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## Electronic Structure of Intercalated Graphite Determined by Magnetothermal Oscillations

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We report the first observation of magnetothermal quantum oscillations in  $C_{12n}(SbCl_5)$  for  $n=2$  and  $n=4$ . We interpret these results assuming that the compound is composed of two phases: pure graphite and intercalated sandwiches which behave like two-dimensional metals. This model explains simultaneously the metallic reflectivity and conductivity and the immeasurably small Hall coefficient observed in these compounds.

The graphite intercalation compounds consist of an alternating sequence of intercalate layers separated by  $n$  graphite layers. These compounds are interesting for two applications: conductors of electricity and catalysts in electrolytic cells. The electrical conductivity is especially high, even higher than that of copper for certain compounds.<sup>1</sup> This metallic conductivity is still not yet well understood, even though many experimental results have been published.<sup>2</sup> The electronic structure is still unknown. One of the major parameters is the fractional free-carrier generation rate per intercalated atom or molecule,  $f$ . Estimations of  $f$  ranging from 0.01 to 1 have been reported.<sup>3</sup>

Quantum oscillatory effects are known as one of the best tools to determine the Fermi surface (FS) of metals. Oscillations in the magnetoresistance (Shubnikov-de Haas effect) have been reported by Bender and Young<sup>4</sup> in graphite bromine residual compounds, with a very low concentrations of bromine ranging (from 1 to 2)  $\times 10^{-2}$  at.%. Dresselhaus, Dresselhaus, and Fischer<sup>5</sup> proposed a rigid-band model valid for very dilute compounds. In their model, the size of the FS increases continuously with donor or acceptor density. This can be directly tested by measuring

the size of the FS for various intercalation stages  $n$ .

We report the first experiments on magnetothermal oscillations for the compounds  $C_{12n}(SbCl_5)$  with  $n=2$  and  $n=4$ . Contrarily to the residual compounds, these compounds are well-defined both chemically and structurally.

We have studied the magnetothermal oscillations (MTO) of the de Haas-van Alphen (dHvA) type. As is well known,<sup>6</sup> a thermally isolated degenerate electron gas at low temperature in a high magnetic field presents oscillations in its temperature versus magnetic field  $B$ . These oscillations, the so-called MTO, arising from the Landau level quantization, are observed by the temperature variation produced in the coupled crystal lattice. The frequency of the MTO is proportional to the extremal section of the FS perpendicular to  $\vec{B}$ .

Among the quantum effects the MTO are particularly well adapted for the study of the FS of the lamellar compounds, because they do not need electrical contacts and can be measured on very small samples ( $\leq 10^{-3}$  g). We have used for these experiments the low-frequency field-modulation technique<sup>7</sup> in an 80-kOe superconducting coil, at 4.2°K. The samples of  $C_{12n}(SbCl_5)$ , small disks of

3–4 mm diameter and 0.15 mm thickness, were glued by silicon grease to a very small carbon thermometer (0.2 mm<sup>3</sup>), thermally isolated from the liquid helium bath. The samples were prepared by direct action of liquid or gaseous SbCl<sub>5</sub> on HOPG graphite.<sup>8</sup> These compounds are particularly stable in air and easy to manipulate. Amplitudes of the MTO, as low as a few times 10<sup>-6</sup> K, have been measured. Fourier transforms were used to analyze the complex structure of the MTO spectra.

Figure 1 shows a typical magnetothermal oscillation (a), and its Fourier spectrum (b). Table I shows the observed frequencies for  $\vec{c}$  axis parallel to  $\vec{B}$ . These frequencies correspond to orbits in the basal plane. Three sets of frequencies were observed. The angular variation (not shown here) for the smallest  $\alpha$  set fits very well a cylindrical FS.

The oscillations appear at a magnetic field as low as  $5 \times 10^3$  G, implying mobilities  $\mu \geq 2 \text{ m}^2 \text{ V}^{-2} \text{ s}^{-1}$  ( $\mu B \geq 1$ ). These high mobilities suggest that the system is well ordered at low temperatures and contains very few defects and impurities.

The characteristic feature of these results is that the MTO frequencies are independent of the state. This fact suggests that the same metallic phase is present in all samples. We think that

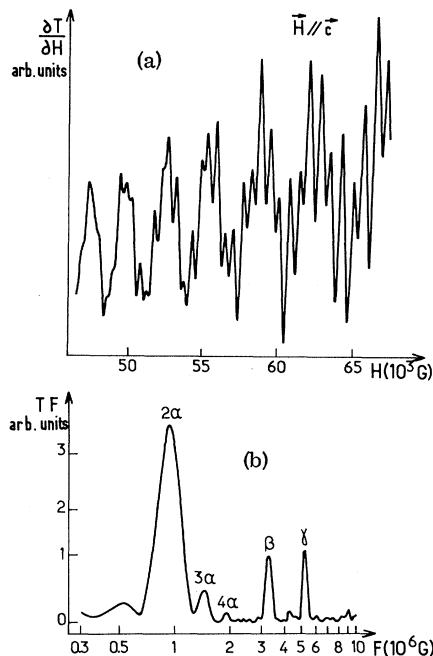


FIG. 1. (a) Typical magnetothermal oscillation for C<sub>24</sub>SbCl<sub>5</sub>; (b) its Fourier transform.

TABLE I. The observed MTO frequencies in C<sub>12n</sub>(SbCl<sub>5</sub>) with  $n = 2$  and  $n = 4$ .

