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Pressure and temperature dependences of the electronic conductivity of boron carbides

G. A. Samara and David Emin
Sandia National Laboratories, Albuquerque, New Mexico 87185

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

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The effects of combined hydrostatic pressure (0—25 kbar) and temperature (300—600 K) on the electronic conductivities of the high-temperature semiconductors B_4C and B_9C were investigated. The conductivities of both materials decrease with pressure. In particular, both the preexponential factor and the activation energy of the conductivities increase with pressure. These results are in semiquantitative agreement with predictions of a model which ascribes electronic transport in these materials to the hopping of small bipolarons between the $B_{11}C$ icosahedra of the boron carbides.

I. INTRODUCTION

The boron carbides $B_{1-x}C_x$ in the composition range $0.1 \lesssim x \leq 0.2$ represent a class of single-phase solids with remarkable mechanical and electronic properties.[1] They are believed to crystallize in a rhombohedral structure D_{3d}^5 ($R\bar{3}m$) consisting of twelve-atom deformed-icosahedral units (B_{12} and $B_{11}C$) bound together by strong intericosahedral linkages.[2,3] These linkages are (a) direct boron-boron bonds (b) three-center boron bonds, and (c) covalent structural units. The latter units are thought to be (i) carbon-boron-carbon chains,[3] (ii) carbon-carbon-carbon chains,[4] and (iii) B_4 parallelepiped structures.[5] The distribution of icosahedral compositions, carbon locations within icosahedra, and intericosahedral linkages impose disorder upon the crystalline superstructure. The boron carbides are highly stable (melting temperature ~2600 K) and have high electrical conductivities and Seebeck coefficients as well as low thermal conductivities.[1] These features have stimulated considerable interest in these materials for possible applications in efficient high-temperature thermoelectric generators.[1] More generally, these materials have potential applications as very-high-temperature semiconductors.

Recent investigations of the high-temperature electronic transport properties including dc conductivity, Hall effect, and Seebeck coefficient measurements, have shown that these properties deviate qualitatively from those of the more conventional high- or low-mobility crystalline semiconductors.[1] Most strikingly, the large Seebeck coefficients increase strongly with temperature. In view of the strong increase of the conductivity with temperature, the temperature dependence of the Seebeck coefficients is anomalous. Analysis of the transport results, along with consideration of the chemistry, indicate that the charge carriers are holes which move by a succession of phonon-assisted hops between electronic states (on inequivalent $B_{11}C$ icosahedra) which are strongly coupled to the atomic motion.[6] This is essentially small-polaron hopping motion. However, the charge carriers provide neither an ESR signal nor a contribution to the magnetic susceptibility,[7] i.e., they are spinless. Thus, they are singlet small-bipolarons[6]—pairs of electronic charge carriers bound together in their mutual polaronic potential well with a state of zero spin.

Since the motion of a small-polaron (or bipolaron) is dependent on the strength of the electron-lattice interaction, on the vibratory excursions of the atoms in the lattice and on the overlap of wave functions between adjacent sites, the application of pressure can be expected to strongly influence this motion. Consequently, we have investigated the effects of combined hydrostatic pressure and temperature on the electronic conductivities of two boron carbides at the extremes of the single-phase region; B_4C and B_9C. As we shall see, the pressure results are consistent with the view that charge transport occurs by small-polaron (small-bipolaron) hopping.

II. EXPERIMENTAL DETAILS

The samples were in the form of thin rods ~0.5—1.0 mm^2 in cross-sectional area and 1—1.5 cm long. They were cut from previously studied[1] polycrystalline slabs prepared from high-purity C and B by vacuum (10^{-5}—10^{-6} Torr), reactive hot pressing (2400 K) at ~400 bars. The grain size was in the range 1—10 μm. Leads were attached by either air-drying silver paint or with an indium-gallium alloy.

