de Haas–van Alphen effect of the stage-2 bismuth chloride graphite intercalation compound

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The stage-2 intercalation compound made from the intercalation of $BiCl_3$ and Cl_2 in highly oriented pyrolytic graphite was investigated by the de Haas–van Alphen (dHvA) effect. There are two dHvA frequencies of 327 and 1012 T from extremal cross-sectional Fermi surface areas of 0.0312 and 0.0966 $Å^{-2}$, respectively, with the magnetic field parallel to the c axis. The charge transfer per carbon atom is $0.017e^+$. The results are interpreted by the two-dimensional band-structure model proposed by Blinowski. The Fermi energy is -0.73 eV.

I. INTRODUCTION

The stage-2 bismuth chloride graphite intercalation compound (GIC) is a compound in the group of metal chloride GIC's that can be prepared with high staging fidelity.[1] In the present work, samples of the stage-2 $BiCl_3$ GIC were prepared and measured by the de Haas–van Alphen (dHvA) effect. The two dHvA frequencies that are expected from Blinowski's model[2] for a stage-2 compound were observed. The work was done to determine the Fermi surface and band structure of the compound and to compare it with other stage-2 compounds.[3,4]

II. EXPERIMENTAL RESULTS

Highly oriented pyrolitic graphite (HOPG) and $BiCl_3$ in a sealed reaction tube were heated at a temperature of 253 °C with chlorine gas at a pressure of 800 mbar in the tube. The intercalation time was 14 days. X-ray (001) diffraction showed that the samples were in a pure stage-2 state with a c-axis repeat distance I_c of 13.06 Å.

The dHvA effect from the stage-2 compound obtained at 4.2 K with the apparatus used previously[5] is shown in Fig. 1. There is essentially a single oscillation for magnetic fields up to 4.7 T. However, a second oscillation is apparent above 4.8 T and changes the shape of the dHvA signal with increasing magnetic field. Actually, the second oscillation with a higher dHvA frequency could become stronger for magnetic fields above 5.4 T, but the maximum field of the superconducting solenoid that was used was 5.5 T. Figure 2 shows the Fourier-transform spectrum of the dHvA oscillations in the field range 4.0–5.4 T at a temperature of 2.1 K. The dHvA frequencies are $F_1=(327\pm5)$ T and $F_2=(1012\pm10)$ T, which correspond to the Fermi areas of 0.0312 and 0.0966 $Å^{-2}$, respectively, according to the relation between the Fermi area and dHvA frequency $[A_F=(2\pi e/\hbar)F]$. There is a weak second harmonic of F_1 with a frequency of 655 T between F_1 and F_2. The third harmonic will be even weaker, with a frequency of 981 T which is less than F_2. It therefore contributes very little to the peak of the second dHvA oscillation. The small peak at 1330 T is at the sum of F_1 and F_2 and confirms the existence of F_2.

The temperature dependence of the dHvA amplitude A was measured from 2.1 to 4.2 K. Figure 3 shows the plot of $\ln(A/T)$ versus T for both F_1 and F_2. The carrier effective masses corresponding to F_1 and F_2 obtained from the temperature dependence are $m_1^*=0.147m_0$ and $m_2^*=0.265m_0$.

All the results were reproducible with different samples

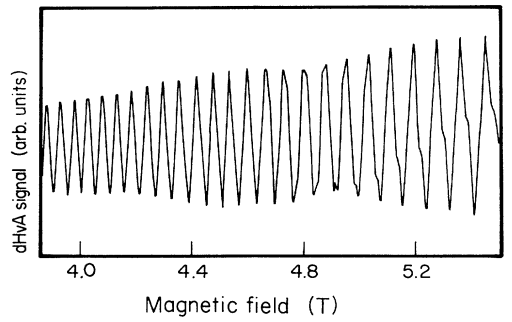

FIG. 1. de Haas–van Alphen oscillations of the stage-2 $BiCl_3$ GIC.

