Three-dimensional energy band in stage-1 acceptor graphite intercalation compounds

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(Received 6 March 1995)

The low-frequency de Haas–van Alphen (dHvA) oscillation of the stage-1 $CdCl_2$ graphite intercalation compound (GIC) and of the SbF_6^- compound was investigated as a function of magnetic-field direction θ with respect to the c axis. For the angular range of measurement of $0<\theta<20°$ the frequency was independent of θ within experimental uncertainty in both compounds and did not follow the relation $f_\theta = f_0 \sec\theta$ for a cylindrical Fermi surface. For the angular range of measurement, the extremal cross-sectional areas of the Fermi surface for the low-frequency are that of a sphere. This indicates a significant three-dimensional component of the graphitic energy band for the low frequency.

I. INTRODUCTION

There is charge transfer from graphite to acceptor molecules in acceptor graphite intercalation compounds (GIC's). This makes the GIC a p-type material with holes in the graphite energy bands. For stage-1 GIC's, according to band theories,[1,2] there is one energy band that is two dimensional in the single graphite layer. The Fermi surface is a cylinder with its axis along the c axis. A high-frequency de Haas–van Alphen (dHvA) oscillation results from this Fermi surface, and has been identified for a group of stage-1 acceptor GIC's.[3–7] However, there is a second lower-frequency oscillation observed with each of the compounds, and it is not expected from the graphite energy-band calculations.

The low frequency has been observed in the range 300–600 T with the magnetic field parallel to the c axis in the stage-1 GIC's intercalated with $SbCl_5$ (Ref. 3), $SbCl_4F$ (Ref. 4), SbF_6^- (Ref. 5), $CdCl_2$ (Ref. 6), and $AlCl_3$ (Ref. 7). The purpose of this work was to determine the dependence of the low frequency on the angular displacement θ of the magnetic field from the c axis in several of the GIC's. The angular range for the observation of the oscillation was limited to $\theta<20°$ because of scattering of the carriers from their cyclotron orbits by the intercalant layers for larger values of θ. This meant that the complete shape of the Fermi surface could not be derived, although differences from a cylindrical shape could be determined for $\theta<20°$. The choice of the GIC's for this study had the requirement of a large amplitude for the low-frequency oscillation in order to observe it in the fullest possible angular range. This condition was satisfied with the GIC's intercalated with $CdCl_2$ and SbF_6^- which were used in this study.

II. EXPERIMENT

The stage-1 $CdCl_2$ GIC was prepared by heating high-purity $CdCl_2$ and highly oriented pyrolytic graphite (HOPG) in an atmosphere of Cl_2 at a pressure of 600 Torr in a sealed Pyrex tube. A temperature of 500 °C was used for 480 h. The (001) x-ray diffraction consisted of narrow, sharp peaks indexed from (001) to (005) with a stage-1 interlayer spacing and no evidence of other stages. Two samples were used in the dHvA experiments.

For the preparation of the second GIC, NO_2SbF_6 salt was dissolved in nitromethane. Intercalation of HOPG placed in the solution took place at room temperature in one week. All handling and the reaction were done in a dry box. This method of preparation was used in preference to the other methods that have been described,[5] because it resulted in samples with a strong low frequency.

Two dHvA systems were used for the measurements. In both systems the sensitivities were similar and the sample was inserted in a detection coil which could be rotated to set the angular position of the sample. For the study of the angular dependence of the $CdCl_2$ GIC, the sample was cooled with a top-loading dilution refrigerator with a base temperature of 25 mK, and was in a superconducting solenoid with a maximum field of 14 T.[6] This system was not suitable for the measurement of the cyclotron mass because with the small mass there was a small change in the dHvA amplitude for different temperatures below 1K which were accessible easily with the system. Thus the cyclotron mass was measured with the second system operating in the temperature range 1.5–4.2 K.[2] The maximum magnetic field of this system was 5.5 T, which was sufficient to detect the dHvA oscillation. This second system was also used to study the angular dependence of the low frequency of the SbF_6^- GIC.