Two- and four-lead resistance measurements as a function of temperature at 1 bar gave essentially identical results. Consequently, most of the high-pressure data were obtained by two-lead measurements. The measurements were made in a hydrostatic pressure apparatus using a mixture of normal pentane and isopentane as the pressure fluid. Specimen temperature at high pressure was controlled by resistive heating employing a furnace internal to the pressure cell.[8] Sample conductivity was calculated from the measured resistance without corrections for temperature- and pressure-induced dimensional changes as these corrections were quite small, and they do not affect the conclusions to be drawn.

III. EXPERIMENTAL RESULTS

Figure 1 shows the pressure dependence of the conductivity, σ, of the B_4C sample at 300 and 425 K. We note that σ decreases logarithmically with pressure over the pressure range covered. The magnitude of the slope $\partial \ln\sigma/\partial p$ decreases from -3.66%/kbar at 300 K to -2.35%/kbar at 425 K. This latter feature is seen more clearly in Fig. 2 which shows (semilogarithmic) Arrhenius plots of σT versus $1/T$ between 300 and 600 K at different pressures. The data at 1 bar ($P=0$ in Fig. 2) are in good agreement with earlier results.[1] We note that the data exhibit a single activated regime over most of this temperature range, but there are some deviations at low temperatures. The deviation from Arrhenius behavior at low temperature is a general feature of small-polaron hopping. The linear portions in Fig. 2 are fit by the expression

$$\sigma T = A \exp(-E/k_B T) \ . \tag{1}$$

The form of this expression is that appropriate to the adiabatic hopping of a constant number of small polarons (c.f. Sec. IV).

The pressure dependences of the activation energy E and the preexponential factor A are shown in Fig. 3. Both quantities increase superlinearly with pressure for the B_4C sample. Thus, the observed pressure dependence of σ is the result of a competition between these two effects, but it is the pressure dependence of E which dominates, leading to the observed decrease of σ with pressure.

The B_9C sample exhibited qualitatively similar pressure effects. However, the results were complicated by (1) the conductivity exhibiting two thermally activated regimes between 300 and 600 K and (2) the presence of some ir-

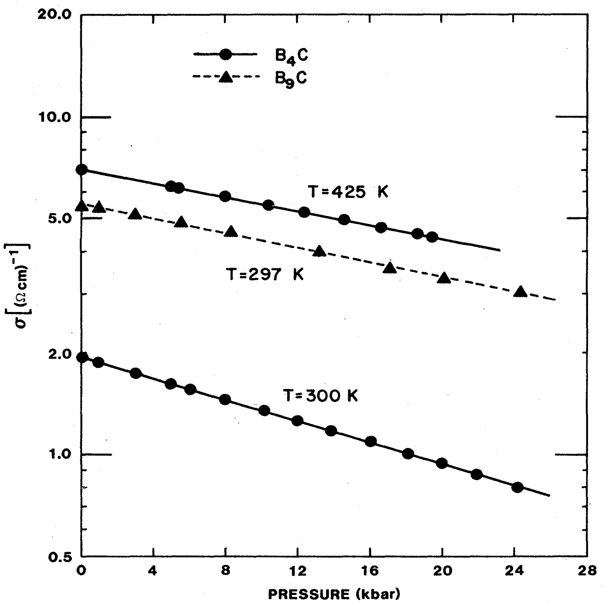

FIG. 1. Pressure dependences of the electronic conductivity σ of B_4C (at 300 K and 425 K) and of B_9C (at 297 K). Note that σ decreases logarithmically with pressure for both materials.