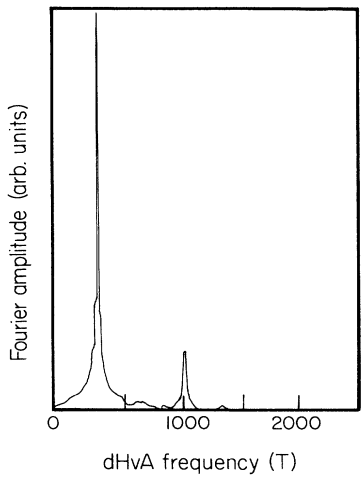

FIG. 2. The Fourier transform of the dHvA signal of the stage-2 $BiCl_3$ GIC.

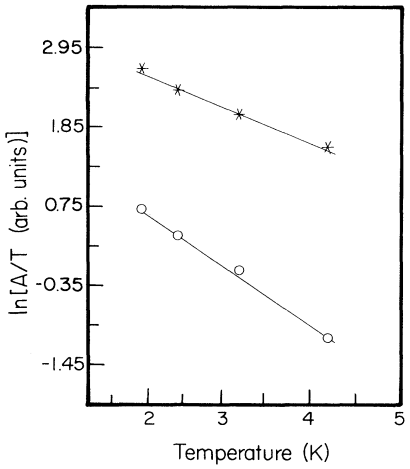

FIG. 3. The temperature dependence of $\ln A/T$, where A is the amplitude of the dHvA oscillation for the first frequency 327 T (*) and the second frequency (0) of the stage-2 BiC_3 GIC.

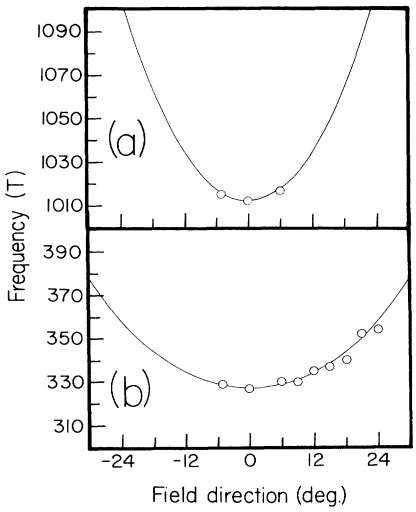

FIG. 4. The dHvA frequency as a function of magnetic-field direction from the c axis for (a) frequency F_2 and (b) frequency F_1.

and the experimental data are summarized in Table I.

The angular dependence of the two dHvA frequencies is shown in Fig. 4. The solid curves represent the predictions for two-dimensional straight cylinders of the Fermi surface given by $F_\theta = F_0/\cos\theta$, where θ is the angle between the field direction and the c axis. The dHvA frequencies follow a cylindrical behavior. This means that the band structure of the stage-2 $BiCl_2$ GIC is quite two-dimensional. However, the angular range of measurement is too limited to distinguish small differences from a cylinder because the amplitudes of the dHvA oscillations decreased with increasing θ. The dHvA signal of F_1 disappeared at $\theta = 27°$. The oscillation of the second frequency F_2 was weaker than that of F_1, and was not observed when the angle exceeded 9°.

III. DISCUSSION

The two valence bands of a stage-2 acceptor compound as derived with the tight-binding method by Blinowski *et al.*[2] are given by

$$-|E_1|^v = \tfrac{1}{2}[(3\gamma_0^2 a^2 k^2 + \gamma_1^2)^{1/2} + \gamma_1] , \quad (1)$$

$$-|E_2|^v = \tfrac{1}{2}[(3\gamma_0^2 a^2 k^2 + \gamma_1^2)^{1/2} - \gamma_1] , \quad (2)$$

TABLE I. Experimental results for the stage-2 $BiCl_3$, $SbCl_5$ (Ref. 3), and BF_4^- (Ref. 4) GIC's for the dHvA frequency F, the cross-sectional area of the Fermi surface A, the cyclotron mass ratio, and the ratio of the energy-band parameters.

	$BiCl_3$	$SbCl_5$	BF_4^-
F_1 (T)	327	422	523
F_2 (T)	1012	1190	1377
A_1 (Å)$^{-2}$	0.0312	0.0403	0.0499
A_2 (Å)$^{-2}$	0.0966	0.114	0.131
E/γ_0	0.304	0.333	0.362
γ_1/γ_0	0.158	0.159	0.162
m_1/m_0	0.147	0.146	0.162
m_2/m_0	0.265	0.267	0.28

where γ_0 is the in-plane interaction parameter, γ_1 is the first in-plane interaction parameter, and $a = 2.46$ Å is the magnitude of the in-plane translation vector. The Fermi energy E_F is negative and has the magnitude of E_1 and E_2, so that with $|E_1| = |E_2| = E$, $E_F = -E$.

