

c-axis electrical resistivity of SbCl_5 -graphites

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c-axis electrical resistivity was measured from 1.5 to 300 K on the acceptor-type SbCl_5 -graphite intercalation compounds of stages 1–6 and 10. The resistivity of the compounds is up to an order of magnitude larger (10^{-3} – 10^{-2} Ω m) than that of the parent highly-oriented pyrolytic graphite material, indicating that the mean free path is comparable to an atomic spacing. In spite of this large resistivity an entirely metallic temperature dependence of resistivity is observed for stages 1–3. Higher-stage compounds show metallic character only at high temperatures; as the temperature decreases one observes a crossover to an activated dependence of the resistivity. A model, based on defect-mediated short-circuiting channels, is proposed in order to reconcile the metallic dependence with the large *c*-axis resistivities observed in these compounds.

The electrical-transport properties of graphite intercalation compounds have been an increasingly active area of research in recent years.¹ Nearly all of these studies, however, are confined to investigations of the in-plane electrical conductivity; very few² address the interesting question of electrical transport in the direction of the *c* axis.

We report here on measurements of the *c*-axis resistivity of various stages of highly-oriented pyrolytic graphite (HOPG) intercalated with SbCl_5 , in the temperature range 1.5–300 K. The structural, thermal, and in-plane electrical properties of these graphite intercalation compounds (GIC's) have recently been investigated at this institution^{3–5} and elsewhere.^{6,7}

The electrical resistivity in the *c* direction was measured by a standard four-probe dc technique. Unlike the case of the in-plane measurements, the large resistivity anisotropy ρ_c/ρ_a does not lead here to difficulties with nonuniform current injection.

Samples (typically $10 \times 10 \times 0.5$ mm³) were intercalated by the standard two-zone vapor method starting with Union Carbide HOPG and highly purified SbCl_5 . Stage fidelity of all compounds has been determined by x-ray diffraction. Electrical contacts, made in the form of thin oxygen-free high-conductivity (OFHC) copper plates (for current probes) and small platinum disks (for voltage probes) were attached to the sample with a silver-loaded General Electric 7031 varnish (see inset in Fig. 1). Sample currents were in the range 1–10 mA and voltages were measured by a Keithley Model 181 nanovoltmeter. We have tested for the Ohmic character and the current independence of the resistivity over the range 10^{-6} – 10^{-1} A cm².

The overall temperature dependence of ρ_c for SbCl_5 graphite of stages 1–3 is shown in Fig. 1, and those of stages 4, 6, and 10 in Fig. 2. For comparison, the *c*-axis resistivity⁸ of the parent material, HOPG, is also shown in both figures. There are several interesting phenomena which we describe in turn.

First, the *c*-axis resistivity of all intercalated samples is significantly larger than the resistivity of HOPG, a feature common to all acceptor type GIC's.⁹ However, what is striking and unexpected is the temperature dependence associated with such

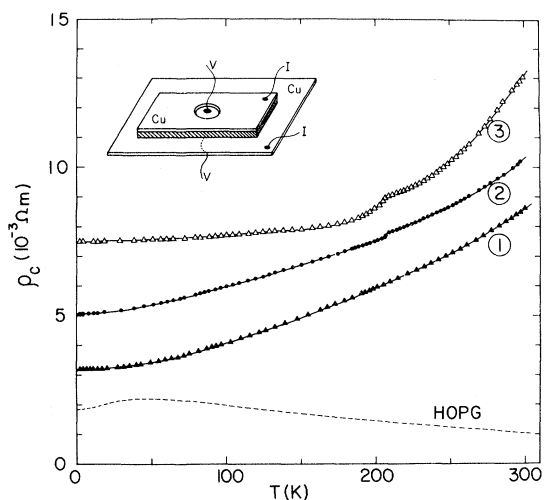


FIG. 1. Temperature dependence of the *c*-axis electrical resistivity of SbCl_5 graphites. Stage index is indicated by a circled number. *c*-axis resistivity of HOPG is shown by a broken curve. Inset illustrates an arrangement of the electrical probes.

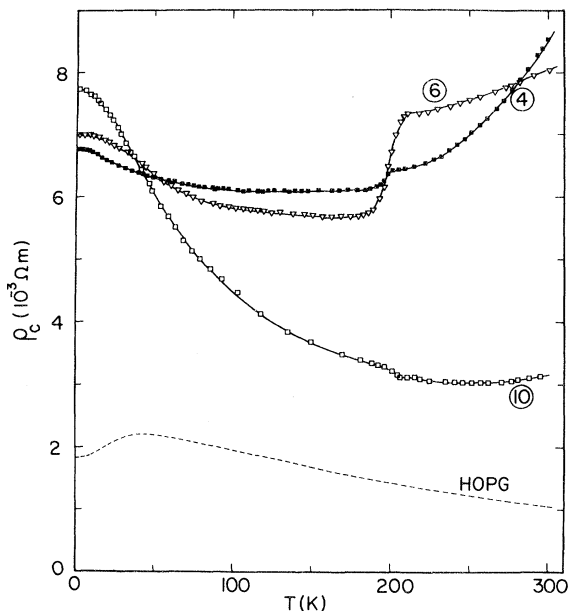


FIG. 2. Temperature dependence of the c -axis resistivity of higher stages of SbCl_5 graphites. Again, a broken curve shows a behavior of the c -axis resistivity of HOPG.

