The de Haas-van Alphen effect of SbF$_5$-intercalated graphite

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Abstract. This paper presents the de Haas–van Alphen (DHVA) effect of the stage-3 SbF$_5$-graphite intercalation compound (GIC). Three groups of DHVA frequencies and carrier cyclotron masses are explained by the Blinowski band structure model with a Fermi energy of −0.73 eV. The highly anisotropic Fermi surface of the compound is measured with the angular dependence of the DHVA frequencies. It is also found that the energy bands and the charge distribution over the graphite layers are similar in the stage-3 SbF$_5$-GIC and the stage-3 SbCl$_5$-GIC.

1. Introduction

Graphite intercalation compounds (GICs) of SbCl$_5$ and SbF$_5$ are similar synthetic metals with a high electrical conductivity (Wortmann *et al* 1988). The SbCl$_5$ GICs have been studied extensively with respect to structure, electrical properties and chemical composition while the SbF$_5$ GICs have received considerably less attention. In this paper, we present the first report of the de Haas–van Alphen (DHVA) effect in the stage-3 SbF$_5$ GIC.

The Blinowski rigid band model (Blinowski and Rigaux 1980, Blinowski *et al* 1980) is based on the tight-binding approximation with nearest neighbour interactions. It was used to interpret the DHVA effect in the stage-2 SbCl$_5$ GIC (Zaleski *et al* 1987), the stage-3 SbCl$_5$ GIC (Wang *et al* 1988) and stage-1 and stage-2 SbCl$_4$F GIC (Zaleski *et al* 1989); and it describes the energy bands and the Fermi surfaces of the GICs to within 10%.

This paper presents the detailed results of the investigation of the electronic structure of the stage-3 SbF$_5$-graphite compound by the DHVA technique. Both the temperature dependence and the angular dependence of the DHVA frequencies were measured. The experimental data related to the band structure are interpreted with Blinowski's theoretical model. The results of the stage-3 SbF$_5$ GIC and the stage-3 SbCl$_5$ GIC, reported previously, are compared.

2. Experimental details

The stage-3 SbCl$_5$ GIC was made with the method of Wu *et al* (1981). The starting material was highly oriented pyrolitic graphite (HOPG) cut into 2 mm × 3 mm squares approximately 0.3 mm thick. The HOPG and SbF$_5$ were loaded into an H-shaped tube.
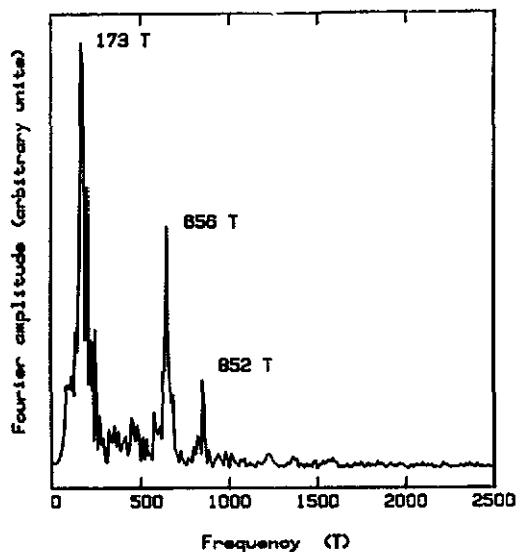
Figure 1. The Fourier transform of the DHVA oscillations of stage-3 SbCl$_5$ graphite.

The SbF$_5$ side was placed in a constant-temperature bath at 20 °C, and the other side containing the sample was put into a tube furnace at a temperature of 100 °C. The reaction time was about seven days. The mass uptake showed that the sample had the chemical composition C$_{27}$SbF$_5$ which is also that of the stage-3 SbF$_5$ GIC.

The DHVA effect was observed with the low-frequency, field-modulation technique in magnetic fields up to 5.5 T. The temperature dependence of the amplitude was measured with the c-axis of the sample parallel to the direction of the magnetic field. The angular dependence was obtained by turning the sample to different orientations with respect to the magnetic field direction. Samples were cooled slowly from room temperature to liquid nitrogen temperature because it was shown previously that fast cooling of the SbCl$_5$ GIC results in a complex DHVA spectrum (Zaleski *et al* 1987). The frequencies were measured with a sample temperature of 4.2 K.

3. Results

Figure 1 shows the Fourier transform spectrum of the DHVA oscillations measured between 2.5 and 4.2 T with the c-axis of the sample parallel to the direction of the magnetic field. There are three groups of DHVA frequencies. The first group consists of a dominant frequency 173 T and four close frequencies, 154 T, 198 T, 222 T and 247 T with smaller amplitude. The second group has a dominant frequency of 656 T and two close frequenciess of 624 T and 685 T. The third group has two frequencies; the dominant one is 852 T and the other 834 T.

