

## Resistivity and Hall effect of the stage-1 CdCl<sub>2</sub> graphite intercalation compound

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The resistivity and Hall effect of the stage-1 CdCl<sub>2</sub> graphite intercalation compound were investigated in the temperature range between 4 and 300 K with the current parallel or perpendicular to the *c* axis. The resistivity for both directions is of the form  $\rho_0 + AT + BT^2$  that results from electron-phonon scattering. The anisotropy of the resistivity is of the order of  $10^3$  and is explained by the undulating cylindrical Fermi surface of the compound. The Hall coefficient is independent of temperature to within the experimental uncertainty and has a value of  $7.0 \times 10^{-9} \text{ m}^3 \text{ C}^{-1}$  from a net carrier density of  $8.9 \times 10^{26} \text{ m}^{-3}$ .

### I. INTRODUCTION

The intercalation of CdCl<sub>2</sub> in graphite forms a stage-1 graphite intercalation compound (GIC) with a *c*-axis repeat distance  $I_c$  of 9.58 Å. It was prepared first<sup>1,2</sup> with graphite powder and flakes, and more recently<sup>3</sup> with highly ordered pyrolytic graphite (HOPG). The use of samples made with HOPG permits the investigation of its electronic properties. A study of the de Haas-van Alphen (dHvA) effect provided details about the Fermi surface.<sup>3</sup> The resistivity and Hall effect give additional information about the electron scattering, electrical anisotropy, and carrier density.

The method of preparing samples and the experimental procedure for measuring the resistivity and Hall effect are given in Sec. II. The resistivity with the current either parallel or perpendicular to the *c* axis for temperatures between 4.2 and 300 K is given in Sec. III. This section also presents the Hall coefficient for the current perpendicular to the *c* axis, and the magnetic field of 1.5 T parallel to the *c* axis. These results are discussed in Sec. IV in terms of the Fermi surface determined previously by the dHvA effect. The conclusions are given in Sec. V.

### II. EXPERIMENTAL METHOD

The intercalation of HOPG with CdCl<sub>2</sub> was carried out with cleaved pieces of HOPG that had been cleaned ultrasonically in anhydrous methanol. The area of the pieces was approximately 1 cm<sup>2</sup>. The HOPG and CdCl<sub>2</sub>, 99.99% pure, were heated in an atmosphere of Cl<sub>2</sub> with a pressure of 800 mb in a sealed pyrex tube. The intercalation was done at a temperature of 500 °C for a time of 480 h. The composition of the stage-1 compound determined by the change of weight by intercalation was C<sub>5.5</sub>CdCl<sub>2</sub>.

The (001) x-ray diffraction using Cu *K*α radiation was indexed from (001) to (006) with increasing 2θ. The (002) peak for the stage-1 compound was the most intense. There was no evidence of diffraction from other stages and from graphite. The *c*-axis repeat distance  $I_c$  was 9.58 Å. This value is between the values reported previously by Rudorff<sup>1</sup> of 9.51 Å, and by Colin and Durizot<sup>2</sup> of 9.63 Å.

Electrical contacts to the sample were made with silver paste. The contacts were put at the corners of a rectangular sample to measure the resistivity in the *ab* plane by the Montgomery<sup>4</sup> method. This method gave more reliable results than those obtained using linear current and potential contacts. For the measurement of the resistivity along the *c* axis, the current contacts in the shape of a ring were on opposite cleaved surfaces and the potential contacts were in the center of the ring. The contacts for the Hall measurements were on a cleaved surface of a thin sample with a length-to-width ratio of 3. The potential probes were on opposite edges and the current was along the length of the sample.

In order to cancel the resistive voltage caused by a small misalignment of the Hall potential probes, the magnetic field was rotated by 180°, and the odd component with respect to the field direction was determined for each measurement.

The measurements were made with the sample in a Dewar. The temperature in the Dewar was varied between 4.2 and 300 K and was measured with platinum and carbon glass thermometers. The potentials across the samples were measured with a Keithley 181 nanovoltmeter and were recorded with a computer. The magnetic field for the Hall measurement was provided by an electromagnet with a maximum field of 1.8 T. The data were recorded while the sample was cooled slowly and while it warmed slowly to room temperature during a period of about 10 h. This slow procedure ensured temperature equilibrium between the sample and the thermometers.