It is necessary to comment on whether our stage-2 GIC is a donor or an acceptor compound. $BiCl_3$ is always a donor because it has an excess of electron density. However, the prior addition of elemental chlorine is necessary to make the stage-2 compound. It is likely that this process changes the bismuth from the +3 to the +5 oxidation state. Then the molecule is known to be a Lewis acid which functions as an acceptor of electron density. Thus we consider the stage-2 compound made from $BiCl_2$ with the addition of Cl_2 to be an acceptor. This will be confirmed by the similarity of its energy-band parameters with those of other stage-2 acceptor compounds.

The cross-sectional areas of the Fermi surface of the two bands are

$$A_1 = \frac{4\pi}{3\gamma_0^2 a^2}(E^2 - E\gamma_1) , \quad (3)$$

$$A_2 = \frac{4\pi}{3\gamma_0^2 a^2}(E^2 + E\gamma_1) . \quad (4)$$

Equations (3) and (4) can be solved for E/γ_0 and γ_1/γ_0 with

$$E = \left[\frac{3a^2\gamma_0^2}{8\pi}(A_1 + A_2)\right]^{1/2} . \quad (5)$$

Thus γ_0 is a scaling factor which must be determined.

The two dHvA frequencies F_1 and F_2 are attributed to the areas A_1 and A_2, respectively. Then the solution of Eqs. (3) and (4) yields $E/\gamma_0 = 0.304$ and $\gamma_1/\gamma_0 = 0.158$.

There are several ways to obtain a value for γ_0. First, we calculated the energy bands for E_1^v and E_2^v for a set of band parameters (γ_0, γ_1) and the Fermi energy was ad-

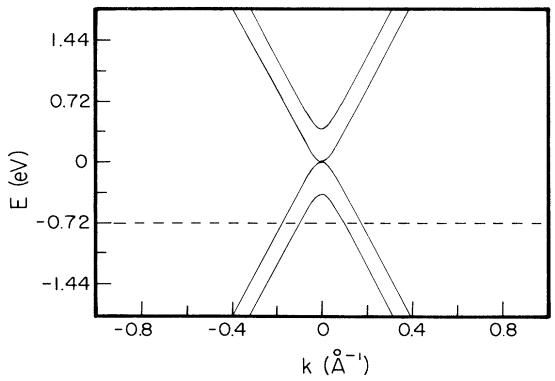

FIG. 5. The band structure of the stage-2 $BiCl_3$ GIC. The dashed line is the Fermi level of -0.73 eV.

justed to fit the sum of the experimental areas according to Fig. 5. This value was then used to calculate the Fermi areas from (3) and (4). The band parameters $(\gamma_0,\gamma_1)=(2.4,0.38$ eV) gave satisfactory agreement with a Fermi energy of -0.73 eV. The energy bands are shown in Fig. 5.

The parameter γ_0 was also determined from E/γ_0 and γ_1/γ_0 and the cyclotron masses which are given by

$$m_1=\frac{2\hbar^2}{3\gamma_0^2a^2}(2E-\gamma_1)\ , \tag{6}$$

$$m_2=\frac{2\hbar}{3\gamma_0^2a^2}(2E+\gamma_1)\ . \tag{7}$$

Equations (6) and (7) are the band masses, and in using the measured cyclotron masses in (6) and (7) it has to be assumed that other contributions to the mass from the electron-phonon and electron-electron interactions are negligible and that $m=(\hbar^2/2\pi)dA/dE$. Since only one equation is required to solve for γ_0, we obtained values of γ_0 from (6) and (7). It was found that $\gamma_0=2.58$ eV from m_1 [Eq. (6)] and $\gamma_0=2.50$ eV from m_2 [Eq. (7)].

