de Haas–van Alphen effect of stage-1 $CdCl_2$ intercalated graphite

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The de Haas–van Alphen (dHvA) effect of the stage-1 compound intercalated with $CdCl_2$ has been investigated with magnetic fields up to 14 T and for temperatures between 50 mK and 1.87 K. There are two dominant oscillations with values of 1144 and 1190 T with the magnetic field parallel to the c axis. The average value of the mass for these two frequencies is $(0.26\pm0.01)m_0$, where m_0 is the mass of the electron. The change of the frequencies with magnetic-field direction shows that the Fermi surface is an undulating cylinder directed along the c axis with a 4% difference between the minimum and maximum cross-sectional areas. The Fermi energy determined from the Holzwarth band model is -1.113 eV. There is also a dHvA frequency of 334 T with the magnetic field parallel to the c axis from a minority carrier.

I. INTRODUCTION

A stage-1 graphite intercalation compound (GIC) has alternating layers of carbon and the intercalant and provides the opportunity to study a system with a small coupling between two-dimensional layers. The electronic structure in the region of the Fermi energy is expected to be similar to that of a single graphite sheet in a hexagonal lattice. The Fermi surface of the two-dimensional system is a straight cylinder with its axis along the c direction. The interaction between the carbon sheets results in a warping of the straight cylinder along the c axis, which takes the form of an undulating cylinder.

The band structure of a stage-1 acceptor GIC has been determined by Holzwarth.[1] The calculation includes four in-plane and four interplanar interactions and a difference in energy for nonequivalent carbon sites. A simpler model that was used by Blinowski *et al.*[2] is a first-order expansion of energy *versus* momentum near the corners of the Brillouin zone.

$CdCl_2$ reacts with graphite in the presence of Cl_2 to form a stage-1 compound.[3–5] The chlorine pressure must exceed a certain threshold value to initiate the intercalation process. A good stage-1 compound suitable for dHvA experiments can be produced with a reaction temperature of 500 °C.

The sample preparation and the dHvA detection system with a top-loading dilution refrigerator and a 14-T superconducting magnet are described in Sec. II. The dHvA frequencies and their dependence on magnetic-field direction are given in Sec. III. The cyclotron mass of the carriers in the graphite π band is also presented. The results are discussed in Sec. IV in terms of the theories of Holzwarth[1] and Blinowski *et al.*[2] The conclusions are given in Sec. V.

II. EXPERIMENTAL METHOD

The dHvA effect was detected with a system capable of magnetic fields up to 14 T in a superconducting magnet and temperatures down to 25 mK produced with a top-loading dilution refrigerator. The modulation coil in He^4 provided a field of 9.4×10^{-3} T at a frequency of 18 Hz. The detection coils that were immersed in the He^3-He^4 mixture had an inside diameter of 3 mm with 5000 turns on the pickup coil and 3000 turns on the balance coil wound on top of the pickup coil. The sample and coils were turned to set the orientation of the sample with respect to the field direction.

The dHvA oscillations could be detected for magnetic fields between 6 and 14 T. The data were taken as the field was changed from 13.8 to 7.8 T at a rate that was linear in reciprocal field with 2048 data points taken at time intervals of 1.52 s. The frequencies and their angular dependence were measured with a sample temperature of 50 mK. The temperature dependence of the amplitude was measured at temperatures between 50 mK and 1.78 K. This temperature range was used because it was the working range of the refrigerator, although the dHvA oscillation could have been observed at higher temperatures. The temperature was measured with a carbon resistor in the mixing chamber calibrated with a Ge resistor near the sample position at zero magnetic field.

The intercalation of highly oriented pyrolytic graphite (HOPG) was carried out with cleaved pieces of HOPG that had been cleaned ultrasonically in anhydrous methanol. The HOPG and 99.99% pure $CdCl_2$ were heated in a sealed pyrex tube at a temperature of 500 °C for 480 h with an atmosphere of Cl_2 at a pressure of 600 Torr in the tube. This resulted in a fully developed, stage-1 GIC with a composition, determined by the change in weight by intercalation, of $C_{5.5}CdCl_2$. This has a higher concentration of $CdCl_2$ than that reported previously[4] ($C_{6.76}CdCl_2$) for a saturated stage-1 GIC.