### III. RESULTS

The dc electrical resistivity  $\rho_c$  and  $\rho_a$  of the stage-1 CdCl<sub>2</sub> GIC was measured with the current parallel and perpendicular to the *c* axis, respectively, as shown in Figs. 1 and 2.  $\rho_2$  is 0.02 Ω cm at 4.2 K, and increases with increasing temperature. It has a value of 0.072 Ω cm at room temperature. It can be fit very well to

$$\rho = \rho_0 + AT + BT^2, \quad (1)$$

with  $\rho_0 = 0.0189 \text{ } \Omega \text{ cm}$ ,  $A = 4.25 \times 10^{-5} \text{ } \Omega \text{ cm K}^{-1}$ , and

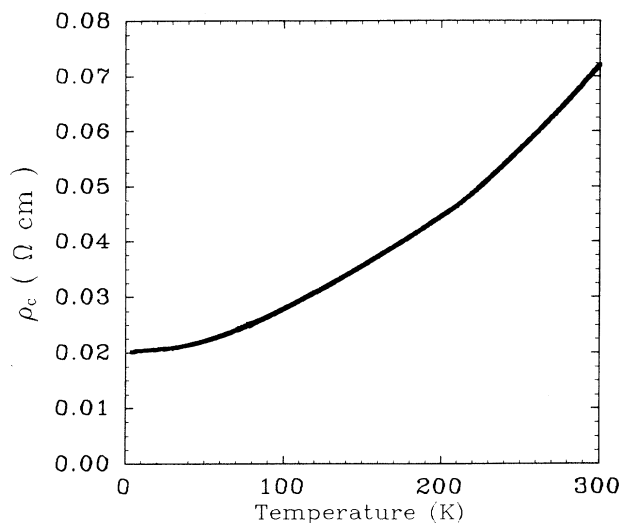


FIG. 1. Resistivity of the stage-1 CdCl<sub>2</sub> GIC vs temperature with the current parallel to the *c* axis.

$$B = 4.4 \times 10^{-7} \Omega \text{ cm K}^{-2}.$$

In the temperature dependence of  $\rho_a$  in Fig. 2,  $\rho_a$  is  $1.6 \times 10^{-5} \Omega \text{ cm}$  at 4.2 K, and increases with increasing temperature to a value of  $7.8 \times 10^{-5} \Omega \text{ cm}$  at room temperature. The temperature dependence of  $\rho_a$  can also be expressed by Eq. (1). The best-fit parameters for  $\rho_a$  are  $\rho_0 = 1.57 \times 10^{-5} \Omega \text{ cm}$ ,  $A = 5.07 \times 10^{-8} \Omega \text{ cm K}^{-1}$ , and  $B = 5.8 \times 10^{-10} \Omega \text{ cm K}^{-2}$ . The calculated curve is not evident in Fig. 1 because it is within the data points of the figure. It is worthwhile to mention that the ratios of the three coefficients of  $\rho_c$  to the corresponding coefficients of  $\rho_a$  are similar and have an order of magnitude of  $10^3$ .

The temperature dependence of  $R_H$ , the Hall

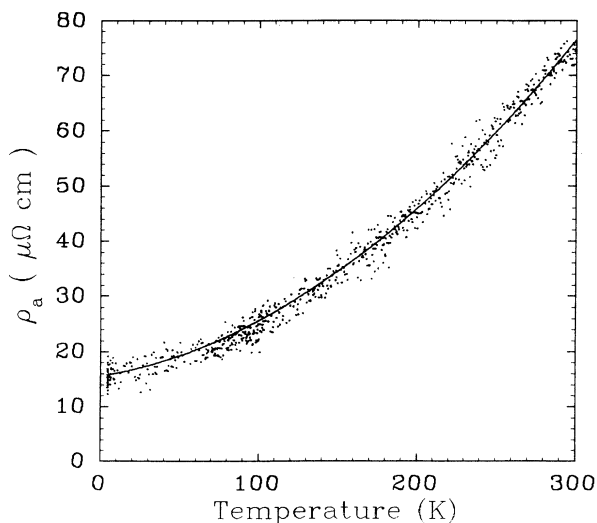


FIG. 2. Resistivity of the stage-1 CdCl<sub>2</sub> GIC vs temperatures with the current perpendicular to the *c* axis.