The cyclotron masses coresponding to the three dominant frequencies were determined from the temperature dependence of the DHVA amplitudes between 1.4 K and
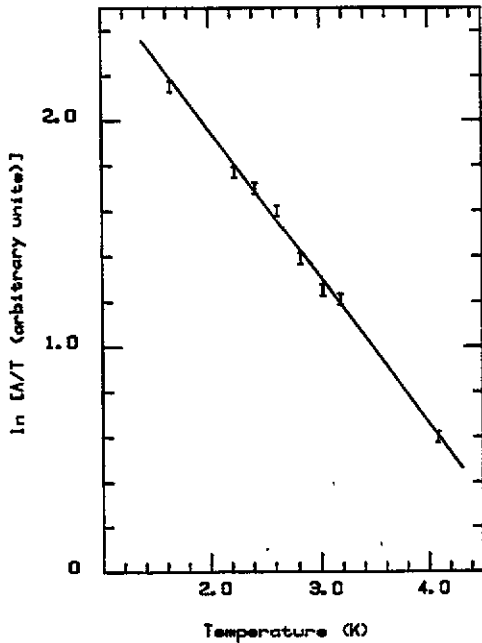
Figure 2. Temperature dependence of A/T where A is the amplitude of the 173 T DHVA oscillation of stage-3 SbF₅ graphite.
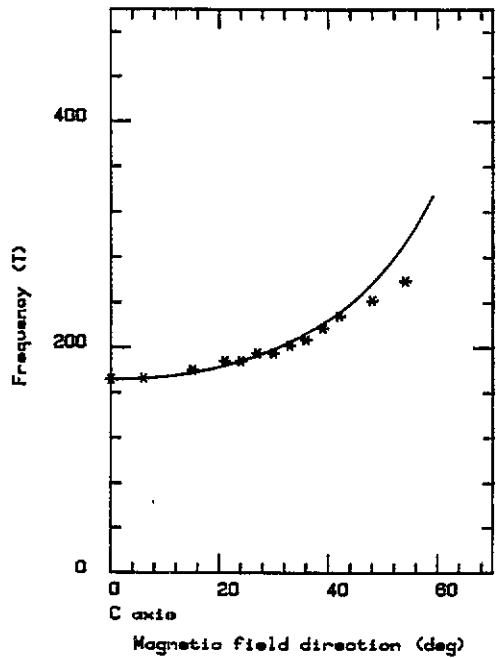
Figure 3. DHVA frequency of the lowest frequency dominant oscillation as a function of magnetic field direction from the c-axis of stage-3 SbF₅ graphite. The full curve is for a cylindrical Fermi surface.

4.2 K. Figure 2 shows a plot of $\ln A/T$ against T. The effective masses were determined from the proportionality of the amplitude A

$$A \propto T/\sinh(bm_c T/Bm_0)$$

by a computer program. The results are $m_1 = 0.184\, m_0$. $m_2 = 0.226\, m_0$ and $m_3 = 0.109\, m_0$.

In order to investigate the actual shape of the Fermi surface for this compound, the angular dependence of the DHVA frequencies was measured from $\theta = 0°$ to $\theta = 54°$. Here θ is the angle between the direction of the magnetic field and the c-axis of the sample. Figure 3 shows the plot of the dominant DHVA frequency in the first group as a function of the angle θ. The full curve represents the prediction for a straight cylinder of the Fermi surface given by $f = f_0/\cos\theta$. From figure 3 one can see that the DHVA frequency does follow a cylindrical behaviour for angles up to about 40°. For larger angles, there are deviations from the cylindrical fit. At $\theta = 54°$ there is a substantial difference between the frequency and the prediction for a Fermi surface cylinder.

4. Discussion

The simple, tight-binding model proposed by Blinowski *et al* assumes that the in-plane unit vectors are the same as in graphite and the c-axis unit vector is equal to the

Table 1.

Area (Å^{-2})		Frequency (T)		Mass (m_0)	
Exp.	Cal.	Exp.	Cal.	Exp.	Cal.
0.0164	0.0163	172	168	0.109	0.101
0.0626	0.0651	656	684	0.184	0.184
0.0813	0.0814	852	849	0.226	0.212

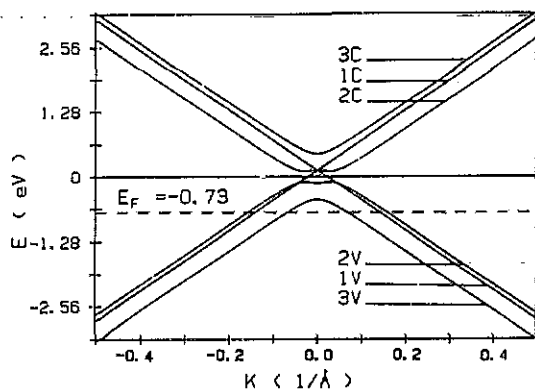**Figure 4.** The band structure of stage-3 SbF$_5$ graphite with the band structure parameters $\delta = 0.13$, $\gamma_0 = 2.8$ and $\gamma_1 = 0.31$.

intercalate–intercalate spacing. This gives n valence–conduction pairs of bands for a stage-n compound. The electron dispersion is assumed to be independent of the intercalated species and the number of electrons transferred from the graphite.

