The de Haas-van Alphen effect of $SbCl_4F$-intercalated graphite

The de Haas–van Alphen effect of SbCl$_4$F-intercalated graphite

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Abstract. The de Haas–van Alphen (DHVA) effect of the SbCl$_4$F graphite intercalation compound in stage 1 and stage 2 was investigated in magnetic fields of up to 5.5 T. The DHVA frequency spectrum of the stage-1 compound consists of two frequencies. The higher one is associated with the single graphitic energy band of the stage-1 compound. In some stage-1 samples, the two frequencies are split further into two. There is a single strong DHVA oscillation with a frequency between 400 and 450 T from the stage-2 compound. It is assigned to one of the graphitic energy bands.

1. Introduction

SbCl$_4$F graphite is a new graphite intercalation compound (GIC), which is prepared by a vapour-phase technique (Preiss *et al* 1986, Preiss and Fichtner-Schmittler 1986, Ummat *et al* 1986). The formulae determined using x-ray analysis by Preiss and co-workers are $C_{12.5}$ SbCl$_4$F and C_{24} SbCl$_4$F for stage 1 and stage 2, respectively. The SbCl$_4$F is in a sandwich structure between carbon layers but, unlike in the classical model, the antimony atoms are not located at the central plane of the sandwich. The in-plane structure of the SbCl$_4$F was reported by Preiss and co-workers to be a $\sqrt{7} \times \sqrt{7}$ lattice oriented with respect to the carbon lattice. Later, Zaleski and Datars (1988) found additional weak x-ray reflections, which index to a $\sqrt{21} \times \sqrt{21}$ lattice of linked SbCl$_4$F molecules.

This new GIC is similar to the SbCl$_5$ GIC, which has been studied extensively. The formula of the stage-2 compound is $C_{24.4}$ SbCl$_5$ from x-ray analysis (Preiss *et al* 1986b). There is a charge transfer of 0.0205 carriers per carbon atom and a Fermi energy of -0.88 eV. The in-plane and intra-layer carbon interaction parameters are $\gamma_0 = 2.4$ eV and $\gamma_1 = 0.377$ eV, respectively (Zaleski *et al* 1987). For stage-1 SbCl$_5$ graphite, the Fermi energy is -1.127 eV, the charge transfer per carbon atom is 0.031 electrons and the carbon interaction parameter is taken to be $\gamma_0 = 2.4$ eV (Zaleski *et al* 1984). It is also known that SbCl$_5$ intercalated graphite has a stable $\sqrt{7} \times \sqrt{7}$ in-plane structure of triangular symmetry (Homma and Clarke 1985) as well as several other structures.

The de Haas–van Alphen (DHVA) frequency is a measure of an extremal cross sectional area of the Fermi surface in the plane perpendicular to the magnetic field. The basic Fermi surface of the SbCl$_5$ GICs is determined from the graphite energy bands that are modified by the intercalant. However, more complex DHVA spectra with many frequencies for one magnetic field direction are obtained with SbCl$_5$ GICs that are not

cooled slowly (Zaleski *et al* 1984, 1987). An understanding in terms of the graphite bands was obtained only from spectra with a few frequencies. Similarly, the simplest DHVA spectra of the $SbCl_4F$ GICs are interpreted in order to gain an understanding of the energy bands of these GICs.

A model of the electronic structure of acceptor GICs was proposed by Blinowski *et al* (1980). The model is based on the tight-binding approximation and includes nearest-neighbour interactions. It describes the energy bands and Fermi surface of the $SbCl_5$ GIC to within 10%. It is used to interpret the results in this paper.

The purpose of this paper is to present results of DHVA experiments with stage-1 and stage-2 $SbCl_4F$ intercalated graphite. The results are compared with those for $SbCl_5$ graphite.

2. Experimental method

The intercalation reactions were performed using highly oriented pyrolytic graphite (HOPG) cut into $3 \times 3 \ mm^2$ pieces and cleaved to a thickness of about 0.5 mm. Liquid $SbCl_4F$ was prepared by the reaction of $SbCl_5$ with AsF_3 and purified by triple distillation (Ummat *et al* 1986).

A stage-1 compound was obtained easily with a piece of HOPG and $SbCl_4F$ in a sealed pyrex tube held at a temperature of 50 °C for three days. The stage-2 GIC was prepared in a two-zone vapour-phase reaction. The $SbCl_4F$ was kept at 54 °C and the HOPG at 104 °C for one week.

The sample stage number was determined by (00*l*) x-ray diffraction with Cu Kα radiation with the sample in a sealed sample holder. The *c* axis identity periods for stage-1 and stage-2 samples were 9.30 and 12.69 Å, respectively. The mass uptake of each sample, $\Delta m/m$, equal to the increase in mass from intercalation relative to the mass of the starting HOPG piece, was measured with a balance situated in a dry box. $\Delta m/m$ was 2.13 ± 0.02 for stage-1 samples and between 1.04 and 1.08 for stage-2 samples.

