from the carbon concentration's departure from the value of the "idealized" insulator, 20 at. %. Thus, if the carriers are regarded as localized, as indicated by their conduction proceeding by phonon-assisted hopping, this result implies that most of the carriers are paired as singlets. As shown in Fig. 4, Hall-effect measurements between 100 and 300 K find the very low thermally activated behavior predicted for the Hall mobility of small-polaronic carriers.¹⁵ Thus, we conclude, in accord with prior studies, that most carriers in boron carbides are localized and paired as singlets.

For completeness, we note finding small ferromagnetic contributions ($g > 3$) to the magnetization of some samples. Ferromagnetic contributions, attributed to impurities, have also been reported in some prior measurements.^{6,13,14} Impurities, such as iron, may be introduced in the process of grinding the (very hard) boron carbides and may exist in some starting materials.

Novel results are observed for temperatures above 100 K. In particular, measurements between 100 and 300 K reveal three unusual results. First, the temperature dependences of the spin susceptibilities of Fig. 3(a) depart from the Curie-like behavior they manifest at low temperatures. Second, the g values associated with these spins' ESR spectra fall with increasing temperature. Third, the linewidths of these spectra, shown in Fig. 3(b), increase with temperature. These features imply that a second spin species is manifesting itself as the temperature is being raised. Furthermore, the two spin species apparently interact strongly enough so as to produce a single line.

The relatively narrow room-temperature ESR line for the sample with the largest carbon content (about 19 at. %) enables us to meaningfully extend its measurement to a much higher temperature than is possible for samples of borides with smaller carbon concentrations. Figure 5(a) shows that the magnetic susceptibility rises steadily with increasing temperature from 100 up to 1200 K. In addition, Figs. 5(b) and 5(c) show the g factor falling and the ESR linewidth

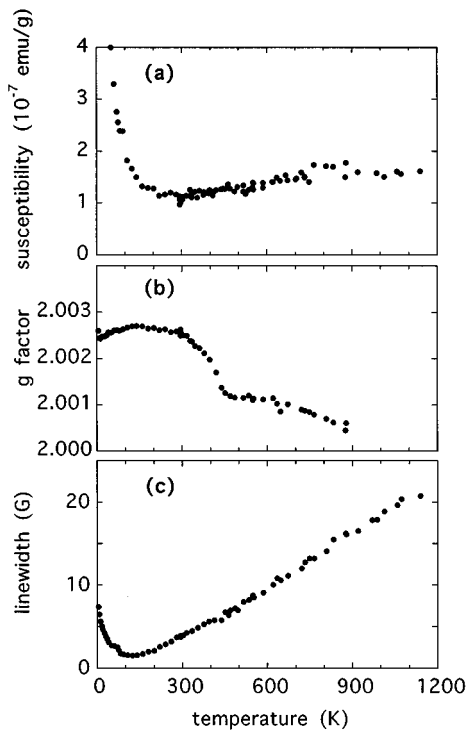


FIG. 5. The spin susceptibility, g value, and linewidths obtained from the ESR spectrum of the boron carbide with the highest carbon content (19 at. %) are shown in (a), (b), and (c), respectively.

increasing with rising temperature. As shown in Fig. 6, the spin density of this sample rises steadily with increasing temperature.

In summary, these results show that most of the ($\approx 10^{21} \text{ cm}^{-3}$) carriers in boron carbides pair as singlets and that electrical transport proceeds by the low thermally assisted mobilities expected of small-polaronic carriers. The low-temperature ($T < 100 \text{ K}$) ESR arises from a temperature-independent density of about 10^{19} cm^{-3} localized spins. These ESR lines are broadest for boron carbides with carbon concentrations of about 13 at. % and narrow with increasing temperature. By contrast, at sufficiently high temperatures ($> 100 \text{ K}$) the densities of localized spins and their ESR linewidths both rise with increasing temperature. Concomitantly, the g values of the ESR resonances tend to fall with increasing temperature at sufficiently high temperatures.

