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Physical Properties of a Novel Layered Compound; Scandium Boron Carbide $Sc_2B_{1.1}C_{3.2}$

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Physical properties of the new compound $Sc_2B_{1.1}C_{3.2}$, with-$[B_{1/3}C_{2/3}]_\infty$- graphite-like layers, were investigated and similarities to GICs observed, i.e. quadratic temperature dependence of resistivity and paramagnetic orbital susceptibility. Interestingly, it was indicated that 2D Anderson localization occurs at low temperatures. This was attributed to possible disorder in the -$[B_{1/3}C_{2/3}]_\infty$-layers.

Keywords: layered material; graphite-like; rare earth borocarbides; conductivity; specific heat; orbital magnetic susceptibility; localization

INTRODUCTION

The properties of layered materials have been extensively studied in recent years, with the graphite intercalation compounds (GIC) providing a particularly fertile field of research[1]. Quite recently, a new scandium boron carbide compound $Sc_2B_{1.1}C_{3.2}$ was discovered[2], having a new structure type of rare-earth boron carbides. The trigonal crystal structure (a=b=23.710(9)A, c=6.703(2)A, P3m1) is composed of alternate –$[B_{1/3}C_{2/3}]_\infty$-Sc-C-Sc-$[B_{1/3}C_{2/3}]_\infty$- layers (Fig. 1). A particularly interesting structural feature was that the boron and carbon atoms –$[B_{1/3}C_{2/3}]_\infty$-appear to form a puckered graphite-like layer within the compound. To our knowledge, only three compounds have been reported with the $[BC]_\infty$ graphite like framework, LiBC[3], MgB_2C_2[4] and BC_3[5]. Furthermore, the -Sc-C-Sc- layers could be removed from the compound with

the application of nitric acid. In other words, the Sc-C-Sc constituents are reminiscent of intercalants in a graphite-like compound and therefore of high practical and fundamental interest. It is to be noted that these compounds were synthesized by solid state reaction. In order to investigate the physical properties of this compound, the following measurements were performed on single crystals.

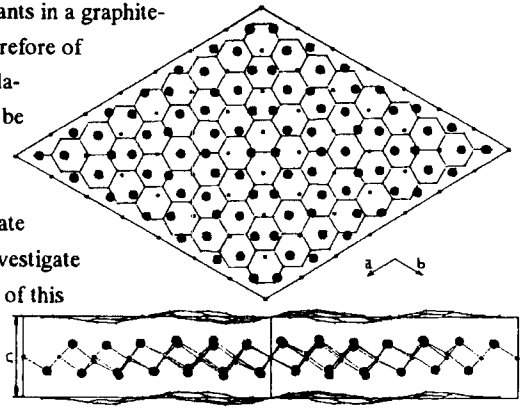

Figure 1: Structure of $Sc_2B_{1.1}C_{3.2}$ determined from crystallographic measurements. Projection of $Sc_2B_{1.1}C_{3.2}$ structure on a-b plane (top) and (110) plane (bottom). The large filled circles represent scandium atoms in different layers. Small solid circles represent the boron and carbon mixed layer, while medium gray circles indicate carbon atoms.

Experimental

The $Sc_2B_{1.1}C_{3.2}$ crystals measured were grown and characterized as described previously[2]. The typical four-probe method was used to measure the resistivity and the Hall effect. The specific heat was measured by a transient heat pulse method. Magnetic susceptibility was measured with a SQUID magnetometer.

Results and Discussion

The temperature dependence of the in-plane resistivity is given in Fig. 2. A metallic type temperature dependence is observed down to 80 K. A fit of the temperature dependence of the resistivity between 300 K and 80 K as

$$\rho = \rho_0 + \rho_1 T^n \qquad (1)$$

yielded n=2.02. Since it is indicated that the major conduction mechanism in this temperature region is quadratic, we refit with n=2, and obtained ρ_0=490 $\mu\Omega$, ρ_1=2.0x10^{-10} Ω/K^2. The temperature independent resistivity takes a relatively large value.

The quadratic temperature dependence of the resistivity has been observed in GICs and has been attributed to a carrier-carrier scattering mechanism[6,7]. This temperature dependence indicates that we are observing the conduction pertaining to the graphite-like layers, i.e. there is charge transfer from the scandium atoms and it is not simply conduction of metallic scandium, for example. A low temperature upturn of the resistivity is observed around 70 K.

The origin of this will be discussed later.