The model is used by assuming the band parameters γ_0(2.8 eV), γ_1(0.31 eV), and δ(0.13 eV) for stage-3 SbCl$_5$ graphite and calculating the areas of the three bands as a function of energy. The value of the Fermi energy is adjusted to fit the experimental Fermi areas obtained from the equation $A = \hbar f/2\pi e$. The fitted Fermi energy (-0.73 eV) and the band parameters (γ_0, γ_1, δ) are then used to calculate the DHVA frequencies ($f = 2\pi e A/\hbar$) and cyclotron masses ($m_c = (\hbar^2/2\pi)(\partial A/\partial E)_{E_F}$) with the area functions from the band model. The comparison of the experimental data with the model is shown in table 1.

One can see from table 1 that the model of Blinowski *et al* predicts the areas and frequencies to within 4% and the values of the effective masses to within 7% of the observed ones. This is within the accuracy expected for the model.

The energy bands for the stage-3 SbCl$_5$ GIC are shown in figure 4. There are three valence bands and three conduction bands. There is little overlap between the valence and conduction bands. The valence bands are unoccupied because some electrons are transferred to the acceptor intercalate species. The Fermi energy is negative with a value of -0.73 ev and is shown by the broken line in figure 4.

The fraction, z, of the excess charge accumulated on the internal layer of the stage-3 acceptor compound can be found from the relation (Blinowski and Rigaux 1980)

$$2\delta = 0.1 + (f/l)(57.6\,z - 2.7) \text{ ev} \tag{1}$$

where the parameter 2δ is the potential energy difference between the external and

internal layers and f is the charge-transfer coefficient per intercalated molecule in the compound with a composition C_X.

The charge transfer per carbon atom, f/l, is directly proportional to the sum of the DHVA frequencies

$$f/l = (f_1 + f_2 + f_3)/118371 \tag{2}$$

With the values for $f_1 + f_2 + f_3$ given in table 1, $f/l = 0.0142$. Then with $\delta = 0.13\,\text{eV}$, the fraction z of the excess charge accumulated on the internal layer is 0.242. This value of z being larger than zero and smaller than $\frac{1}{3}$ means that the charge distribution along the c-axis of the sample is neither a metallic sandwich nor a uniform charge distribution. There is a deficiency of charge on the internal graphite layer relative to the layer next to the intercalant.

The angular dependence of the DHVA frequencies gives insight into the actual shape of the Fermi surface. From figure 3, it is evident that the Fermi surface is not a straight cylinder because the observed frequency does not follow the cylindrical prediction at high angles. The negative deviation from the prediction means that the cross-sectional area of the Fermi surface is gradually decreasing with wave vector k_z along the z direction. The change in the area could arise from an undulation of the Fermi surface. The undulation of the Fermi surface could cause the splitting of the DHVA frequency for each band because it has more than one external cross-sectional area.

The Blinowski model predicts a straight, cylindrical Fermi surface. The reason the real Fermi surface is not this simple is that the potential energy variation in the graphite subsystem, that is neglected in the model, must be included. Imperfections, particularly the domains of intercalated monolayers, can play a critical role in the perturbation of the graphite–graphite and graphite–intercalant interactions. This affects the band structure of the graphite compound and makes the Fermi structure more complicated than a cylinder.

The stage-3 SbF$_5$ and SbCl$_5$ GICs have many things in common as shown by the comparison of data for the two compounds in table 2. They are similar with respect to intercalate structure, energy band structure and charge distribution along the c-axis. This occurs because SbF$_5$ and SbCl$_5$ have similar chemical properties and a similar electron affinity, and results in a similar charge transfer from graphite to SbCl$_5$ and SbF$_5$. The properties of their energy bands are, then, expected to be similar to those predicted by the rigid band model.

5. Conclusions

The DHVA measurements for stage 3 SbCl$_5$ GIC show three groups of DHVA frequencies which are identified with the basic graphite bands.

These frequencies are used to determine the Fermi energy of the compound by using Blinowski's band model. The band parameters γ_0, γ_1 and γ are taken to be the same as those in the stage-3 SbCl$_5$ GIC and the observed frequencies agree with the theoretical predictions. The values of the measured cyclotron masses agree with the three values calculated from the model.

The fractional charge distribution shows that there is a deficiency of charge in the internal graphite layer relative to the layers next to the intercalant.

Table 2.

		$SbCl_5$	SbF_5
Repeat d-spacing	I	16.02 Å	15.05 Å
Chemical composition	C_nX	$C_{36}SbCl_5$	$C_{27}SbF_5$
Band parameters (eV)	E_F	−0.71	−0.73
	δ	0.13	0.13
	γ_0	2.8	2.8
	γ_1	0.31	0.31
DHVA frequencies (T)	F_1	654	656
	F_2	811	852
	F_3	152	172
Effective masses (m_0)	m_1^*	0.16	0.184
	m_2^*	0.22	0.226
	m_3^*	0.086	0.109
Charge transfer/carbon	f/l	0.0137	0.0142
Fractional charge on internal layer	z	0.25	0.24

The comparison of the SbF_5 GIC with the $SbCl_5$ GIC shows that they are similar in intercalate structure, Fermi structure and charge transfer.

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