The (001) x-ray diffraction with Cu $K\alpha$ radiation in Fig. 1 has narrow, large peaks indexed from (001) to (006) with the (002) peak being the most intense as expected for a stage-1 GIC. There is no evidence of diffraction from other stages and from graphite. The c-axis repeat dis-

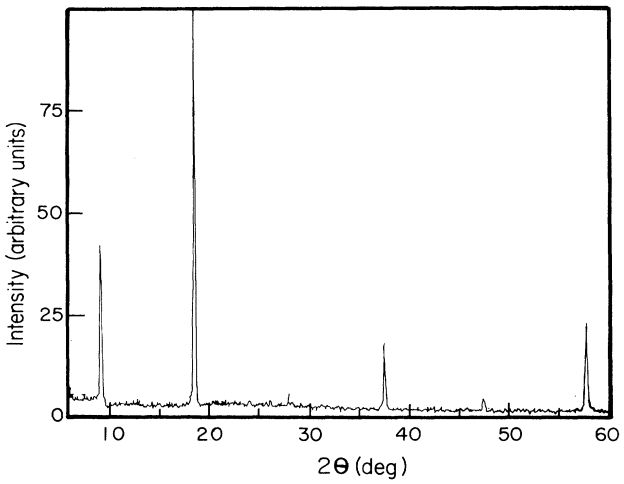

FIG. 1. (001) x-ray diffraction of the stage-1 $CdCl_2$ GIC with Cu $K\alpha$ radiation.

tance, I_c, is 9.58 Å, which is between the values reported previously.[3,4]

III. EXPERIMENTAL RESULTS

The dHvA oscillations with the field parallel to the c axis are shown in Fig. 2. A beat in the dominant oscillation indicates that there are two close frequencies. The Fourier transform of the c-axis data in Fig. 3 shows that these frequencies have values of $f_1=1144$ T and $f_2=1190$ T. There is also a frequency $f_3=334$ T from a minority carrier.

The dHvA oscillations were observed for magnetic-field directions within 16° of the c axis. Beating of the oscillations indicated two close frequencies at each direction. The frequencies were resolved in the Fourier-transform analysis for magnetic-field directions within 3° of the c axis and 8°–10° from the c axis. At other directions the frequencies were not resolved in the Fourier transform probably because the amplitude of F_2 was much larger. However, a beat pattern indicating the

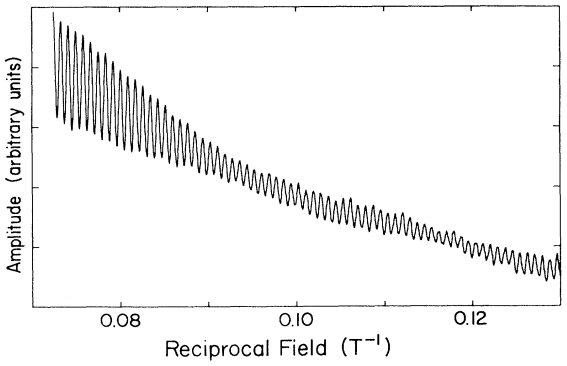

FIG. 2. dHvA oscillations as a function of reciprocal field for fields between 7.68 and 13.8 T with a sample temperature of 50 mK of the stage-1 $CdCl_2$ GIC. The magnetic field is parallel to the c axis.