III. RESULTS

The dHvA effect of the $CdCl_2$ GIC shown in Fig. 1 for the magnetic field parallel to the c axis has two dominant oscillations. One is observed at fields above 3.8 T, and the other above 7 T. The latter is dominant at high fields and originates from the undulating Fermi surface, as reported previously. The oscillation with the lower fre-

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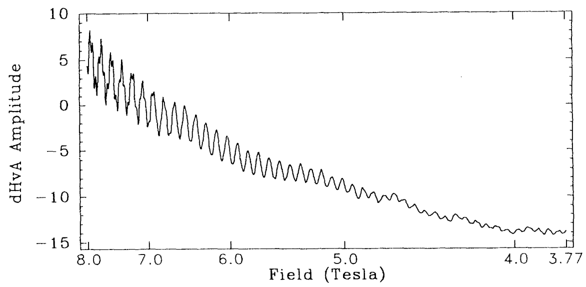

FIG. 1. dHvA oscillations as a function of reciprocal magnetic field for the stage-1 $CdCl_2$ GIC with the magnetic field parallel to the c axis.

quency, which is of interest in this study, was measured to as low a field as possible to have a large number of cycles for the determination of the frequency. Approximately 50 oscillations were recorded, which gave an accuracy of better than 1%.

The Fourier transform of the data of Fig. 1 is shown in Fig. 2. The two components of the high frequency are in excellent agreement with the previous result[6] for the undulating Fermi-surface cylinder. The low frequency is 328 T, and is within 2% of the value of 334 T measured previously.

The angular dependence of the frequency is shown in Fig. 3. The frequency of the oscillation was determined by a least-square Lorentzian fit of seven points between 300 and 360 T in the Fourier transform of the data. The error bars were estimated from the range of best-fit frequencies for sets of data taken at the same field direction, and each data point is the average of several determinations for the field direction. The frequency is independent of magnetic-field direction to within experimental uncertainty and does not increase as θ increases. In contrast, the $\sec\theta$ dependence shown as the solid curve in Fig. 3 expected from a straight cylindrical Fermi surface increases by 6% at $\theta=20°$.

The low-frequency oscillation was measured between 4

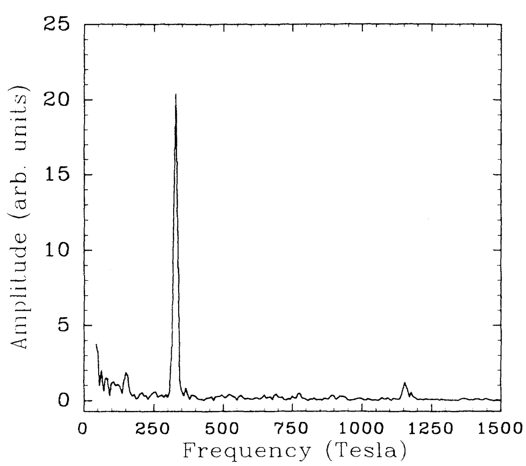

FIG. 2. Fourier transform of the dHvA oscillations of Fig. 1 for the stage-1 $CdCl_2$ GIC.

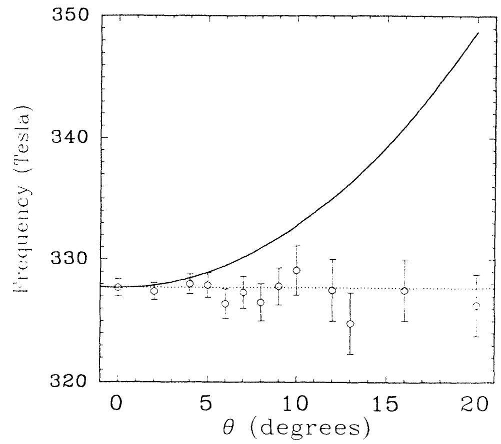

FIG. 3. dHvA frequency as a function of magnetic-field direction from the c axis of the stage-1 $CdCl_2$ GIC. The solid curve is the angular dependence for a cylindrical Fermi surface, and the dashed line is for a spherical Fermi surface section.

