

Magnetic susceptibility study of boron carbides

L. J. Azevedo, E. L. Venturini, and D. Emin

Sandia National Laboratories, Albuquerque, New Mexico 87185

C. Wood

Jet Propulsion Laboratory, California Institute of Technology, Pasadena, California 91109

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We have measured the magnetic susceptibility of several boron carbides, including B_4C , $B_{15}C_2$, and B_9C , over the temperature range 2–400 K with magnetic fields between 1 and 50 kOe. In general, the susceptibility follows a Curie law with a temperature-independent diamagnetic contribution. There is some ferromagnetic contribution to the susceptibility. However, the density of ferromagnetic impurities is considerably less in our samples than in commercial samples. The paramagnetic spin concentration is compared with the carrier concentration determined by transport measurements (conductivity, Hall effect, and Seebeck effect) on the same samples. The spin concentration is about 2 orders of magnitude smaller than the carrier concentration. We attribute the observed spins to defects and impurities. Thus, our results support the view that the charge carriers are spinless, small, singlet bipolarons.

I. INTRODUCTION

The series of boron carbides B_xC , where x ranges between 4 and 8, hold technological promise as very high temperature semiconductors. For example, these refractory solids are candidate materials for use in thermoelectric generators operating up to 1600 K. However, the physics of the charge transport differs from the conventional semiconductors. In particular, there is very strong evidence to suggest that the charge transport in these degenerate semiconductors is via the hopping of $\sim 10^{21} \text{ cm}^{-3}$ small polarons between geometrically inequivalent sites within the solid.^{1–4}

We have undertaken magnetic susceptibility studies on the same samples used in transport studies in order to help characterize these materials and the nature of charge transport in them. Specifically, if the charge carriers were to possess spin these studies would provide an independent measure of the carrier concentration. In fact, the relatively low estimates of the spin densities ($\sim 10^{19} \text{ cm}^{-3}$) suggest that the charge carriers are spinless, small singlet bipolarons.

Collateral measurements of electronic transport and the spin density of B_4C have been made before. In particular, Geist *et al.* have measured the Hall effect and ESR signal at 300 K on three B_4C samples.⁵ In addition, the electrical conductivity was measured over a significant temperature range (2–200 K). The Hall coefficient was used to determine the carrier density. The carrier density n is generally related to the Hall coefficient R_H by the relation $n = (qR_H)^{-1}(\mu_H/\mu_D)$, where q is the carrier's charge and μ_H and μ_D are the Hall and drift mobilities, respectively. Geist *et al.* assumed that the carriers were high mobility ($\gg 1 \text{ cm}^2/\text{V sec}$) itinerant carriers. As such, the Hall mobility is nearly equal to the drift mobility. Then, the Hall constant directly yields an estimate of the carrier density. In two of the three samples the carrier densities Geist

et al. find are of the order of the ESR-determined spin densities. In the other case, the spin density is three orders of magnitude *smaller* than the carrier density. Furthermore, the mobilities deduced by Geist *et al.* are low (between 10^{-4} and $2 \text{ cm}^2/\text{V sec}$) and increase with temperature. That is, they differ qualitatively from the presumed itinerant carrier behavior. Thus, the analysis is not self-consistent. Nonetheless, Geist *et al.* conclude that the carrier density generally equals the spin density in boron carbides. We believe that the analysis and conclusions are both incorrect.

II. EXPERIMENTAL DETAILS

Our boron carbide samples were bars of dimensions $1 \times 4 \times 8 \text{ mm}^3$, which typically weight 100 mg. The method of preparation of these samples has been described elsewhere.²

Susceptibility measurements were performed with a computer controlled superconducting quantum-interference device (SQUID) magnetometer.⁶ Scatter in the data is typically 0.5% or less. The field dependence of the magnetic moment was studied at 300 and 7 K with fields between 1 and 50 kOe. From the zero-field intercept of the magnetic moment versus magnetic field data we determine the ferromagnetic contribution to the susceptibility. To estimate the concentration of ferromagnetic impurities we assume that the only ferromagnetic impurity is Fe, a major impurity in some commercially available boron. Our cleanest samples have a ferromagnetic contribution equivalent to 6 ppm of Fe. However, the concentration of ferromagnetic impurities in some commercial (Eagle, Picher, and Callery) samples is considerably greater, equivalent to 150 ppm of Fe. Having measured the ferromagnetic contribution to the magnetic moment, the diamagnetic and paramagnetic contributions were determined. This is accomplished by setting the

magnetic field at 5 kOe and measuring the magnetic moment as a function of temperature. We routinely carried out these measurements between 7 and 400 K, although for some samples the measurements were extended down to 2 K.