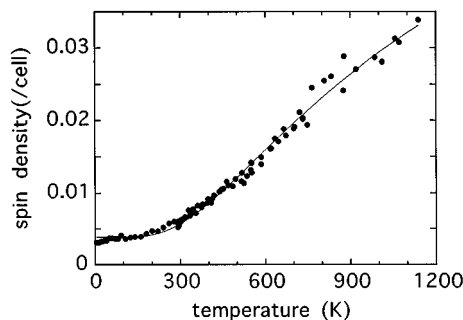


FIG. 6. The spin density of the boron carbide with the highest carbon concentration (over 19 at. %) is plotted against temperature.

IV. DISCUSSION

The principal observation of this paper is the increase of the density of boron carbides' localized spins with rising temperature at sufficiently high temperatures, $T > 100 \text{ K}$. In what follows we describe the high-temperature thermally induced rise of the spin density as being a general feature of a system composed of singlet small bipolarons.

Recent work argues that the high-temperature electrical conductivity of a system in which most carriers form singlet small bipolarons is dominated by the hopping motion of the small bipolarons produced by dissociation of some small bipolarons.¹⁶ This situation occurs for two reasons. First, small polarons hop more rapidly than do small bipolarons. Second, small polarons readily pass through small bipolarons by a process in which *one* of a small bipolaron's carriers transfers to a neighboring small polaron. In the bulk of this section the temperature and carbon-concentration dependences of the densities of spins we measure are shown to agree with what we expect from small polarons produced by splitting small bipolarons.

Our measurements also enable us to study the ESR of small polarons as a function of their density since the carrier density of boron carbides is controlled by their carbon content. In particular, we discuss how the linewidths of small polarons varies with boron carbides' carbon content and the temperature in Appendix A. Finally, we discuss the linewidth of the defect spins that predominate at low temperatures in Appendix B. There the carbon-composition dependence of the low-temperature ($T < 100 \text{ K}$) ESR linewidths is rationalized in terms of the model within which boron carbides' electronic properties are described.

A. Pair breaking and the magnetic susceptibility

A convenient means of modeling small-bipolaron formation utilizes the Holstein-Hubbard model.¹⁷ In this model the ground-state energy of a small polaron is $-E_b$, where E_b is termed the small-polaron binding energy. Doubling the number of carriers on a site doubles the magnitude of the atomic displacements stabilized by the carriers' presence. By itself, this effect produces a small-bipolaron binding energy of $4E_b$ since each of the two carriers have their energy lowered twice that of a small polaron's carrier. In addition, a small bipolaron's two carriers experience a mutual on-site Coulomb repulsion of U . If the two carriers form a singlet and thereby share a common local electronic state, the small-bipolaron's ground-state energy is thus $-4E_b + U$. Small-bipolaron formation is energetically favorable when $-4E_b + U$ is lower than the formation energy of two separate small polarons, i.e., when $2E_b > U$.

For small bipolarons or small polarons to hop between sites, the atomic displacement pattern responsible for localizing a carrier at one site must be removed and a similar atomic displacement pattern produced about another site.¹⁸ Thus, small-polaronic carriers seldomly hop at low temperatures since appropriate atomic displacements rarely occur when most atomic vibrations are frozen out. As the temperature is increased from absolute zero, small-polaronic hopping rates first increase in a non-Arrhenius manner.¹⁹ Once the

temperature is high enough for atomic vibrations to be treated classically the rates for small-polaronic hopping then become Arrhenius.

Recently, the jump rates for small-bipolaron and small-polaron hops have been calculated in this high-temperature ‘‘semiclassical’’ regime.¹⁶ One-electron transfers that involve small polarons are found to always be faster than small-bipolaron hops when small-bipolaron formation is stable, $2E_b > U$. As a result, even when most carriers pair as small bipolarons, the dc conductivity in the high-temperature semiclassical regime is dominated by the hopping of small polarons. Thus, the temperature dependence of the high-temperature conductivity arises from two sources: from decomposing small bipolarons into small polarons and from small polarons’ thermally assisted hopping.

The density of small polarons may be determined (independently of measuring the conductivity) by measuring the thermally induced Curie paramagnetism arising from small polarons’ spins. In particular, the small polarons’ paramagnetic susceptibility is¹⁶

$$\chi_m = \frac{N(g\mu_B)^2}{4k_B T} c_p, \quad (1)$$



The spin densities we measure are reasonably consistent with those associated with Eq. (2). In particular, Fig. 6 compares our measurements of the spin density with the sum of a constant (defect) density plus the calculated polaron density for $2E_b - U = 0.2$ eV. The temperature dependence of the polaron concentration becomes increasingly mild as it approaches saturation at high temperatures. Furthermore, in accord with the theory, the temperature dependence of boron carbides’ conductivities exceed those of the spin density.

