Hall effect and resistivity of stage-2 SbCl$_5$ intercalated graphite

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The Hall coefficient and the dc resistivity were measured in the basal plane of stage-2 SbCl$_5$ intercalated graphite between 4.2 and 300 K. The Hall coefficient R_H during the first cooling of a sample is 0.57×10^{-8} m^3 C^{-1} and is from the carriers in the two basic graphitic energy bands. R_H is larger and has a maximum between 100 and 150 K in subsequent coolings. The change is attributed to the truncation of the basic Fermi surface by the periodicities of the in-plane intercalant structures. The resistivity at room temperature is $(8\pm2) \times 10^{-5}$ Ω cm. It decreases as the temperature is lowered from the change in electron-phonon scattering. There is also a large decrease of resistivity in a small temperature range during the first cooling of some samples. This is attributed to an initial change from disorder to order of the in-plane structure. The resistivity anisotropy is 1.6×10^4.

The stage-2 graphite-intercalation compound (GIC) made from SbCl$_5$ has been studied extensively because it has many interesting properties. The in-plane structures of the ions are ordered with respect to the hexagonal graphite lattice and include the $(\sqrt{7} \times \sqrt{7})R$ 19.11° commensurate lattice and the $(\sqrt{39} \times \sqrt{39})R$ 16.1° discommensurate structure. Most interestingly, there is a commensurate-incommensurate phase transition at 210 K. These structures have been detected by x-ray[1] and electron[2-4] scattering experiments. The phase transition is evident in some other properties such as the specific heat[5] and magnetic susceptibility.[6]

Several structures can coexist because there may be several phases that contain SbCl$_6^-$ and SbCl$_3$ in two ionic states Sb^{5+} and Sb^{3+}, as indicated by Mossbauer experiments.[7] There can also be a glassy phase in the low-temperature region below the transition. However, the appearance of this phase is strongly dependent on samples and sample conditions during cooling.

Several de Haas–van Alphen (dHvA) spectra can be observed in the stage-2 compound. There are two dominant frequencies of 422 and 1190 T with samples that are examined immediately after they are made, and are cooled slowly from room temperature to 4.2 K for the experiments.[8] These frequencies are identified with the two basic graphitic energy bands that are expected from energy-band calculations.[9] There is no indication of the in-plane intercalant structure in this simple dHvA spectrum. However, with old samples and samples that are cooled quickly from room temperature, the dHvA spectrum consists of many frequencies. Some of these have been identified with the effects of the in-plane structure.[10] The periodicities of the phases form periodic zones in reciprocal space that divide the Fermi surface of the basic bands into electron and hole sections, each of which has a characteristic dHvA frequency.

The purpose of the present work is to present properties of the Hall effect and the resistivity in the (001) plane of the stage-2 SbCl$_5$ GIC and to relate them to the electronic properties of the compound. Previously, the in-plane resistivity was studied by a 40-kHz power absorption method,[11] as a function of pressure by a contactless

method[12] and to accompany a transmission-electron-microscopy experiment.[13] The c-axis resistivity was measured by a standard four-probe dc technique.[14] The Hall effect of the SbCl$_5$ GIC has not been reported previously.

The stage-2 SbCl$_5$ GIC samples were made by immersing small pieces of highly oriented pyrolytic graphite in liquid SbCl$_5$ and heating the reaction vessel for one week at 110 °C. The samples were examined by x-ray diffraction, which showed no evidence of diffraction from other stages and from graphite. The dimensions of the samples were of the order $3 \times 3 \times 0.5$ mm^3. More than ten samples were used to provide a complete study. In order to have a thin and narrow sample, the samples were cut in half and peeled off by Scotch tape. A cryostat was used for measurements in the temperature range between 4.2 and 300 K. Magnetic fields up to 1.8 T were provided by an electromagnet. The classical, four-probe method was used with silver paste contacts with apparatus that has been described previously.[15] The Hall coefficient was calculated from

$$R_H = \frac{Vd}{BI}, \qquad (1)$$

where V is the Hall voltage, d is the sample thickness, B is the applied magnetic field, and I is the current.