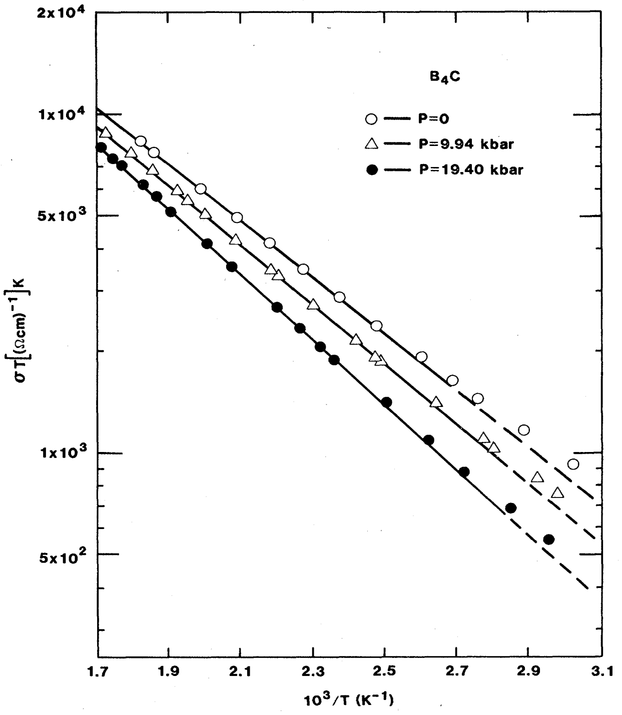

FIG. 2. Arrhenius plots showing the temperature dependence of the electronic conductivity of B_4C at three pressures.

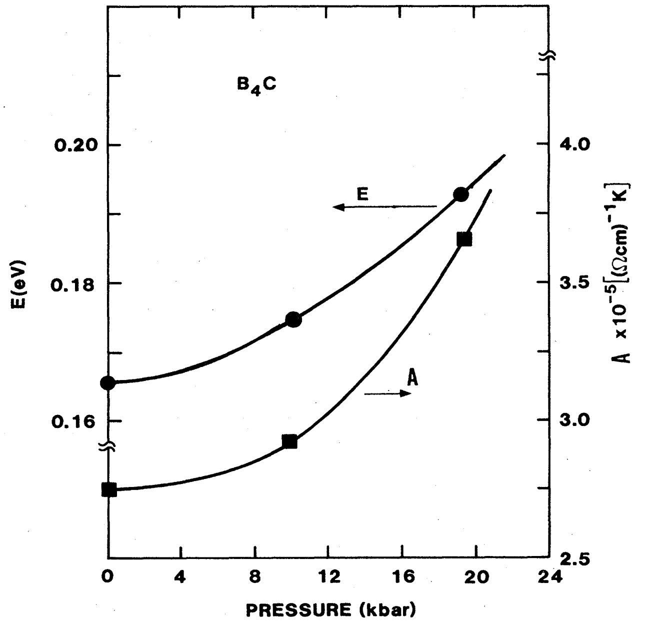

FIG. 3. Pressure dependences of the conductivity activation energy and prefactor for B_4C.

reversible effects after pressure and temperature cycling. At 1 bar, the first (or low-temperature) activated regime was observed below ~ 430 K with $E \approx 0.09$ eV and the second regime was observed above 550 K with $E \simeq 0.15$ eV. Because of the limited temperature range over which linear Arrhenius plots could be measured, it was difficult to accurately determine the pressure dependences of E and A, but we can definitively state that both quantities increase with pressure and the effects in both regimes are of the same order of magnitude as for the B_4C sample. The pressure dependence of σ of B_9C is also comparable to that of B_4C as shown by the dashed line in Fig. 1. At 297 K, i.e., in the low-temperature regime, σ decreases at a rate $(\partial \ln\sigma/\partial p) = -1.8\%/\text{kbar}$.

In view of the above-mentioned difficulties with the B_9C sample, the analysis and discussion in Sec. IV will deal with B_4C only. However, the qualitative arguments should be applicable to B_9C as well.