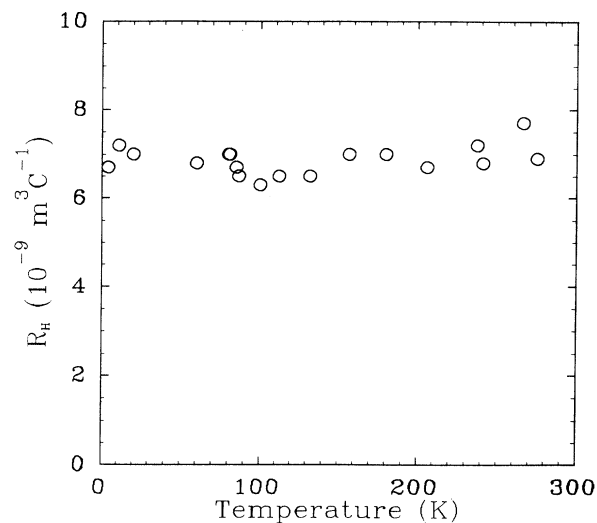


FIG. 3. The Hall coefficient of the stage-1 CdCl<sub>2</sub> GIC for temperatures between 4.2 and 300 K.

coefficient, of the stage-1 CdCl<sub>2</sub> GIC is presented in Fig. 3 for temperatures between 4.2 and 300 K.  $R_H$  is independent of temperature to within experimental uncertainty, with a value of  $(7.0 \pm 0.3) \times 10^{-9} \text{ m}^3 \text{ C}^{-1}$ . The sign of  $R_H$  was identified by determining the magnetic field and current directions and by comparing them to the positive sign of the Hall coefficient of polycrystalline copper that was measured at room temperature. Our results show that  $R_H$  is positive, and confirm that the stage-1 CdCl<sub>2</sub> GIC is an acceptor compound.

#### IV. DISCUSSION

The temperature dependence of the resistivity of most graphite intercalation compounds in the low stages can be described by Eq. (1), although the values of  $\rho_0$ ,  $A$ , and  $B$  depend on the intercalation compound and the stage number.<sup>5</sup> This equation describes contributions to the carrier scattering by both in-plane and out-of-plane scattering. Electron-electron scattering is ineffective in contributing to the resistivity.<sup>6</sup> Since the resistivity of the stage-1 CdCl<sub>2</sub> GIC is described by Eq. (1), the electron-phonon scattering is the dominant process. Also, the hopping mechanism, which is suggested<sup>7</sup> to explain the temperature dependence of  $\rho_c$  in some intercalated compounds, is not applicable to the stage-1 CdCl<sub>2</sub> GIC because the ratios of the coefficients of  $\rho_c$  and  $\rho_a$  are similar.

The ratio of  $\rho_c/\rho_a$  at 4.2 K for the stage-1 CdCl<sub>2</sub> GIC is  $1.2 \times 10^3$ . The finite value of  $\rho_c$  and the ratio of  $\rho_c/\rho_a$  can be explained by the departure of the Fermi surface from a two-dimensional structure. It is obvious that a straight cylindrical Fermi surface results in zero electrical conduction along the cylindrical axis because the electron velocity is perpendicular to the Fermi surface. The shape of the Fermi surface can be determined by a study of the dHvA spectrum. A recent study by Datars *et al.*<sup>3</sup>

of the dHvA effect in the state-1 CdCl<sub>2</sub> GIC shows that the dHvA spectrum of this compound consists of two high, close frequencies of  $f_1=1140$  T and  $f_2=1190$  T, and a low frequency of  $f_3=334$  T with the magnetic field parallel to the  $c$  axis. A study of the angular dependence of these oscillations indicates that  $f_1$  has a cylindrical behavior, and that  $f_2$  is almost independent of the field direction until it joins the cylindrical branch. This indicates that these two frequencies come from an undulating Fermi-surface cylinder. It can be approximated by a straight section with a spherical cap with radii  $k_1$  and  $k_2$ , respectively. The Fermi area  $A_F$  and the dHvA frequency  $f$  are related by<sup>8</sup>

$$A_F = (2\pi e / \hbar) f . \quad (2)$$

Substituting the values of  $f_1$  and  $f_2$  into Eq. (2) yields  $k_1=0.186 \text{ \AA}^{-1}$  and  $k_2=0.189 \text{ \AA}^{-1}$  for the radii of the straight section and the maximum cross section, respectively. The Fermi surface of  $f_3$  is not known, since there should be only one Fermi-surface piece for a stage-1 compound. Possible origins of this piece are suggested in the discussion of the Hall effect.