We now compare these results with those for the stage-2 $SbCl_5$ GIC and the stage-2 BF_4^- GIC. There are two frequencies for the stage-2 $SbCl_5$ GIC that is cooled slowly from room temperature.[3] The values are 422 ± 2 and 1190 ± 5 T. Two narrow peaks in the Fourier-transform dHvA spectrum of the BF_4^- GIC yield frequencies of 523 ± 1 and 1377 ± 2 T.[4] These data were interpreted with the band model of Holzwarth.[6] It includes four in-plane and four interplane interactions and a difference in energy for nonequivalent carbon sites. The Fermi energy was adjusted to fit the sum of the Fermi areas obtained from the dHvA frequencies. The Fermi energy was -0.88 eV for the $SbCl_5$ GIC and -0.96 eV for the BF_4^- GIC.

The experimental results for the stage-2 GIC's of $BiCl_3$, $SbCl_5$, and BF_4^- are summarized in Table I. Here, E/γ_0 and γ_1/γ_0 were determined from Eqs. (3) and (4). The ratio γ_1/γ_0 is the same to within experimental error for these compounds. This confirms that the $BiCl_3$ GIC is an acceptor compound. It also suggests that the energy-band parameters are very similar for the three compounds. However, they are different from those of pure graphite, for which $\gamma_1/\gamma_0=0.123$ with $\gamma_0=3.16$ eV and $\gamma_1=0.38$ eV.

The values of γ_0, γ_1, and E_F that were determined in different ways are compared in Table II for the three GIC's. The value of γ_0 from the Blinowski model is less than that for the Holzwarth model, but for each model a similar value is suitable for all the compounds. It depends as much on the mass that is used for one compound as on the compound that is analyzed when Eqs. (6) and (7) are used. Nevertheless, it is always smaller for the stage-2 GIC's than for pure graphite. The same value of γ_1 is suitable for all the compounds for the calculation of the energy bands for either the Holzwarth model or the Blinowski model. The Fermi energy increases as the charge transfer per carbon atom increases for different stage-2 compounds. It can be noted that there is an increase in the charge transfer with a decrease in the d-repeat spacing.

IV. CONCLUSIONS

The measurements of the dHvA effect on the stage-2 $BiCl_3$ GIC were performed. Two dHvA frequencies were obtained and were interpreted in terms of the electronic structure of the Blinowski model, with the parameters γ_0 and γ_1 having values of 2.40 and 0.38 eV, respectively, and the Fermi energy equal to -0.73 eV. The parame-

TABLE II. Energy-band parameters determined in different ways for the stage-2 $BiCl_3$, $SbCl_5$, and BF_4^- GIC's.

	$BiCl_3$	$SbCl_5$	BF_4^-
γ_0 (eV) Blinowski model	2.40	2.40	2.40
γ_0 (eV) Holzwarth model		2.64	2.66
γ_0 (eV) from m_1	2.58	2.60	2.91
γ_0 (eV) from m_2	2.50	2.92	2.78
γ_1 (eV) Blinowski model	0.38	0.38	0.38
γ_1 (eV) Holzwarth model		0.42	0.43
γ_1 (eV) from m_1	0.41	0.41	0.47
E_F (eV) Blinowski model	-0.73	-0.80	-0.87
E_F (eV) Holzwarth model		0.88	-0.96
$f/l(e^+)$ charge transfer/carbon	0.017	0.020	0.024
d (Å) repeat spacing	13.00	12.72	11.13

ters determined from the cyclotron masses were larger by up to 10%. The results were compared with those obtained previously[3,4] for the stage-2 GIC's with $SbCl_5$ and BF_4^-. The same band structure is suitable for all the stage-2 compounds. However, there is a different charge transfer from the graphite to the acceptor in each stage-2 compound. This gives each GIC a unique Fermi energy.

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[1]P. Behrens, V. Woebe, K. Jopp, and W. Metz, Carbon **26**, 641 (1988).

[2]J. Blinowski, H. H. Nguyen, C. Regaux, J. P. Vieren, R. letoullec, G. Furdin, A Herold, and J. J. Melin, J. Phys. (Paris) **41**, 47 (1980).

[3]H. Zaleski, P. K. Ummat, and W. R. Datars, Phys. Rev. B **35**, 2958 (1987).

[4]H. Zaleski, P. K. Ummat, and W. R. Datars, Solid State Commun. **55**, 401 (1985).

[5]G. Wang, H. Zaleski, P. K. Ummat, and W. R. Datars, Phys. Rev. B **37**, 9029 (1988).

[6]N. A. W. Holzwarth, Phys. Rev. B **21**, 3665 (1980).