Frequencies in 10 <sup>6</sup> G	State	
	$n = 2$	$n = 4$
$\alpha$	0.475 ± 0.01	0.475 ± 0.01
$2\alpha$	0.95 ± 0.01	0.95 ± 0.01
$3\alpha$	1.43 ± 0.02	1.44 ± 0.02
$4\alpha$	1.91 ± 0.03	2.00 ± 0.03
$\beta$	3.32 ± 0.05	3.30 ± 0.05
$\gamma$	5.35 ± 0.1	5.50 ± 0.1

this metallic phase is a two-dimensional one, consisting of a sandwich of one intercalate plane of SbCl<sub>5</sub> molecules between two carbon layers.

To determine the two-dimensional (2D) electronic structure of this metallic sandwich (MS), we use the nearly-free-electron model (NFE) with the Harrison method<sup>9</sup> for constructing the 2D FS. If we assume the C<sub>12</sub>-SbCl<sub>5</sub>-C<sub>12</sub> composition for the MS, the direct lattice is deduced from that of the graphite by multiplication  $2\sqrt{3}$ ,  $2\sqrt{3}$  and a rotation of 30°. The area of the unit cell in direct space is twelve times that of graphite. The area of the Brillouin zone is

$$S_{\text{BZ}} = \frac{4\pi^2}{9\sqrt{3}a^2} = \frac{4\pi^2}{31.43} \text{ \AA}^{-2}$$

(see Fig. 2).

The construction of the FS (here a circle) needs a knowledge of  $k_{\text{F}}$  which is determined by

$$\frac{1}{2\pi^2} \pi k_{\text{F}}^2 = n_{\text{S}},$$

$n_{\text{S}}$  being the number of free electrons per unit surface. Assuming that the transfer coefficient is  $f = 1$ , with two electrons transferred to the

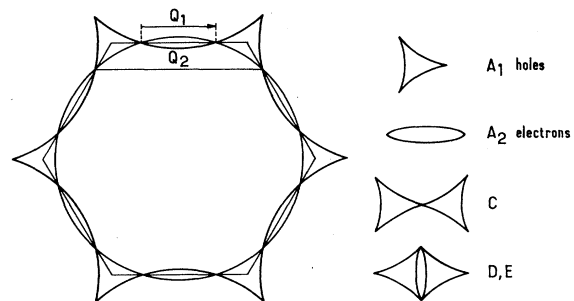


FIG. 2. Nearly-free-electron Fermi surface of 2D C<sub>12</sub>M, with possible orbits indicated on the right.

SbCl<sub>5</sub> molecule, we obtain a "hole" FS given by

$$\pi k_F^2 = S_{BZ}. \quad (1)$$

This implies one hole in the 2D band structure of graphite for 12 carbon atoms. Equation (1) gives

$$k_F = 0.63 \text{ \AA}^{-1}.$$

The Fermi circle is drawn in Fig. 2. This construction yields two orbits of respective areas  $A_1$  and  $A_2$ . The fact that  $\pi k_F^2 = S_{BZ}$  gives exactly  $A_1/A_2 = \frac{3}{2}$ , and an exact compensation  $n_e = n_h$ , where  $n_e$  and  $n_h$  are the densities of electrons and holes, respectively. The calculated values  $A_1$  and  $A_2$  give the following values for dHvA frequencies:

$$F_1 = 2.44 \times 10^6 \text{ G}, \quad F_2 = 1.63 \times 10^6 \text{ G}.$$

We obtain two frequencies instead of the three observed experimentally. The highest two observed frequencies,  $F_\beta$  and  $F_\gamma$ , are almost twice  $F_2$  and  $F_1$ , respectively. We can interpret this fact by either assuming a distortion of the FS from the exact circular shape, or by a crystallographic structure corresponding to  $C_6^+M^-$  instead of  $C_{12}^+M^-$  for the MS. The latter structure gives an area of the BZ twice as large as previously.

However, our model gives a ratio  $F_1/F_2 = \frac{3}{2}$ , which is exactly the value observed experimentally (within 5%). This ratio is directly related to the exact compensation ( $n_e = n_h$ ) in this compound. The compensation seems to be a general feature of the intercalated compounds, as seen from the Hall-effect measurements made by many authors<sup>10,11</sup> in a great variety of systems.

In the layered dichalcogenides, charge-density waves (CDW) have been observed.<sup>12</sup> Rice and Scott<sup>13</sup> have shown that a 2D energy band with saddle points at the Fermi energy is unstable against CDW formation. If we apply to our model the CDW instability driven by saddle points in the FS, we can find other orbits (Fig. 2). If the CDW vector is  $\vec{Q}_1$  we find the orbit C with a frequency  $2F_1$ . If the vector is  $\vec{Q}_2$ , we find two new orbits D and E. With our values we have  $F_0 = 0.54 \times 10^6 \text{ G}$

and  $F_E = 2F_1 + F_D = 5.4 \text{ MG}$ . Experimentally, the value of  $F$  is close to  $F_D$  giving some evidence for CDW formation. This should be confirmed by structural studies.

At very high magnetic fields, higher frequencies appear which we relate to magnetic breakdown. More detailed measurements will be published elsewhere.<sup>14</sup>

In conclusion, we believe that our MTO measurements have shown strong support in favor of a two-phase model, one of the phases being a 2D compensated metal. This model explains (a) the observed dHvA frequencies, (b) the very small Hall coefficient, (c) the metallic in-plane conductivity and reflectivity, and (d) the high density of states  $N(E_F)$  at the Fermi level obtained by specific-heat and magnetic-susceptibility measurements.

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