III. RESULTS

The magnetic moment is the sum of ferromagnetic, paramagnetic and diamagnetic contributions. We assume the validity of the standard expression for the magnetic moment,

$$M = M_f + CH/T + \chi_d H. \quad (1)$$

Here M_f is the ferromagnetic contribution; CH/T is the Curie-law paramagnetic contribution with C being the Curie constant, H is the magnetic field strength, and T is the temperature; $\chi_d H$ is the diamagnetic contribution.

The ferromagnetic contribution is taken to be independent of the magnetic field strength. As such it is measured by the zero-field intercept when the magnetic moment is plotted against magnetic field strength. In Fig. 1 we plot the measured magnetic moment versus the strength of the applied magnetic field for our samples measured at room temperature. We note that the ferromagnetic contribution, as measured by the zero-field intercept, is both small and positive. In addition, the ferromagnetic contribution is independent of temperature. In Table I we list the corresponding values of these ferromagnetic contributions to the magnetic moments.

To determine the paramagnetic and diamagnetic contributions to the magnetic moment, we presume that the paramagnetic contribution follows a Curie law and that the diamagnetic contribution is temperature independent. We therefore plot the magnetic susceptibility dM/dH against reciprocal temperature $1/T$. The occurrence of a straight line implies the validity of our use of Eq. (1). The slope of such a curve is the Curie constant C and the $1/T=0$ intercept is the diamagnetic portion of the susceptibility. Plots of the magnetic susceptibility versus reciprocal temperature for our samples are shown in Fig. 2.

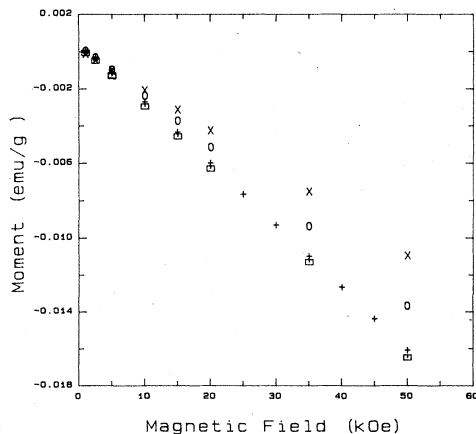


FIG. 1. Room temperature (300 K) magnetic moments of several boron carbides are plotted against magnetic field strength: (+) B_4C ; (\square) $B_{6.5}C$; (\times) $B_{7.5}C$; (\circ) B_9C .

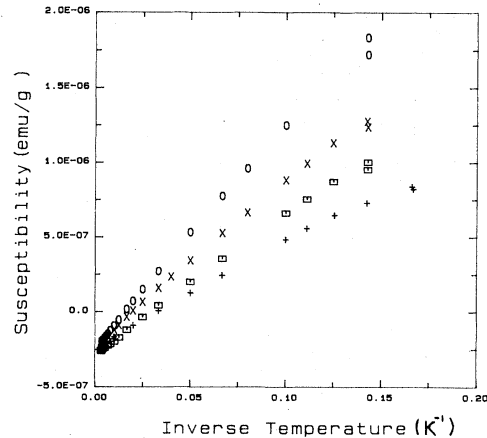


FIG. 2. Magnetic susceptibility measured at 5 kOe is plotted against reciprocal temperature for several boron carbide compositions: (+) B_4C ; (\square) $B_{6.5}C$; (\times) $B_{7.5}C$; (\circ) B_9C .

Except at the lowest temperatures, Eq. (1) is obeyed. Expressing the Curie constant as

$$C = N\mu^2/3k_B, \quad (2)$$

where N is the spin concentration and μ is the magnetic moment of an isolated spin ($g=2$ and $s=\frac{1}{2}$), we can estimate the spin concentrations for our samples. Table I lists the concentrations of paramagnetic spins of our samples. We find that there is one spin for every several thousand atoms. These concentrations are two orders of magnitude less than the carrier concentrations. Furthermore, although the carrier concentration of B_xC generally rises with increasing x , the spin concentration falls with increasing x . We conclude that the spins we are observing are not those of the charge carriers. Indeed, since the spin concentration is very much less than the determined carrier concentration, the carriers must be spinless.