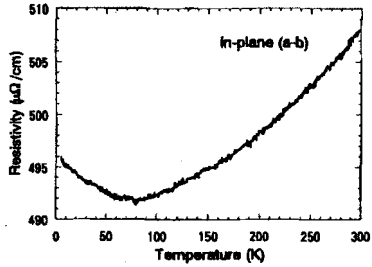

Figure 2: Temperature dependence of the in-plane resistivity of $Sc_2B_{1.1}C_{3.2}$. The dotted line indicates the fitted curve of $\rho = \rho_0 + \rho_1 T^2$.

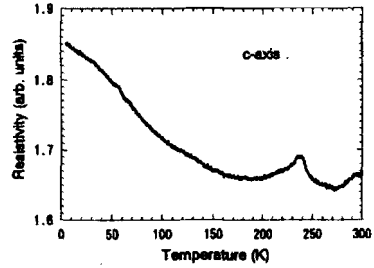

Figure 3: Qualitative temperature dependence of the c-axis resistivity of $Sc_2B_{1.1}C_{3.2}$. The data is plotted versus an arbitrary scale.

The absolute values of the c-axis resistivity was difficult to measure, as dimensions of the samples in this direction were very small. Therefore, we only present qualititative results in Fig. 3. The particular temperature dependence was reproducible and observed for different methods of measurement.

In contrast to the in-plane resistivity, the c-axis resistivity increases with decreasing temperature. An anomaly is observed at around 240 K and a bend in the curve can be seen around 60 K. Some kind of structural transition may account for this behavior. However, at present it is not clear.

The Hall coefficient R_H was determined to be $-1.5 \times 10^{-3} cm^3/C$ at 300 K. The negative value indicates that the majority of carriers are electrons and corresponds to 4.1×10^{21} carriers $/cm^3$ or 0.14 carriers/Sc atom. Little temperature dependence was observed with 3.6×10^{21} carriers/cm^3 at both 80 K and 5 K. Although the band structure of the compound is not clear, the small number of carriers/Sc atom may be due to the fact that the [BC] graphite-like layer is expected to be electron deficient compared to graphite. A broad minimum is observed in the in-plane resistivity (Fig. 2). To investigate this behavior further we investigated the magneto-

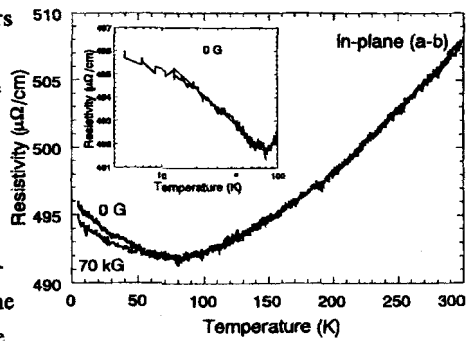

Figure 4: Temperature dependence of the in-plane resistivity of $Sc_2B_{1.1}C_{3.2}$ at zero field (bold line) and 70 kG (gray line). The zero field data is the same as that of Fig. 1. The inset figure is the in-plane resistivity below 100 K plotted versus logT. The line is a guide to the eye.

resistance. A negative magnetoresistance is observed at low temperatures, as shown in Fig. 4. Furthermore, the increase in resisitivity plotted in the inset of Fig. 4, appears to follow a logT dependence, with a little saturation at low temperature.

Two possibilities to account for this behavior come to mind:

(1) the Kondo effect, due to magnetic impurities[8], or

(2) 2D Anderson localization in the weakly localized regime, due to disorder[9,10].

Since the residual resistivity of our sample is rather large, and the impurity content not so high (to be given later), we judge that case (1), the Kondo effect is not likely. Furthermore, the idea that appreciable disorder exists in the sample leading to a localized state, is also supported by the structure. X-ray results indicated that the graphite-like layer of boron and carbon atoms is disordered, i.e. bond lengths could not be assigned to an ordered array of B and C within the plane.

The magnetic field dependence of the resistivity at 5 K and 100 K is shown in Fig 5(a) and 5(b), respectively. The negative magnetoresistance is observed at 5 K, with none at 100 K. Although, the signal to noise ratio is not good, the field dependence is not inconsistent with that expected for 2D Anderson localization in the weakly disordered regime[11].

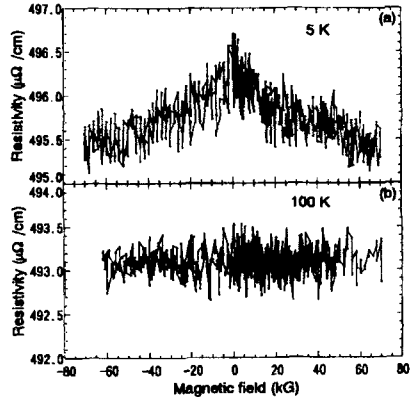

Figure 5: Magnetic field dependence of the in-plane resistivity of $Sc_2B_{1.1}C_{3.2}$ at (a) 5 K and (b) 100 K.