B. The Hall effect and the small-polaron density

We have also performed Hall-effect measurements to verify that charge transport is by phonon-assisted hopping. In particular, the Hall mobility μ_H the product of the Hall coefficient and the conductivity, measures the deflection of carriers’ current by a magnetic field. Since the Lorentz force only affects carriers during their motion, measuring a low ($\mu_H < 1$ cm²/V sec) thermally activated Hall mobility indicates that the intrinsic motion is by hopping rather than by freeing high-mobility itinerant carriers from traps. The mobilities of Fig. 4 clearly indicate small-polaronic hopping.¹⁵

The Hall mobility generally differs from the mobility that enters into the conductivity μ , a measure of the current induced by an electric field. As a result, the Hall coefficient, $R \equiv (1/ne)(\mu_H/\mu)$, for hopping carriers does not generally measure just the carrier density n .¹⁵ Only for free carriers, where the drift and Hall mobilities equal one another, does the Hall coefficient measure only the carrier density.²⁰

Below 400 K in boron carbides the conductivity becomes non-Arrhenius. In this regime the temperature dependences

where the concentration of small polarons (number of small polarons per site) is

$$c_p = \frac{\sqrt{1 + c(2 - c)[e^{(2E_b - U)/k_B T} - 1]} - 1}{e^{(2E_b - U)/k_B T} - 1}, \quad (2)$$

N is the density of possible sites for both small polarons and bipolarons, g is a small polaron’s Lande g factor, μ_B is the Bohr magneton, $k_B T$ is the thermal energy, and c is the carrier concentration (e.g., c carriers can produce $c/2$ bipolarons). The number of unpaired spins contributing to χ_m rises in a thermally activated manner from an arbitrarily small value at low temperatures, $\exp[-(E_b - U/2)k_B T]/\sqrt{c} \ll 1$. However, the spin density saturates at a value equal to c at high temperatures, $\exp[-(E_b - U/2)k_B T]/\sqrt{c} > 1$. Thus, plotting the spin density against temperature results in an S-shaped curve.

The carrier density c and N can be related to a boron carbide’s carbon concentration. The model of Ref. 3 has c rising from 0 to 1 as the carbon content is reduced from 20 to 13 1/3 at. % carbon. In addition, N , the number of B₁₁C icosahedra, falls by a factor of 2 as the carbon concentration is reduced from 13 1/3 to 10 at. %:

of μ_H and μ both weaken and thus the temperature dependence of μ_H/μ should become especially weak. In this circumstance the predominant contribution to the temperature dependences of boron carbides’ Hall coefficients arise from the carrier densities. As shown, in Fig. 7, temperature dependences of the reciprocals of boron carbides’ Hall constants

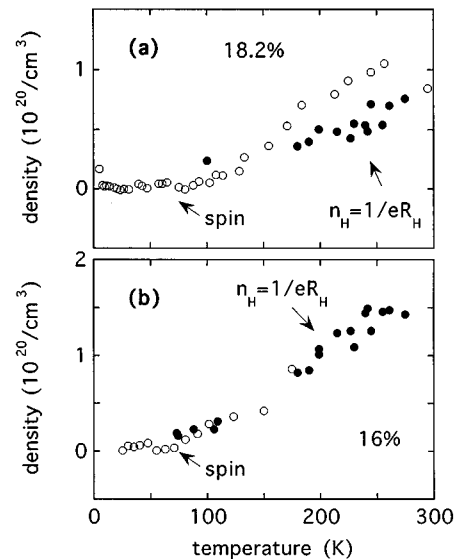


FIG. 7. The temperature dependences of the spin densities are compared with those of the reciprocals of the Hall constants for boron carbides with 18.2 and 16 at. % carbon in (a) and (b), respectively.

compare reasonably well with the spin densities obtained from ESR. Consistent with Eq. (2), the rise of the carrier concentration with increasing temperature steepens as the carrier concentration c increases (as the carbon concentration is decreased from 20 toward 13 at. %). These measurements of the Hall coefficient therefore provide additional support for the conclusion that the carriers and the spins in boron carbides both arise from small polarons produced by dissociating singlet small bipolarons. Thus, the Hall-effect measurements are consistent with the high densities of thermally induced spins in boron carbides being associated with small-polaron production rather than with occupation of some defect states.