IV. DISCUSSION

Electronic transport data clearly indicate that the charge carriers in the boron carbides move via thermally activated hopping.¹⁻⁴ Namely, the dc conductivities of all samples are activated with an activation energy of 0.16 eV. In addition, the Hall mobilities are low, <1 $\text{cm}^2/\text{V sec}$, and thermally activated with activation energies of about 0.05 eV. These results are consistent with

TABLE I. Ferromagnetic impurity concentration, in ppm, and inverse spin density, in atoms/spin, for several boron carbide compositions. The ferromagnetic impurity concentration is determined from the zero-field intercept of the magnetization. The inverse spin density is dominated from the paramagnetic contribution to the magnetic susceptibility.

Composition	Ferromagnetic contribution (ppm)	Inverse spin density (atoms/spin)
B_4C	6 ± 1	4400 ± 300
$B_{6.5}C$	11 ± 2	3570 ± 220
$B_{7.5}C$	9 ± 4	2720 ± 240
B_9C	27 ± 7	2100 ± 130

the hopping of a temperature-independent density of small polarons. From the magnitude of the preexponential factor of the dc conductivity one estimates carrier densities of B_xC which fall with x but remain of the order of 10^{21} cm^{-3} . Furthermore, analysis of the Seebeck coefficient¹⁻⁴ indicates that the carriers are holes which hop between inequivalent sites. One would like to understand the nature of the charge carriers and the sites between which they hop.

The boron carbides are composed of 12-atom icosahedral units (B_{12} and $B_{11}C$) which are linked together by carbon-containing chains.⁷ It is widely, but not universally,⁸ believed that these chains are carbon-boron-carbon chains.⁷ At the high-carbon end of the single-phase region of the phase diagram B_4C , these materials appear to be regular crystals. At this composition each icosahedron is a $B_{11}C$ units and every potential intericosahedral chain position is filled with a C—B—C chain.⁷ However, the carbon atoms do not generally occupy geometrically equivalent positions within different icosahedra. Thus, there is some disorder. With less carbon some of the intericosahedral chains are removed and some $B_{11}C$ icosahedra are replaced by B_{12} icosahedra.

The boron carbides are examples of boron compounds with electron-deficient bonding.⁷ Here the boron icosahedra contain far fewer electrons than would be required to link all adjacent pairs of boron atoms by two-center bonds. Indeed, within the well-known scheme of two-center bonding it would be impossible to understand the bonding of a boron icosahedron. Namely, how can a boron atom, with only three second-shell electrons, be bonded to five intraicosahedral neighbors and at least one external neighbor? In essence, the answer is that the bonding orbitals in these compounds are molecular orbitals which transcend a single pair of atoms.⁷

Furthermore, in boron compounds with electron-deficient bonding, a fully bounded molecular unit is often not electrically neutral. In particular, it is well known in boron chemistry that the stable state of a boron icosahedron, as in the molecule borane ($B_{12}H_{12}$), is not the neutral state. Rather, the stable state is when the icosahedron garners two extra electrons.^{3,7} In particular, the two added electrons fill the empty bonding orbitals of the neutral icosahedron; that is, they act as a diamagnetically paired singlet. This is energetically favorable because the extra

bonding energy associated with the two added electrons is greater than their Coulomb repulsion. Furthermore, as might be expected, with the addition of the two electrons there is a significant conformational change of the icosahedron.⁷ In other terms, the two added electrons may be regarded as forming a singlet bipolaron.

In the boron carbides the icosahedra involved in electronic transport are the $B_{11}C$ icosahedra rather than B_{12} icosahedra.^{2,3} Here substituting a carbon atom for a boron atom contributes one of the two electrons required to fill the icosahedron's bonding orbitals. Thus, the stable state of a $B_{11}C$ icosahedron is that when it is charged only *singly* negative to form a $B_{11}C^-$.

If a $B_{11}C$ icosahedron were to remain neutral, it would have one unpaired electron, a net spin of $\frac{1}{2}$. However, with bipolaron formation it is energetically favorable for electrons to pair. For example, it is energetically favorable for $2B_{11}C$ icosahedra to form a $B_{11}C^+ - B_{11}C^-$ pair. Namely, two electrons added to two $B_{11}C^+$ icosahedra would both occupy the same icosahedron. Thus, all of the icosahedra's electrons are diamagnetically paired. Electronic transport occurs when a pair of electrons moves from a $B_{11}C^-$ icosahedron to a $B_{11}C^+$ icosahedron. Thus, all of the icosahedra involved in electronic transport are spinless.

In summary, we can understand the small number of paramagnetic spins in the boron carbides relative to the carrier density. Namely, the electronic transport is completely diamagnetic. It involves the hopping of small singlet bipolarons between $B_{11}C$ icosahedra. The observed paramagnetism is associated with defects and impurities (perhaps, "free carbon"). With ESR we hope to elucidate the nature of these paramagnetic states.

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