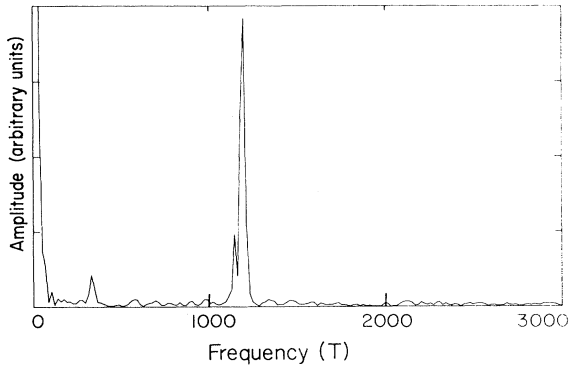

FIG. 3. Fourier transform of the dHvA oscillations of Fig. 2 for the stage-1 $CdCl_2$ GIC.

presence of two frequencies was analyzed to obtain the frequencies. The analysis of the Fourier transform and the beat patterns gave the angular dependence of the frequencies in Fig. 4. The error bars of the frequencies resulted from the closeness of the two frequencies which resulted in only two minima in the beat pattern and peaks in the Fourier transform that were not resolved completely.

The cyclotron mass was determined from the temperature dependence, as shown in Fig. 5, of the amplitude of the Fourier-transform peak with the field 4° from the c axis for which the two peaks were not resolved. The uncertainty of the mass analysis resulted from its dependence on the temperature and magnetic-field ranges that were used. The mass determination from the analysis is $(0.26\pm0.01)m_0$.

IV. DISCUSSION

The curve in Fig. 4 is a plot of $f_0\sec\theta$ with $f_0=1144$ T and θ is the angle between the c axis and the magnetic-field direction. This shows that the lower-frequency

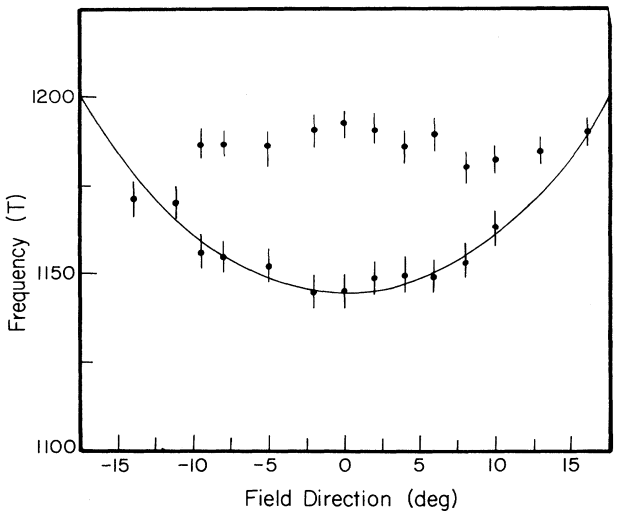

FIG. 4. dHvA frequency as a function of magnetic-field direction from the c axis of the stage-1 $CdCl_2$ GIC.

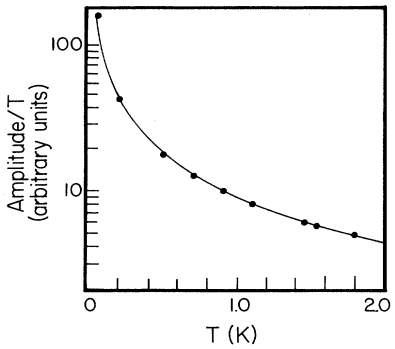

FIG. 5. $\log_{10}$ [(Fourier amplitude)/T] versus temperature for the dominant dHvA frequency of the stage-1 $CdCl_2$ GIC. The curve is calculated for $m/m_0=0.256$.

branch is from a straight cylindrical Fermi-surface section. The frequency of the upper branch does not change significantly with field direction and tends to join the lower branch being only slightly above the lower branch at $\theta=10°$. It, therefore, comes from a maximum cross section which joins the cylindrical section. The areas of the sections are 0.109 and 0.114 Å^{-2} and have a difference of 4%. The Fermi surface may be represented by an undulating cylinder with its axis along the c axis.