The Hall mobility due to hopping conduction is often anomalously signed.²¹ That is, μ_H/μ often negative. The Hall effect then does not give the sign of the carriers. This situation is commonly observed in glasses. These sign anomalies can arise when, as is common in disordered systems, the shortest closed hopping path by which a carrier can return to a starting site is odd-membered.²¹ However, Hall-effect sign anomalies are predicted to not occur for hopping between nearest neighbors along the edges of a cubic lattice (since the smallest hopping loop then has four members).²¹ Similarly, since the icosahedra in boron carbides occupy vertices of a rhombohedral cell, hopping along the edges of the cell should not yield sign anomalies. Thus, observation of p -type Hall coefficients for holes in boron carbide is consistent with having nearest-neighbor hopping of holes between boron carbides' icosahedra.

C. Triplet bipolarons in boron carbides?

Thermally induced local spins can also arise from exciting singlet small bipolarons into triplet states.²² For small-bipolaronic holes in boron carbides this excitation involves promoting one of a $(B_{11}C)^+$'s electrons into an excited state. The characteristic energy separation between icosahedral energy levels ($\approx \hbar^2/mR^2$, where R is the icosahedral radius and m is the electronic mass) is of the order several eV, since an icosahedral radius is only about an Angstrom. Therefore, the excitations required to produce triplet excitons might seem to be far too high in energy to correspond to the excitations we observe. However, the splitting of degeneracies of the primary icosahedral levels can yield energy separations that are smaller than the characteristic splitting. In particular, the energy separations between the relevant energy levels in a $B_{11}C$ icosahedron have been estimated to be about 0.5 eV.²³ This energy is still larger than the binding energy we observe.

V. CONCLUSIONS

In summary, our ESR measurements indicate the thermal generation of spins as the temperature is raised above 100 K for all carbon concentrations within boron carbides' single-phase regime. Our measurements of boron carbides' Hall coefficients suggest that the thermally induced spins we observe are associated with thermally generated charge carriers. We associate these spins with small polarons produced by dissociation of boron carbides' singlet small bipolarons. These results are consistent with the finding that the high-temperature charge transport of a system for which singlet

small bipolarons formation is stable will be dominated by the hopping of small polarons produced by splitting the singlets.¹⁶

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APPENDIX A: LINEWIDTHS OF THE SPINS OBSERVED ABOVE 100 K

The spins observed above 100 K are attributed to small polarons produced by dissociating singlet small bipolarons. There are two processes by which small polarons undergo thermally assisted hops.¹⁶ Small-polaron motion occurs when either a small polaron's unpaired carrier jumps to a vacant adjacent site or when one of the two carriers of a bipolaron hops on to the site of an adjacent small polaron. Both types of hops occur at the same rate.¹⁶

We now estimate the small-polaron jump rate in boron carbides by considering their electrical conductivities. The temperature dependence of the small-polaron conductivity arises both from the increase of the small-polaron density with increasing temperature and from the rise of small-polaron jump rate with increasing temperature. To estimate the small-polaron jump rate from the conductivity we must be able to identify each of these two effects.