The samples were put into a sealed sample holder for the DHVA measurements. Each sample was oriented for measurement with the *c* axis parallel to the direction of the magnetic field provided by a 5.5 T superconducting magnet. Data were taken as a function of the magnetic field with a sample temperature in the range 1.3–4.2 K by the modulation method, with detection at the first harmonic of the modulation frequency of 517 Hz. The output was recorded digitally for computer Fourier transform analysis.

3. Results

Figure 1 shows the DHVA spectrum from a stage-2 sample intercalated with a mass uptake of $\Delta m/m = 1.08$. There is one oscillation with a frequency of 450 T. There is no beating with a second oscillation of similar frequency. There is also no evidence of a high frequency up to 2000 T. The DHVA spectra of all the stage-2 samples that were measured are characterised by a strong oscillation with a frequency between 400 and 450 T. The frequency of the oscillation decreased slightly from 450 to 400 T as the mass uptake of the sample decreased from 1.08 to 1.04.

Figure 2 shows the DHVA spectrum of a stage-1 $SbCl_4F$ GIC. It exhibits two strong oscillations. One has a frequency of 1250 T and the second has a lower frequency of 480 T. The peak below 100 T is not a DHVA frequency. This is the simplest spectrum
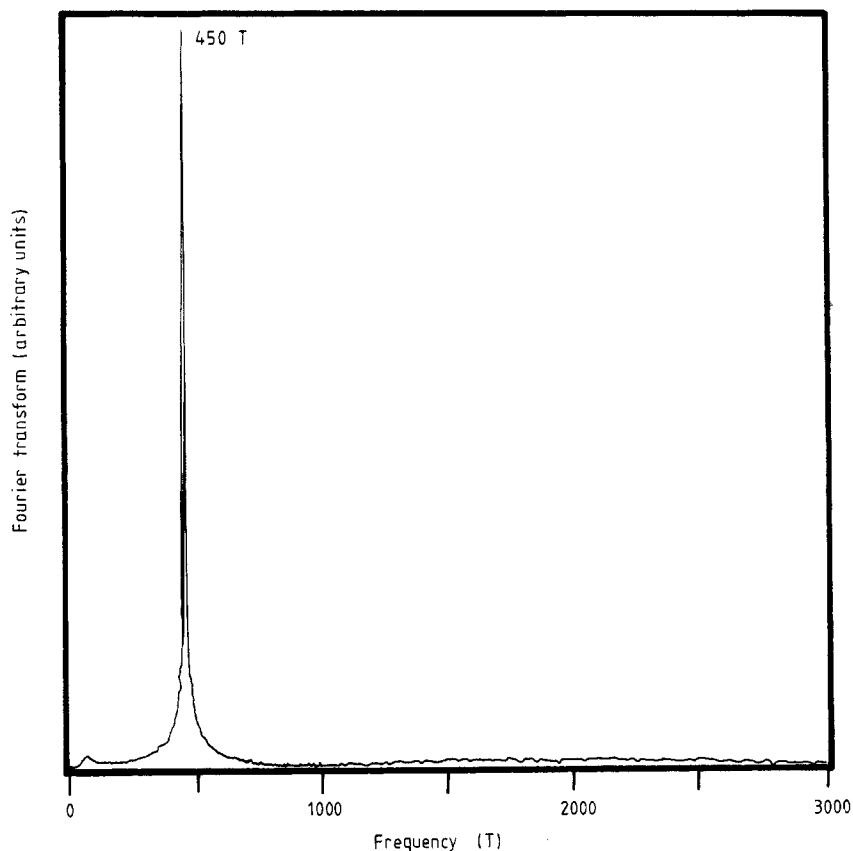
Figure 1. The Fourier transform of the DHVA oscillations of stage-2 SbCl$_4$F graphite.

obtained with stage-1 samples. One sample showed more frequencies; the high and low frequencies are each split into a pair with a frequency difference of 20%.

4. Discussion

The total charge per carbon atom for an n-stage compound with l carbon atoms per unit cell is

$$\frac{f}{l} = \frac{a^2\sqrt{3}}{4\pi^2 n} \sum_i A_i.$$ (1)

The areas A_i are directly proportional to the DHVA frequencies F_i:

$$F_i = (\hbar c/2\pi e)A_i.$$ (2)

Thus, the DHVA effect measures the charge transfer directly.