The Hall coefficient of the stage-2 SbCl$_5$ GIC depends on the thermal history of a sample. The temperature dependence of two samples that were measured shortly after they were made is given in Fig. 1. R_H has a value of 0.57×10^{-8} m^3 C^{-1} between room temperature and 4.2 K during the first cooling cycle a to b in Fig. 1. It increases from 0.57×10^{-8} to 1×10^{-8} m^3 C^{-1} at room temperature during the first return warming cycle. In subsequent cycles, there is no difference in R_H for the cooling and warming cycles. R_H follows c to d in Fig. 1 with a maximum of 1.25×10^{-8} m^3 C^{-1} at 150 K and a value of 1×10^{-8} m^3 C^{-1} at 4.2 K. The similar results in Fig. 1 for two samples with different thicknesses indicate the reproducibility of the temperature dependence and that it is not dependent on sample thickness.
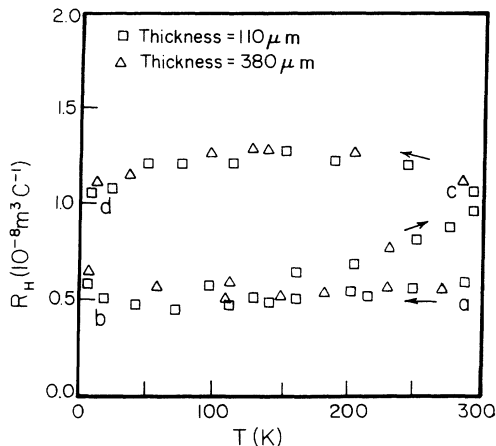
The Hall coefficient is larger with older samples (six

FIG. 1. Temperature dependence of the Hall coefficient for the first two temperature cycles of a stage-2 SbCl$_5$ GIC sample.

FIG. 3. Temperature dependence of the in-plane resistivity of a stage-2 SbCl$_5$ GIC sample for its first two temperature cycles.

months to two years old) and has a maximum at about 100 K as shown in Fig. 2. The temperature dependence is the same for warming and cooling and there is no indication of a transition at 210 K.

The sign of R_H was also determined by identifying the direction of the magnetic field with a small bar magnet and by measuring the Hall coefficient of copper. Both methods confirm that R_H is positive in the stage-2 SbCl$_5$ GIC, and that it is an acceptor compound as was shown previously by thermopower measurements.[16]

Figure 3 shows the resistivity of a sample for the first two thermal cycles after it was made. Upon cooling from room temperature (point a in Fig. 3), there was a decrease in the resistivity of a factor of 2 between 225 and 200 K. The resistivity continued to decrease as the temperature was lowered from 200 to 4.2 K with a second small step down in resistivity at 120 K. The resistivity gradually increased upon warming from b to c in Fig. 3 with no rapid changes in the curve. The resistivity decreased from c to d while the sample was held at room temperature for one day. The second temperature cycle (between d and b on cooling and b and e upon warming) gave a gradually decreasing resistivity curve on cooling and a gradually increasing curve on warming that followed nearly the same
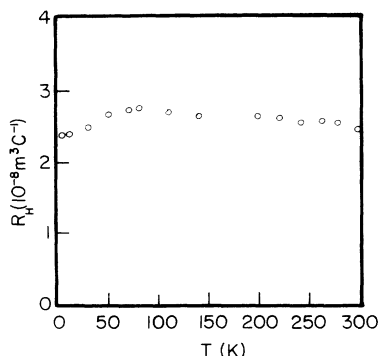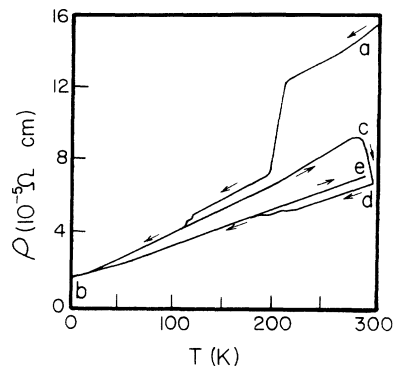
slope with no rapid changes. The resistivity of subsequent temperature cycles followed eb in Fig. 3.

Several samples exhibited resistivity temperature similar to that in Fig. 3. Several other samples showed no step in resistivity between 200 and 225 K but rather displayed a factor of 2 decrease in resistivity at approximately 120 K, where the second small step was observed in Fig. 3. Still other samples did not exhibit any sharp change in the resistivity in any temperature interval.

The temperature-dependent resistivity curve of a sample that did not exhibit a sharp change in resistivity is shown in Fig. 4. There is a smooth change with temperature from 12.3×10^{-5} to 3.2×10^{-5} Ω cm.

The resistivity of our samples after the first temperature cycle was $(8 \pm 2) \times 10^{-5}$ Ω cm at room temperature and $(2 \pm 1) \times 10^{-5}$ Ω cm at 4.2 K. The large uncertainty was a result of variations from sample to sample.