At low temperatures the temperature dependence of the small-polaron density, $c_p N$ with c_p given by Eq. (2), depends on the carrier concentration c . However, at high enough temperatures the small-polaron density approaches saturation at a value of c . In this high-temperature regime the temperature dependence of the conductivity is primarily due to small polarons' thermally assisted motion. The near constancy of the activation energy of boron carbides' high-temperature (>800 K) conductivity ($E_\mu \approx 0.09$ eV) as the carbon concentration is varied suggests that the density of hopping carriers has approached temperature independence.²⁴ As the temperature is lowered from this high-temperature limit, the temperature dependence of the small-polaron jump rate generally weakens.¹⁹ This effect manifests itself in boron carbides' conductivities having significantly weaker temperature dependences at and below room temperature than they have at very high temperatures (>800 K).²⁴ For this reason, the semiclassical adiabatic small-polaron jump rate [$\cong \nu \exp(-E_\mu/k_B T)$, where ν is the characteristic frequency of the phonons involved in the hops] underestimates the jump rate by an increasing amount as the temperature is reduced. Taking $E_\mu = 0.09$ eV and $\nu = 10^{13}$ sec⁻¹ for our boron carbides, the underestimated room-temperature jump rate is 2.7×10^{11} sec⁻¹. The mean jump time is thus very much shorter than the times corresponding to the ESR linewidths we observe, between 10^{-7} and 10^{-9} sec at room temperature.

This rapid hopping of these small polarons can therefore

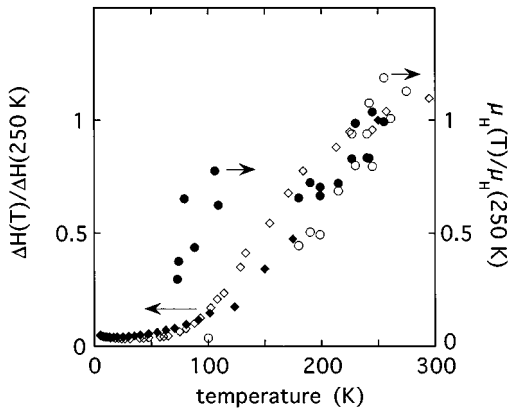


FIG. 8. The temperature dependence of the linewidth (diamonds) is compared to that of the Hall mobility (circles) between 100 and 300 K for boron carbides with 16 (solid symbols) and 18.2 (open symbols) at. % carbon.

motionally narrow their ESR line. Indeed, the extreme narrowing regime is achieved experimentally; by performing a saturation measurement we find $T_1 = T_2$ at room temperature for the sample with the highest carbon content (19 at. %). In this regime the ESR linewidth arises from processes in which spins are flipped as energy is exchanged between the spin and the lattice.

The dependences of the ESR linewidths on temperature and on carbon concentration may provide insight into the nature of the predominant spin-flip process. We observe in Figs. 3(b) and 5(c) that the ESR lines broaden with increasing temperature above 100 K. In addition, the linewidths of Fig. 3(b) vary nonmonotonically with carbon concentration, with their maximum values occurring at 13 at. % carbon.

The temperature dependences of the linewidths of Figs. 3(b) and 5(c) resemble that expected of the small-polaron jump rate. In particular, Fig. 8 shows the similarity of the temperature dependence of the linewidth to that of the Hall mobility between 100 and 300 K for two samples. A proportionality of the linewidth to the small-polaron jump rate would imply that the spin-flip process involves small-polarons' hopping. Furthermore, the dependence of the linewidths on the carbon concentration, by itself, suggests that the spin-flip process is associated with spins encountering small bipolarons or small polarons since both their densities peak at 13 at. % carbon. However, our data also indicates that the temperature dependences of the linewidths below 800 K are weaker than that of boron carbides conductivities. In other words, the linewidth's temperature dependences are not strong enough to be associated with encounters between small polarons, since these events would be proportional to the product of the small-polaron jump rate and the small-polaron density (a strongly increasing function of temperature). For these reasons we speculate that the widths of the ESR lines observed above 100 K occur as unpaired spins flip while an electron is transferred between a small bipolaron and a small polaron that are adjacent to one another. Since polaron-bipolaron transfers occur at rates ($>10^{11} \text{ sec}^{-1}$) that are much larger than the measured relaxation rates (10^7 to 10^9 sec^{-1}), spin flips only occur during a small fraction of these charge transfers.

It has been shown that the spin of a polaron can flip when

a carrier is transferred between doubly and singly occupied sites.²⁵ These spin-flip transfers can occur when the state of the doubly occupied site shifts between the $M_S=0$ states of a singlet and a triplet. The transfer-matrix element for such spin-flip transfers is comparable to that for non-spin-flip transfers.²⁵ However, the relaxation rates do not manifest the strong temperature dependences that we expect would arise from these spin-flip transfer processes creating or annihilating triplet bipolarons. Thus, while our empirical evidence suggests that polarons' spin relaxation primarily occurs when charge is transferred between bipolarons and polarons, we do not herein propose a microscopic mechanism for this relaxation.