The specific heat of $Sc_2B_{1.1}C_{3.2}$ is plotted in Fig. 6, in the conventional C/T versus T^2 plot in the temperature range between 2 K and 42 K. A linear curve is obtained, indicating that the specific heat can be described well as the sum of a linear electronic specific heat term and phonon T^3 term:

$$C=\gamma T + C_2T^3. \qquad (2)$$

The parameters γ=3.59 mJ/mol/K^2 and C_2=48.3 μJ/mol/K^4 are determined. The density of states at the Fermi energy $D(E_F)$ and the Debye temperature θ_D are determined to be 2.3x10^{22} states/eV cm^3 and 633 K, respectively. θ_D is higher than that of many GICs, and probably reflects a higher phonon density of states

at higher energies due to the lighter boron atoms.

The static magnetic susceptibility perpendicular to the c-axis of $Sc_2B_{1.1}C_{3.2}$ is given in Fig. 7. The data can be fit well as a temperature independent term $5.7x10^{-5}$ emu/mole and Curie-Weiss term with a Curie constant of $1.6x10^{-3}$

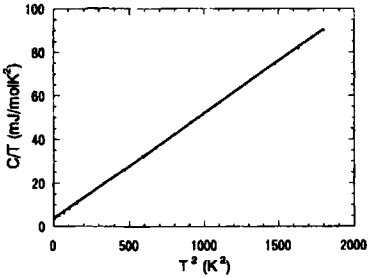

Figure 6: Specific heat of $Sc_2B_{1.1}C_{3.2}$ plotted as C/T versus T^2. The line indicates the fitted curve to eq. (2), with γ=3.59 mJ/mol/K^2 and C_2=48.3 μJ/mol/K^4

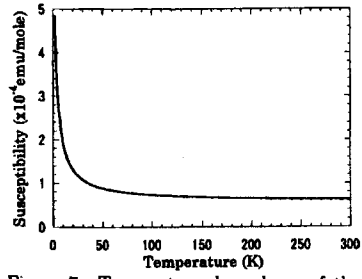

Figure 7: Temperature dependence of the static magnetic susceptibility of $Sc_2B_{1.1}C_{3.2}$. The dotted line indicates the fitted curve as a sum of a temperature independent term and Curie-Weiss term.

emu/moleK and Curie-Weiss temperature θ= -1.8 K. We attribute the Curie-Weiss term to magnetic impurities and/or paramagnetic localized spins in the sample. If a single kind of magnetic impurity is assumed, the maximum number of impurities in our sample can be calculated to be $1.3/p^2$%, where p is the effective number of Bohr magnetons.

The total susceptibility χ in these kinds of systems is comprised of

$$\chi=\chi_0+\chi_{orb}+\chi_C+\chi_P \quad (3)$$

where χ_0 is the diamagnetism from core electrons, χ_{orb} is the orbital susceptibility and χ_C is the Curie (or Curie-Weiss) contribution from paramagnetic spins and χ_P the Pauli paramagnetism from free carriers, which we estimate from the specific heat results, ignoring effects from electron-phonon and electron-electron enhancement. As a result, we obtain the orbital susceptibility χ_{orb} of $Sc_2B_{1.1}C_{3.2}$ to be $47x10^{-6}$ emu/mole, which is paramagnetic. Orbital paramagnetism has been observed in GICs. This was attributed to both interband and intraband effects[12,13]. However, it is not clear at present whether the same physical picture applies to $Sc_2B_{1.1}C_{3.2}$.

Conclusions

Finally, to summarize, we have observed properties similar to those of GICs in the new layered compound $Sc_2B_{1.1}C_{3.2}$, which has a boron and carbon mixed

graphite-like layer. Namely, anisotropy of the temperature dependence of resistivity, the quadratic temperature dependence of in-plane resistivity, and paramagnetic orbital susceptibility.

A further interesting characteristic was that a logT increase in resistivity and negative magnetoresistance was observed, indicative of 2D Anderson localization. We take the origin to be disorder in the boron and carbon graphite-like layer, possibly due to the fact that the boron and carbon composition of $-[B_{1/3}C_{2/3}]_\infty-$ has never been observed before, and may not be the optimum composition to form well ordered graphite-like layers.

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