There is one graphite energy band in an acceptor stage-1 GIC. It is given by (Blinowski *et al* 1980)
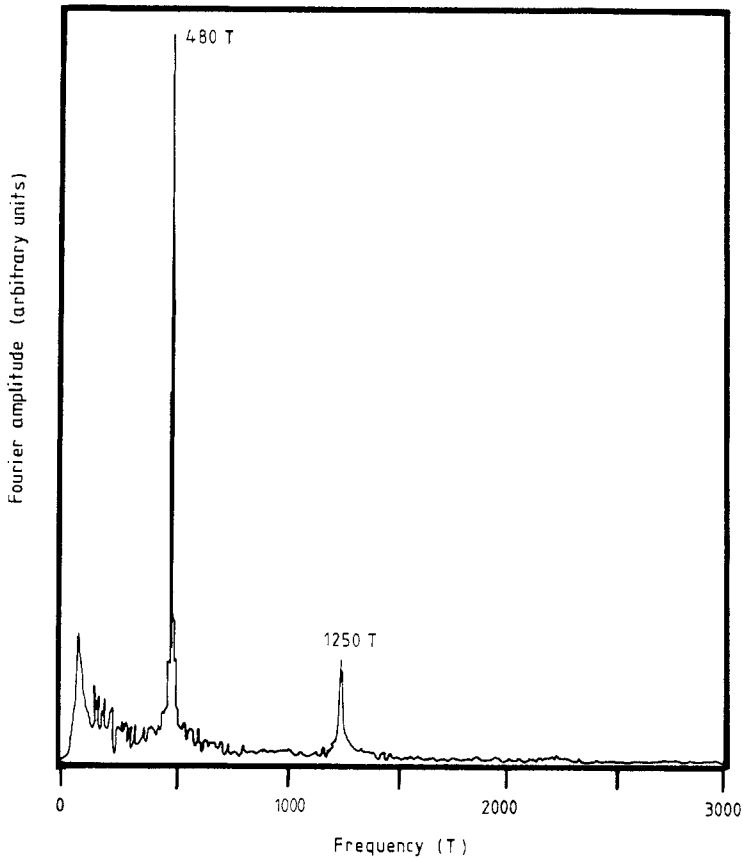
$$E = -\tfrac{3}{2}\gamma_0 a|K|$$ (3)

Figure 2. The Fourier transform of the DHVA oscillations of stage-1 SbCl₄F graphite.

where $|K| = |k - k_U|$ is the wavevector from the U point in the Brillouin zone, a is the in-plane carbon–carbon distance and γ_0 is the in-plane interaction parameter.

The two graphite bands in the stage-2 GIC are given by (Blinowski *et al* 1980)

$$E = -\tfrac{1}{2}[(\gamma_1^2 + 9\gamma_0^2 a^2 K^2)^{1/2} \pm \gamma_1] \tag{4}$$

where γ_1 is the interaction energy of nearest atoms in two layers. The Fermi areas of the bands are given by

$$A_1 = 4\pi(E^2 - E\gamma_1)(9\gamma_0^2 a^2)^{-1} \tag{5}$$

$$A_2 = 4\pi(E^2 + E\gamma_1)(9\gamma_0^2 a^2)^{-1}. \tag{6}$$

The charge transfer per carbon atom is 0.031 and 0.041 for stage-1 SbCl₅ and stage-1 SbF₆ GICs, respectively. These values are derived from a DHVA frequency of 1211 T in stage-1 SbCl₅ (Zaleski *et al* 1984) and 1627 T in stage-1 SbF₆ (Zaleski *et al* 1985). A similar charge transfer and DHVA frequency in stage-1 SbCl₄F are expected since there is a similar number of carbon atoms per intercalant. Thus, the higher DHVA frequency of stage-1 SbCl₄F is assigned to the graphite energy band. Since the area of the Fermi surface cylinder is πK^2, the value of 1250 T yields $E_F = -1.13$ eV from equations (2) and (3) with $\gamma_0 = 2.3$ eV.

The lower frequency of the stage-1 compound cannot be from the basic graphite energy band since there is only one energy band in the stage-1 compound and it does not indicate sufficient charge transfer from equations (1) and (2). Another possible cause of the lower frequency is a remapping of the basic Fermi surface by a periodic structure of the $SbCl_4F$ intercalate. A $\sqrt{7} \times \sqrt{7}$ structure is known, but the addition of the periodicity of this structure in reciprocal space does not change the Fermi surface. Another periodicity such as that of the $\sqrt{21} \times \sqrt{21}$ structure may cause a change in the Fermi surface.

The DHVA spectrum of the stage-2 $SbCl_4F$ GIC is unusual because there is a single strong frequency. There are no weak oscillations that beat with the strong one as in the $SbCl_5$ stage-2 GIC. Since these oscillations in $SbCl_5$ come from regions of different structure, the single frequency indicates that several periodicities are not found in a well prepared sample.

The single frequency comes from the energy band with an area A_1 given by equation (5). The values $\gamma_1 = 0.377$ eV and $\gamma_0 = 2.4$ eV for the stage-2 $SbCl_5$ GIC are used because they cannot be derived from the present data without the second area. This gives an estimate of the Fermi energy: -0.8 eV.

The parameters observed and used for A_1 are used in equation (6). This yields an area $A_2 = 0.11$ Å^{-2} and a frequency $F_2 = 1200$ T for the second frequency. An oscillation at or in the region of this frequency is not observed. The reason for this is not yet known.

There is a small decrease in F_1 when $\Delta m/m$ is changed from 1.08 to 1.04. This indicates that there is a small change in the Fermi energy and charge concentration in the stage-2 compound with a change in the mass caused by intercalation.

5. Conclusions

There is a strong DHVA effect from $SbCl_4F$ graphite intercalated compounds. In the stage-1 compound, there are two DHVA frequencies which are split further into two in some samples. The higher frequency is associated with the single graphite energy band. In the stage-2 compound, there is a single strong DHVA oscillation with a frequency between 400 and 450 T. It is assigned to one of the graphite energy bands.

Acknowledgments

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