APPENDIX B: LINEWIDTHS OF THE SPINS OBSERVED BELOW 100 K

All investigations of the low-temperature ESR of boron carbide ceramics and crystals find temperature-independent localized-spin densities of about 10^{19} cm^{-3} . These localized spins are generally attributed to defects. These defects have been modeled as arising from carbon replacing boron at the central position within a boron carbides' three-atom chains.¹⁴ Thus, a small fraction ($\approx 1/100$) of CBC chains are presumed replaced by CCC chains and a similarly small fraction of CBB chains are presumed replaced by CCB chains. These replacements are expected to produce localized spins because carbon has one more electron than does boron and the ionization potential for carbon's extra electron (carbon's second ionization potential, $\approx 25 \text{ eV}$) is too large to expect it to be relinquished. Concomitantly, having carbon in three-atom chains' central position is energetically unfavorable since the electron is not involved in bonding. Therefore, the fraction of these defects that are frozen in when the material is synthesized is estimated to be about $\exp(-E_{\text{bond}}/k_B T_{\text{syn}})$, where E_{bond} is the loss in bonding energy arising from the carbon atom's electron not being involved in bonding and T_{syn} is the synthesis temperature, about 2400 K. A value of 1/100 is not unreasonable for this fraction. Furthermore, the angular dependence of the dipolar broadening of the narrow low-temperature (4 K) ESR line from a single crystal of high-carbon concentration is consistent with the localized spins being on three-atom chains.¹⁴

The unpaired localized electron on a chain's central carbon atom will tend to spread onto empty states on adjacent locations with comparable energies. A $(B_{11}C)^+$ icosahedron should provide such an opportunity since it has an empty orbital below its principal gap onto which the carbon electron might spread. By contrast, a $(B_{11}C)^-$ icosahedron would not readily accept an electron since all electronic energy levels below its large principal gap ($\approx 10 \text{ eV}$) (Ref. 23) are filled. Furthermore, a B_{12} icosahedron's empty orbitals lie well above those of the isoelectronic $(B_{11}C)^+$ icosahedron due to the absence of the attraction caused by an icosahedral carbon's nucleus. Thus, the electron of a chain-center carbon is presumed more likely to spread onto adjacent $(B_{11}C)^+$ icosahedra than onto adjacent $(B_{11}C)^-$ or B_{12} icosahedra.

The spreading of specific defect spins onto adjacent $(B_{11}C)^+$ icosahedra is dynamic since $B_{11}C$ icosahedra convert between being positively and negatively charged as carriers move through the solid: $(B_{11}C)^- + (B_{11}C)^+ \rightarrow (B_{11}C)^+ + (B_{11}C)^-$.^{3,6,8} Sufficiently rapid changes in spins'

environments result in their having Lorentzian ESR line shapes.

A chain-center-carbon spin's g value is presumed to depend on its spreading onto some of the six icosahedra immediately adjacent to it. At carbon concentrations near 19 at. %, the carbon's electron cannot spread much since most of the adjacent icosahedra are $(B_{11}C)^-$. As the carbon concentration is reduced toward 13 at. % carbon, the density of $(B_{11}C)^+$ icosahedra increases and chain-center carbon's electrons will have increasing opportunities to spread. At 13 at. %, on average three $(B_{11}C)^+$ icosahedra are adjacent to a chain-center carbon. The dispersion in g values will also

increase as the carbon concentration is reduced toward 13 at. %. As the carbon concentration is reduced below 13 at. %, an increasing fraction of the icosahedra become B_{12} 's, while the $B_{11}C$ icosahedra are divided almost equally between $(B_{11}C)^-$ icosahedra and $(B_{11}C)^+$ icosahedra. As a result, on average, the spreading of the carbon's spin should decrease as the carbon concentration is reduced below 13 at. %. The dispersion of the spin's spreading will also fall as the carbon concentration is reduced below 13 at. %. In this manner, the maximizing of the low-temperature ESR line-width at a carbon concentration of 13 at. % is rationalized within the structural model for boron carbides.

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