The temperature independence of the Hall coefficient during the first cooling cycle in Fig. 1 suggests that all the carriers have the same mobility and $R_H = 1/ne$ where n is the concentration of all the carriers. For $R_H = 0.57 \times 10^{-8}$ m^3 C^{-1}, $n = 12.5 \times 10^{26}$ m^{-3}. The carriers are in two bands in the rigid band model with dHvA frequencies of 422 and 1190 T. Using the method of

FIG. 2. Temperature dependence of the Hall coefficient of an older stage-2 SbCl$_5$ GIC sample.
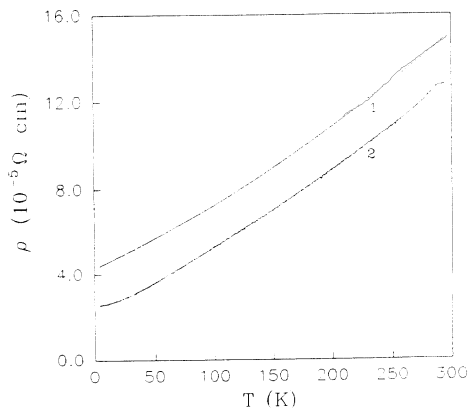

FIG. 4. Temperature dependence of the in-plane resistivity of a stage-2 SbCl$_5$ GIC sample, which does not exhibit a sharp change from ordering: The fitted curve is vertically offset by 2×10^{-5} Ω cm to distinguish it from the experimental curve.

analysis described previously,[15] the carrier concentrations in the two bands are 3.2×10^{26} and 9.05×10^{26} m^{-3}. The total number of carriers is 12.2×10^{26} m^{-3} which is the same, within experimental error, as that determined from the Hall coefficient. Thus, the carrier concentration is the same for slowly cooled samples in dHvA experiments and for the first cooling cycle of the present experiment. The carriers are in the basic graphitic bands and there are no effects of the in-plane intercalant structure. The Hall coefficient increased as the sample is warmed indicating a change in the electronic structure. The temperature dependence of R_H in subsequent cycles indicates that there are groups of carriers with different mobilities. The change in electronic structure and the different groups can be caused by the in-plane intercalant structure. This results in many sections of the Fermi surface with electron or hole character which have a net carrier concentration that can be different from that in the basic graphitic bands. The larger Hall coefficient indicates that the net carrier concentration is less. Since there can be different in-plane structures, the net carrier concentration and Hall coefficient can be sample dependent.

The large resistivity of a sample before it is cooled probably results from disorder rather than a reduced carrier concentration since the Hall coefficient is not anomalously large. The initial room-temperature resistivity suggests that the sample is in a disordered state with no in-plane structural order. The large decrease between 230 and 200 K indicates that ordering is taking place. For some samples this ordering takes place in one step at approximately 120 K rather than in the two steps shown in Fig. 3. As the temperature is lowered below this change, the resistivity becomes smaller from reduced electron-phonon scattering. After the in-plane structures are formed, the commensurate-incommensurate transition has a small affect

The resistivity in Fig. 4 can be fit to

$$\rho = \rho_0 + AT + BT^2 , \qquad (2)$$

where $\rho_0 = 2.27 \times 10^{-5}$, $A = 2.66 \times 10^{-7}$, and $B = 3.19 \times 10^{-10}$. The form of Eq. (2) is expected for intercalated graphite compounds from electron-phonon scattering by in-plane and out-of-plane phonons.[17] Electron-electron scattering is an ineffective process.[17]

The in-plane resistivity of the stage-2 $SbCl_5$ GIC is $(8 \pm 2) \times 10^{-5}$ Ω cm at room temperature. This is consid-erably larger than the value of $(4.8-6) \times 10^{-6}$ Ω cm reported by Melin and Herold.[11] Their measurement was made with a 40-kHz absorption technique with which it is difficult to determine the absolute value of the resistivity, while our measurement was done by a four-contact method. The anisotropy with the c-axis resistivity ρ_c of 1 Ω cm determined by Morelli and Uher[14] is $\rho_c / \rho_a = 1.6 \times 10^4$ at room temperature.

The present resistivity results extend the previous work by Clarke et al.,[13] which showed thermal hysteresis of a stage-4 sample and indicated that there was an unusual effect during the first cooling cycle of a virgin sample. A commensurate-incommensurate transition was observed in stages 1–6. The present results, for stage-2, clearly show the large decrease in resistivity that can occur during the first cooling cycle and that it is sample dependent. The large resistivity before a sample is cooled indicates a large disorder after it is prepared with probably no in-place structural order.

In conclusion, the resistivity and Hall effect measurements have provided additional new information about the stage-2 $SbCl_5$ GIC in addition to that given previously.[13] Some samples are in a disordered state after they are made and order during their first cooling from room temperature as indicated by the change in resistivity. The room-temperature resistivity is $(8 \pm 2) \times 10^{-5}$ Ω cm at room temperature and $(2 \pm 1) \times 10^{-5}$ Ω cm at 4.2 K. The reduced resistivity with decreasing temperature is a result of a change in the electron-phonon scattering described by an equation of the form $\rho = \rho_0 + AT + BT^2$. The Hall coefficient is temperature independent during the first time a sample is cooled and corresponds, in the single-carrier approximation, to the carrier density in the two basic graphitic energy bands. In subsequent coolings, the Hall coefficient is larger than for the first cooling and exhibits a maximum at a temperature between 100 and 150 K. This Hall coefficient reflects the changes to the basic Fermi surface from truncation by the in-plane periodicity of the intercalant.

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