IV. DISCUSSION

The conductivity σ is given by the usual expression

$$\sigma = n\mu q \ , \tag{2}$$

where n is the number of charge carriers (holes), N, per unit volume V, (i.e., $n = N/V$), μ is the mobility of the charge carrier, and q is the electronic charge. The earlier analysis of the transport data on the boron carbides at 1 bar (Ref. 1) suggested that these data are consistent with the hopping of a large ($\sim 10^{21}$ cm^{-3}), temperature-independent number of small polaronic holes, N. Here, we shall assume that N is also pressure independent. We emphasize that this is an assumption. Without it, it would be difficult to interpret the present conductivity data in the absence of mobility measurements under pressure. Under this assumption, the temperature and pressure dependences of the conductivity are determined by changes in μ and the sample volume V. When the transfer energy characterizing the hopping of bipolarons is sufficiently large (as the Hall mobility and Seebeck coefficient results suggest in this case[1,6]), the charge adiabatically follows the atomic motion. This results in a mobility that varies with temperature as

$$\mu = \left[\frac{qr^2\nu}{k_B T}\right]\exp(-E_a/k_B T) \ . \tag{3}$$

Here, r is the distance between hopping sites, ν is the characteristic vibrational frequency, and E_a is the hopping activation energy. In the boron carbides we envision hopping to occur between icosahedra. Hence, r is an *inter*icosahedral distance and ν is a characteristic *intra*icosahedral vibrational frequency. It is the $1/T$ factor in the prefactor in Eq. (3) which motivated us to plot σT rather than σ versus $1/T$ on a semilogarithmic scale in Fig. 2.

Combining Eqs. (2) and (3) yields

$$\sigma T = \left[\frac{nq^2r^2\nu}{k_B}\right]\exp(-E_a/k_B T) \ . \tag{4}$$

Comparison of this result with Eq. (1) produces the following identifications:

$$E = E_a \tag{5}$$

and

$$A = \frac{nq^2r^2\nu}{k_B} \ . \tag{6}$$

We now examine the pressure dependences of A and E separately. From Eq. (6) it is readily seen that the pressure dependence of A is given by

$$\frac{\partial \ln A}{\partial p} = \left[\frac{\partial \ln n}{\partial p}\right] + 2\left[\frac{\partial \ln r}{\partial p}\right] + \left[\frac{\partial \ln \nu}{\partial p}\right] . \tag{7}$$

Although the exact pressure dependences of n, r, and ν are not known for the boron carbides, we can make good order-of-magnitude estimates of these effects, and therefore, of $\partial \ln A/\partial p$. With compression, the intericosahedral distance r is expected to decrease, and ν to increase. To a good approximation, r should scale with the lattice constant a. For many hard materials such as the boron carbides, the isothermal volume compressibility is

$$\kappa \equiv -(\partial \ln V/\partial p)_T = -3(\partial \ln a/\partial p)_T \simeq 1\times 10^{-3}/\text{kbar} \ ,$$

and the mode Gruneisen parameter γ for vibrational frequencies is

$$\gamma \equiv -(\partial \ln\nu/\partial \ln V) = \kappa^{-1}(\partial \ln \nu/\partial p) \approx 2 \ .$$

Noting that $n \sim a^{-3}$ and $r \sim a$, it is readily seen that Eq. (7) yields

$$(\partial \ln A/\partial p) \simeq 2.3\times 10^{-3}/\text{kbar} \ .$$

This compares quite favorably with our experimentally determined logarithmic pressure derivatives, namely $(\partial \ln A/\partial p) \simeq 1.5\times 10^{-3}/\text{kbar}$ (initial slope) for B_4C. For B_4C, $A(p)$ is nonlinear (as shown in Fig. 3). The average value of $(\partial \ln A/\partial p)$ between 0 and 20 kbar is $\sim 10\times 10^{-3}/\text{kbar}$. For the present purposes we consider this value to also be in reasonable agreement with the above estimate of $2.3\times 10^{-3}/\text{kbar}$.

We now consider the pressure dependence of E. We recall that a hop of a small-polaron between a pair of sites occurs when the atoms surrounding these two sites are displaced from their equilibrium locations in such a manner that the electronic energies associated with the carrier occupying these sites momentarily equal one another.[9] The hopping activation energy, E_A, is the minimum strain energy required to establish this momentary degeneracy. This strain energy varies as the square of the required atomic displacements. These, in turn, are proportional to the electron-lattice coupling parameter, F: the change in the carrier's electronic energy per unit atomic displacement.