a large resistivity. We notice in Fig. 1 that stages 1–3 show a metallic character of the resistivity (positive temperature coefficient) throughout the temperature range, 1.5–300 K, yet their resistivities are of the order of 10^{-3} – 10^{-2} Ω m. This is at least 2 orders of magnitude larger than the inverse of the minimum metallic conductivity,

$$1/\sigma_{\min} = (0.026e^2/\hbar a)^{-1}, \quad (1)$$

which, according to Mott,¹⁰ is a condition for the onset of localization of electron wave functions. An alternative criterion states that the mean free path of charge carriers cannot be smaller than the interatomic spacing. Since the mean free path of carriers in HOPG near the resistivity maximum at 40 K is already quite small¹¹ at 15–20 Å it is obvious from the resistivity of SbCl_5 graphites that their mean free paths cannot be much larger than the interatomic spacing. In any case, it is difficult to reconcile the coexistence of the metallic temperature dependence with such very large resistivities as are observed in our low-stage SbCl_5 graphites. Indeed, the extremely large anisotropy of the resistivity, $\rho_c/\rho_a > 10^6$, observed in SbCl_5 graphites suggests that it is very likely that virtually all carriers are directionally localized, i.e., they can move freely along the planes, but are unable to diffuse across the stack of layers. In order to explain the metallic temperature dependence in Fig. 1 we propose that there exist very narrow, highly-conducting “channels” in

the c direction. The most likely candidates to provide such channels are extensive arrays of defects which have their origin in the intercalation process.^{12,13} Since the density of defects increases with decreasing stage,⁹ one would then expect the metallic character to be particularly strong for the lowest stages; this trend is indeed observed.

Compounds of stages higher than 3 show an additional feature (see Fig. 2): The metallic character of the resistivity crosses over to an activated behavior¹⁴ (negative temperature coefficient). The temperature of the cross-over point is strongly stage dependent, e.g., from 130 K for stage 4 up to 260 K for the stage 10. Note also that for stages $N > 1$ one observes an anomaly near 210 K which has its origin in the commensurate-incommensurate transition that we have described earlier.⁴

The crossover from metallic to activated character of the temperature dependence normally signals an onset of metal-insulator transition. If we adopt this interpretation together with our assumption of the existence of highly-conducting, defect-mediated channels, the data of Figs. 1, 2, and 3 can be explained in the following way.

We suppose that transport along the c axis of low-stage compounds is determined entirely by the conductivity of highly conducting channels, most of the π electrons being localized along the c axis. As the stage increases from 1 to 3, either the number of channels or their cross section decreases, resulting in an increase of the resistivity (Fig. 3) and a concurrent decrease of the magnitude of an otherwise positive temperature coefficient (Fig. 1). For compounds of stages higher than 3, simultaneously with

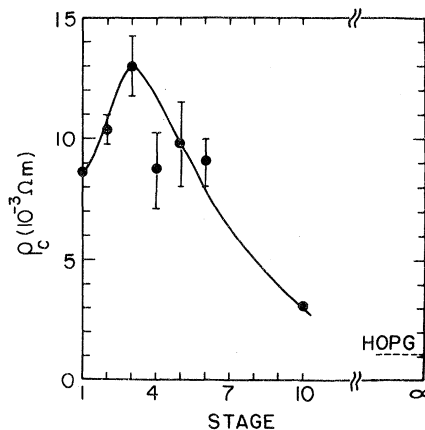


FIG. 3. Stage dependence of the c -axis resistivity measured at room temperature. Error bars indicate the spread of the values obtained on at least four different samples for each stage in the range 2–6. Only a single sample was available for stages 1 and 10.

the decrease of the room-temperature resistivity, one observes a limited temperature range where activation sets in. We believe that this behavior indicates a significant reduction in the density of defects as the stage increases. The strongly stage-dependent crossover temperature of metallic-to-activated behavior shown in Fig. 2 may be related to this reduction of the defect density but the actual mechanism is unclear. The conduction can then proceed only by a thermally activated process among the localized levels such as, e.g., hopping. Of course, as the compounds become more and more dilute, one expects them to approach the behavior of the parent material, in this case HOPG. The wide activation range observed on the stage-10 compound as well as the value of its room-temperature resistivity confirms this trend.

It is important to realize that the activated behavior of the c -axis resistivity for $N > 3$ does not lead to an infinite resistivity as $T \rightarrow 0$; rather, the resistivity curves show saturation below 10 K. In fact, in several cases, we have detected a very small decrease in the resistivity near 1.5 K. This behavior is then reminiscent of the c -axis resistivity of HOPG and exfoliated graphites which is discussed else-

where.¹⁵

In many respects the c -axis transport in graphite and its intercalation compounds is more fascinating than the transport along the graphitic planes. The interplay of the band conduction and localization makes graphite a unique system. The crux of the problem in acceptor-type intercalation compounds such as SbCl_5 graphites is a large c -axis resistivity accompanied by a metallic temperature dependence. We do not see how one can reconcile such an observation without recourse to some kind of spatially limited, highly-conducting channels.

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¹⁴The existence of a region with a negative temperature coefficient of resistivity indicates that the highly-conducting channels cannot be associated with any "short-circuiting" via an in-plane component (path tortuosity effect) because the in-plane resistivity ρ_a of all stages of SbCl_5 graphites is entirely and strongly metalliclike.

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