The conductivity tensor in dyadic notation is given by

$$\sigma = \frac{e^2 \tau}{4\pi^3 \hbar} \int \frac{v_k v_k}{|v_k|} dS_F , \quad (3)$$

where  $\tau$  is the relaxation time and is assumed to be isotropic,  $v_k$  is the carrier velocity in state  $k$ , and  $dS_F$  is a surface element on the Fermi surface.<sup>9</sup> Therefore, the  $c$ -axis conductivity is

$$\sigma_c = \sigma_{zz} = \frac{e^2 \tau}{4\pi^3 \hbar} \int \frac{v_z^2}{|v|} dS_F . \quad (4)$$

Since  $v_z$  is zero except for the spherical section of the Fermi surface, the integral is performed on this section where  $dS_F = k_F^2 \sin\theta d\theta d\phi$ . The azimuthal angle  $\phi$  varies from 0 to  $2\pi$ , and  $\theta$  varies from  $\theta_1$  to  $\pi - \theta_1$  where  $\sin\theta_1 = k_{F1}/k_{F2}$ . Substituting  $v_z = \hbar k_{F2}/m^* \cos\theta$  into Eq. (4), we have

$$\sigma_c = \frac{e^2 \tau k_{F2}^3}{2\pi^2 m^*} \int_{\theta_1}^{\pi - \theta_1} \cos^2\theta \sin\theta d\theta . \quad (5)$$

Therefore, after integration,

$$\sigma_c = \frac{e^2 \tau}{3\pi^2 m^*} (k_{F2}^2 - k_{F1}^2)^{3/2} . \quad (6)$$

The conductivity perpendicular to the  $c$  axis for carriers on the straight cylindrical sector is

$$\sigma_a = \sigma_{xx} = \frac{e^2 \tau}{4\pi^3 \hbar} \int \frac{v_x^2}{|v|} dS_F . \quad (7)$$

(The effect of the spherical section of the Fermi surface in  $\sigma_a$ , which is much smaller than the cylindrical contribution, is neglected.)

In cylindrical coordinates,  $dS_F = k_{F1} d\phi dz$  and  $v_x = (\hbar k_{F1}/m^*) \cos\phi$ . Therefore

$$\sigma_a = \frac{e^2 \tau}{4\pi^3 \hbar} \left[ \frac{\hbar k_{F1}}{m^*} \right] k_{F1} \int_0^{2\pi} \cos^2\phi d\phi \int_0^{2\pi/I_c} dz , \quad (8)$$

and, after integration,

$$\sigma_a = \frac{e^2 \tau k_{F1}^2}{2\pi m^* I_c} . \quad (9)$$

With the measured values of  $k_{F1}$  and  $k_{F2}$ , Eqs. (6) and (9) give  $\sigma_a/\sigma_c = 5 \times 10^2$ . This is smaller by a factor 2.3 than the experimental value.

The ratio  $\rho_c/\rho_a$  can also be estimated by introducing a band energy term  $E_c = 2\delta \cos(k_c I_c)$ , which is the effect of the  $c$ -axis interaction on the two-dimensional part,  $E_a$ , of the energy band.<sup>10</sup>  $\delta$  is the  $c$ -axis interaction energy and is related to  $\Delta A$ , the change in Fermi area along the  $c$  axis, by

$$\delta = \frac{\hbar^2 \Delta A}{8\pi m^*} . \quad (10)$$

With the alternate form of the conductivity tensor,

$$\sigma_i = \frac{e^2}{4\pi^3} \int \frac{dS_k \tau}{|\nabla_k E|} v_i^2 . \quad (11)$$

Thus

$$\sigma_x = \frac{e^2 \tau}{2\pi \hbar^2 I_c} \left[ \frac{\partial E}{\partial k} \right] k_F \quad (12)$$

and

$$\sigma_z = \frac{2e^2 \tau I_c \delta^2}{\pi \hbar^2} \left[ \frac{\partial E}{\partial k} \right]^{-1} . \quad (13)$$

From Eqs. (12) and (13),

$$\frac{\sigma_a}{\sigma_c} = \frac{k_F}{4(I_c \delta)^2} \left[ \frac{\partial E}{\partial k} \right]^2 . \quad (14)$$

With  $I_c = 9.58 \text{ \AA}$  and  $\delta = 6.5 \text{ meV}$  from Eq. (10), Eq. (14) has a value of  $1.6 \times 10^3$  which is very close to the experimental value. However, it should be mentioned that with the assumptions made in this calculation only the order of magnitude of the result is reliable.