and 5.2 T to determine the cyclotron mass. The measured frequency was 325±4 T, which is in satisfactory agreement with measurements at higher fields with a different apparatus. The cyclotron mass determined from the temperature dependence of this amplitude is $(0.13\pm0.01)m_0$ in units of the free-electron mass.

In the study of the second $CdCl_2$ GIC sample, the amplitude of the low-frequency oscillation was smaller and the oscillation could be detected only for $\theta<12°$. The frequencies at $\theta=0$ and $\theta=12°$ were the same to within 1 T, and the measurements at directions between 0° and 12° were mostly smaller by several tesla. Thus measurements with the second sample support that the frequency does not increase as a function of θ.

The dHvA effect of the SbF_6^- GIC was detected in the magnetic field range 3–5 T. The Fourier transform of the data with the magnetic field parallel to the c axis is shown in Fig. 4. The dominant peak of the transform indicates a frequency at 563 T with a shoulder at 578 T. These two components exist at all orientations of the measurement. The small peak at 1772 T is from the

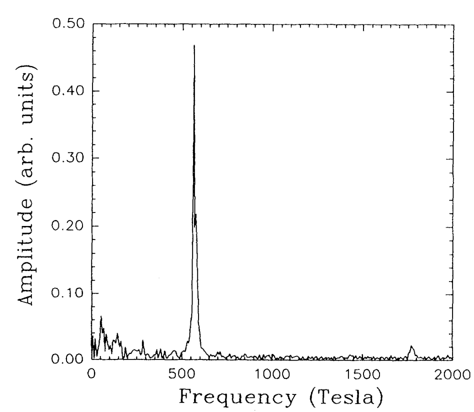

FIG. 4. Fourier transform of the dHvA oscillations of the stage-1 SbF_6^- GIC with the magnetic field parallel to the c axis.

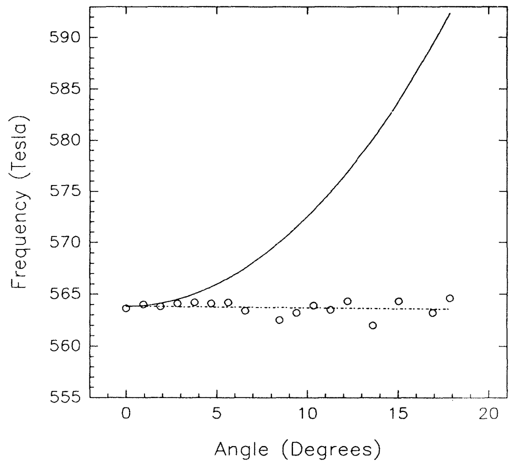

FIG. 5. dHvA frequency as a function of the magnetic-field direction from the c axis for the stage-1 SbF_6^- GIC. The solid curve is for a cylindrical Fermi surface, and the dashed line is a linear fit to the data.

high-frequency oscillation which originates from the graphite cylindrical Fermi surface.

Since the 563-T component was larger, it was used to determine the frequency at each orientation by a fit to the points of the Fourier transform. The angular dependence of the frequency is presented in Fig. 5. The linear fit to the data has an intercept of 563.8 T at $\theta=0$ and a slope of -1.6×10^{-2} T/degree. The frequency difference of the straight line is -0.3 T between 0° and 18°.

IV. DISCUSSION

The angular dependence of the dHvA frequency f_θ from a straight cylinder of the Fermi surface is $f_\theta=f_0\sec\theta$, where θ is the angle between the magnetic field direction and the axis of the cylinder, and f_0 is the frequency at $\theta=0°$. If the cylinder is undulating there are two frequencies at $\theta=0°$ from the minimum and maximum cross sections of the undulating cylinder. These two frequencies become one as θ increases as the areas of the two cross sections approach each other.