As the interatomic separations in the vicinity of the carrier are reduced by pressure, the sensitivity of the carrier's energy to the positions of the atoms about it is increased. That is, the electron-lattice interaction strength, F, is augmented. Due to its proportionality to F^2, the hopping activation energy is increased. We can estimate this effect by considering a square-well model for the trapped carrier. Here, the energy of the carrier in such a well is given by

$$\mathscr{E}=\hbar^2/2mb^2\,, \tag{8}$$

where m is the carrier's mass and b is the width of the well, which we envision to be of the order of the size of an icosahedron. The electron-lattice interaction F is

$$F=-\partial\mathscr{E}/\partial b \propto b^{-3}\,, \tag{9}$$

and the hopping activation energy of the standard small-polaron theory is

$$E_a=F^2/4k \propto b^{-6}\,, \tag{10}$$

where k is the local stiffness. Assuming that b scales with the lattice parameter a, Eq. (10) yields

$$(\partial \ln E_a/\partial p)=2(\partial \ln F/\partial p)\approx -6(\partial \ln a/\partial p)$$
$$\approx 2\times 10^{-3}/\text{kbar}\,.$$

This pressure derivative also compares very favorably with that deduced from the experimental results, namely $\partial \ln E/\partial p=1.6\times 10^3/\text{kbar}$ (initial slope) for B_4C.

In obtaining this estimate, we have ignored the pressure dependence of the *local* stiffness k. Indeed, *lattice* stiffness is generally increased upon compressing the lattice. However, we should also note that, with small-polaron formation, the presence of a charge carrier also stresses the lattice. In fact, the stresses near a localized charge generally exceed that imposed by hydrostatic pressure (at 25 kbar) by at least an order of magnitude. Thus, consistent investigation of pressure-induced stiffness changes requires inclusion of carrier-induced stiffness changes.[10]

For example, with a carrier-induced expansion the local stiffness is reduced. Upon applying pressure the lattice is compressed. However, with this compression the electron-lattice coupling strength is increased. This increases the carrier-induced lattice expansion forces opposing compression. As a result, the compression and the accompanying stiffening of the lattice in the neighborhood of the carrier is less than it otherwise would be. In fact, with typical estimates of the parameters, the pressure-induced increase of the lattice stiffness in the vicinity of the carrier is largely prevented by the increase of the electron-lattice expansionary forces.[10]

Thus, our estimate of the pressure-dependent increase of the hopping activation energy oversimplified matters. It simply ignored the increase of the local stiffness with compression. The fact that the observed hopping activation energy *increases* with pressure implies that this is a reasonable approximation in this instance.

V. CONCLUDING REMARKS

The above considerations have shown that both the preexponential term, A, and the activation energy, E, increase with hydrostatic pressure. It is the predominance of the pressure dependence of E which is responsible for the observed *decrease* of the electronic conductivity of the boron carbides with pressure. The experimental results are in semiquantitative agreement with straightforward predictions of a model which ascribes electronic transport in these materials to the hopping of small bipolarons. Thus, these results provide support for the model. We should caution, however, that although our analysis is based solely on this model, we cannot, on the basis of the present data alone, rule out other mechanisms for electronic transport in these materials.

Finally, we note that, interpreted in terms of a small-polaron model, the present study is one of a few pressure studies on small-polaron systems. However, unlike the case of molecular small-polaron systems, where the conductivity increases with pressure due to increased overlap between adjacent sites (which is reflected by a large and dominant increase in A with pressure),[11] in the present case, the pressure dependence of σ is dominated by the increase in E. In this sense the increase of the hopping conductivity with pressure is anomalous. This is a manifestation of the distinctive bonding of the boron carbides. Namely, *inter*site (intericosahedral) bonding is stronger than *intra*site (intraicosahedral) bonding. Thus, the results indicate that with pressure, the sites (the icosahedron) are compressed more than the intersite (intericosahedral) separations. As a result, the predominant effect is the increase of the hopping activation energy with pressure.

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