The Fermi-surface properties were evaluated as a function of the Fermi level with the Holzwarth band model of the π bands for stage-1 compounds. From the plot for the Fermi-surface area given in Fig. 6, the Fermi level is -1.113 eV for the area of 0.109 Å^{-2} of the cylindrical section. This Fermi energy in the plot for the cyclotron mass in Fig. 6(b) corresponds to $m/m_0=0.266m_0$, which agrees with the measured mass to within experimental uncertainty.

The cross-sectional area A and the cyclotron mass m in the theory of Blinowski *et al.*[2] are

$$A=\frac{4\pi}{3a^2}\left[\frac{E}{\gamma_0}\right]^2, \tag{1}$$

$$m=\frac{4\hbar^2E}{3\gamma_0^2a^2}, \tag{2}$$

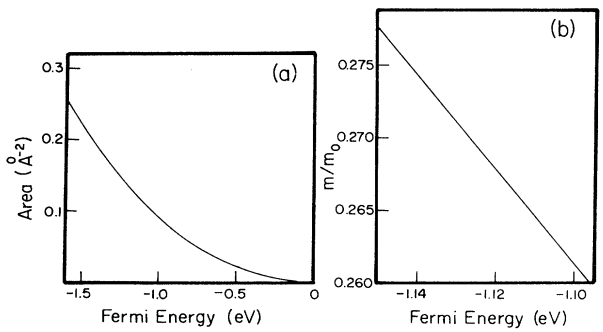

FIG. 6. (a) Cross-sectional area of the stage-1 Fermi surface versus Fermi energy calculated from the theory of Holzwarth. (b) Cyclotron mass of the stage-1 Fermi surface versus Fermi energy calculated from the theory of Holzwarth.

TABLE I. dHvA frequencies, cyclotron mass, and the Fermi energy of some acceptor stage-1 GIC's.

	F_1 (T)	m/m_0	F_3 (T)	E (eV)
$CdCl_2$ (GIC)	1144	0.26	334	−1.113
$SbCl_5$ (GIC)	1211	0.271	328	−1.127
$SbCl_4F$ (GIC)	1250		480	−1.13
SbF_6^- (GIC)	1627	0.321	567	−1.28

where $a=2.46$ Å, γ_0 is the in-plane interaction parameter, and E is the Fermi energy. From Eq. (1) $E/\gamma_0=0.397$ for $A_1=0.109$ Å^{-2}. This yields $\gamma_0=0.28$ eV by using the Fermi energy determined from the Holzwarth model. With these values of γ_0 and E, the cyclotron mass from Eq. (2) is $0.269m_0$. Thus the theories of Holzwarth and Blinowski *et al.* explain both the cross-sectional area and cyclotron mass for $\gamma_0=2.8$ eV and $E=-1.113$ eV.

The present results are compared in Table I with those of stage-1 acceptor compounds intercalated with $SbCl_5$, SbF_6^-, and $SbCl_4F$.[6–8] The dHvA frequency from the graphite π bands in the compounds is in the range 1250–1627 T. The cyclotron mass and the Fermi energy increase with the dHvA frequency. Thus, the electronic properties of the compounds are similar. In each compound, there is also a lower frequency in the range between 328 and 567 T. Although it appears to be a general property of stage-1 acceptor compounds, its origin is not understood at the present time. Two possible causes are a second graphite band that has not been determined by the previous band-structure calculations and the energy band of interlayer states that has been predicted[9] for donor compounds.

V. CONCLUSIONS

The dHvA spectrum of the stage-1 $CdCl_2$ GIC consists of frequencies of 1144, 1190, and 334 T with the field parallel to the c axis. The average mass of the two high frequencies is $(0.26\pm0.01)m_0$. The angular dependence of the high frequencies shows that they are from an undulating Fermi-surface cylinder directed along the c axis. The undulation is larger than that in other stage-1 GIC's. The cyclotron mass and dHvA frequency are explained by the theories of Holzwarth and Blinowski *et al.* with a Fermi energy of -1.113 eV and an in-plane interaction parameter of 2.8 eV. The origin of the lowest frequency is not explained presently.

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