The prediction of a three-dimensional spherical Fermi surface is given by $f_\theta=f_0$, since its area is independent of θ.

Since the dHvA frequency in Fig. 3 is independent of θ to within experimental uncertainty, the data indicate cross sections of a spherical shape for $\theta<20°$. The frequency is no higher at 20° than at 0°. Since it should be 6% higher at 20° for a cylinder, there is no evidence of a straight cylindrical Fermi surface for the low frequency in the $CdCl_2$ GIC. The Fermi surface cannot change suddenly to a cylinder, and so the three-dimensional character exists beyond $\theta=20°$. However, the full shape of the Fermi surface piece is not determined, and it is not known whether the Fermi surface is open or closed. However, the part of the Fermi surface that is observed has three-dimensional properties with a significant component of the electron velocity normal to the graphite planes.

The difference in frequency between the dominant peak and the shoulder observed with the SbF_6^- GIC does not depend on θ, and therefore the angular dependencies of both frequencies are the same. Thus they are not from minimum and maximum cross sections of an undulating cylindrical Fermi surface which merge as θ increases. The two frequencies are likely from two different regions of the sample.

The angular dependence in Fig. 5 shows that the Fermi piece for the low frequency in the SbF_6^- GIC has a spherical cross section for $0<\theta<20°$. The very small slope of the fitted line and its negative value are not significant. This shows that the Fermi surface piece has three-dimensional properties similar to the $CdCl_2$ GIC. This three dimensionality has to exist beyond 20°, but the complete shape of the Fermi surface cannot be determined.

A similar result has been reported for the stage-1 potassium GIC, C_8K.[8] The dHvA frequency of 3126 T was independent of θ for the range of possible measurements of $\theta<22°$. This indicated a three-dimensional part of the Fermi surface of C_8K. This piece was predicted by Ohno, Nakao, and Kamimura[9] with the potassium 4s band crossing the Fermi level to form a nearly spherical Fermi surface. However, it was shown later[10] that the lowest occupied conduction band is an interlayer state at the center of the Brillouin zone.

The interlayer state exhibits a free-electron character parallel to the layers, and forms a band close to the Fermi energy of graphite in the calculation of Posternak *et al.*[11] This band is occupied in the alkali-metal GIC's. However, it is not expected to be occupied in the acceptor GIC's with a Fermi level lower than in graphite. Theoretical calculations are suggested to find whether the interlayer band is lowered in the acceptor GIC's so that it can be occupied. Antibonding π bands with three-dimensional character have also been suggested for the donor GIC's,[12] and may be considered for the acceptor GIC's.

Stage-1 acceptor compounds intercalated with $SbCl_5$, $SbCl_4F$, and $AlCl_3$ have a dHvA frequency similar in magnitude to the ones reported here.[3,4,7] The frequencies are 322 T for the $SbCl_5$ GIC, 480 T for the $SbCl_4$ GIC, and 420 T for the $AlCl_3$ GIC. It is projected that the angular dependencies of these frequencies will be similar to those reported in this paper.

V. CONCLUSIONS

The angular dependence of the low dHvA frequency of the stage-1 acceptor GIC's intercalated with $CdCl_2$ and SbF_6^- has been measured in the angular range of measurement that was possible: $0<\theta<20°$. In both compounds the frequency is independent of θ within experimental uncertainty for $\theta<20°$. This shows that there is a spherical curvature of the Fermi surface for $\theta<20°$, and indicates an energy band with three-dimensional properties.

ACKNOWLEDGMENTS

The HOPG graphite was provided by Dr. A. W. Moore. The research at McMaster was supported financially by the Natural Sciences and Engineering Research Board. Useful discussions with Dr. Y. Iye are acknowledged.

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