It is noted that the  $c$ -axis resistivity of the CdCl<sub>2</sub> GIC is less than those of some other GIC's. At room temperature  $\rho_c$  for the CdCl<sub>2</sub> GIC is 0.08  $\Omega$  cm, while  $\rho_c$  is 1  $\Omega$  cm for the stage-2 SbCl<sub>5</sub> GIC.<sup>11</sup> This results because the undulation of the Fermi surface of the CdCl<sub>2</sub> GIC (4% area charge) is greater than that of the SbCl<sub>5</sub> GIC (0.7%). The larger undulation gives a larger component of velocity along the  $c$  axis, and therefore a greater  $c$ -axis conductivity.

The Hall coefficient of the stage-1 CdCl<sub>2</sub> GIC in Fig. 3 is temperature independent between 4.2 and 300 K. Therefore the one-carrier model with  $R_H = 1/ne$  can be used to calculate the number of carriers per unit volume. The experimental value of  $R_H = (7.0 \pm 0.3) \times 10^{-9} \text{ m}^3 \text{ C}^{-1}$  gives  $n = 8.9 \times 10^{26} \text{ m}^{-3}$ .

The number of carriers can be calculated from the dHvA frequencies. There are three oscillations in the

dHvA spectrum of the stage-1 CdCl<sub>2</sub> GIC. The frequencies are  $f_1=1140$  T and  $f_2=1190$  T, originating from the undulating Fermi surface, and  $f_3=334$  T. The volume of the Fermi surface  $V_F$  is related directly to the Fermi surface area  $A_F$ . For a straight cylindrical Fermi surface,

$$V_F=2A_F(2\pi/I_c). \quad (15)$$

The factor 2 corresponds to the number of Fermi pockets (six) in each corner of the Brillouin zone, with their portion ( $\frac{1}{3}$ ) lying inside the Brillouin zone. With  $A_F$  related to the dHvA frequency by Eq. (2), and the number of carriers per unit volume given by

$$n=2V_F/(2\pi)^3, \quad (16)$$

the use of  $f_1=1140$  T yields  $n=11.5\times 10^{26}$  m<sup>-3</sup>. This is about 25% larger than that determined from  $R_H$ .

The frequency  $f_3=334$  T indicates another pocket of carriers in the Brillouin zone, although it is not suggested by band-structure calculations of the acceptor GIC. There are two possibilities for its origin. It could be either an acceptor hole pocket that has not been predicted, or an electron pocket from an interlayer band.<sup>12</sup> This band has been indicated for donor compounds, and it is suggested that it may also exist with acceptor compounds. From Eq. (16), the number of carriers in this pocket is  $0.7\times 10^{26}$  m<sup>-3</sup> for a spherical shape of the Fermi surface, and  $3.3\times 10^{26}$  m<sup>-3</sup> for a cylindrical surface. Therefore the net number of carriers in the stage-1 CdCl<sub>2</sub> GIC is  $8.2\times 10^{26}$  m<sup>-3</sup> if the second pocket is electronlike with a cylindrical Fermi surface. This is 7% smaller than

the number determined from the Hall coefficient. This is considered to be a satisfactory agreement, because the actual Fermi surface of the interlayer band will be three dimensional and will differ from a straight cylinder.

## V. CONCLUSIONS

The resistivity of the stage-1 CdCl<sub>2</sub> GIC has the form  $\rho_0+AT+BT^2$  for temperatures between 4.2 and 300 K. This form holds for current directions parallel and perpendicular to the  $c$  axis, and indicates that the resistivity is controlled by electron-phonon scattering. The anisotropy of the resistivity is explained by using the undulating cylindrical Fermi surface determined from previous measurements of the de Haas-van Alphen effect. The Hall effect is independent of temperature between 4.2 and 300 K, and indicates a net carrier concentration of  $8.9\times 10^{26}$  m<sup>-3</sup>. This is 25% smaller than the carrier concentration in the cylindrical Fermi surface. Better agreement between the calculated and measured densities is obtained by assuming that there is a pocket of electrons from interlayer states in addition to the holes in the cylindrical Fermi surface.

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