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FERMI SURFACE AND BAND STRUCTURE OF GRAPHITE INTERCALATION COMPOUNDS

Izio Rosenman, Francisco Batallan and Charles Simon

Groupe de Physique des Solides de l'Ecole Normale Superieure
Tour 23, 2 Place Jussieu, Paris 5, France

and

Herve Fuzellier

Laboratoire de Chimie Minerale Appliquee,
Université de Nancy I, 54037 Nancy Cedex, France

Results of quantum magnetothermal oscillations in nitric-acid-graphite intercalation compounds are presented. This includes de Haas-van Alphen frequencies and effective masses. These data are interpreted with a two-dimensionnal band structure proposed by Blinowski & al., coupled with the folding of the Fermi surface in the Brillouin zone of the intercalate. Extensions of this model are proposed.

I. Introduction

Although the pristine graphite is a semimetal its intercalated compounds are metals [1]. The intercalation process is characterized by the charge tranfer occuring between the graphite layers and the intercalate molecules. We shall restrict here to the graphite acceptor compounds (GAC) in which the intercalate accepts electrons from the graphite, leaving delocalized holes in the carbon layers. The high density of electrons produced by the transfer process and localized on the intercalate ions makes an electrostatic screen which prevents the free holes of moving accross it. This results in a two-dimensionnal (2-D) metal. In this case the quantum oscillatory effects are a very useful tool for studying the electronic structure.

II. The electronic structure of graphite acceptor compounds

The electronic structure of such a 2-D metallic zone has been computed by Blinowski & al. in order to explain results of optical reflectivity [2]. Their model is based on a tight binding computation and takes into account the interaction of the nearest graphite layers. It assumes a uniform rigid charge distribution on the intercalate layers. The result is that bands are differents for every stage. For the second stage which we shall describe in detail they find the following dispersion relations for the valence bands near the U and U' points of the Brillouin zone (BZ) of the graphite:

$$E_{v1} = -\frac{1}{2}\left(-\gamma_1 + \sqrt{\gamma_1^2 + 9\gamma_0^2 b^2 k^2}\right)$$

$$E_{v2} = -\frac{1}{2}\left(\gamma_1 + \sqrt{\gamma_1^2 + 9\gamma_0^2 b^2 k^2}\right) \qquad (1)$$

where $b = 1.42$ Å is the distance between carbon atoms in the graphite layer. k is measured from the U and U' points and γ_0 and γ_1 are respectively the resonance integrals for the nearest carbon atoms in the same layer and in two adjacent carbon layers as in pristine graphite. All the other interactions are

neglected in the model of Blinowski & al.Moreover this model neglects a feature which is not important in optical reflectivity but is critical for quantum oscillatory effects namely the inplane order of the intercalate.Indeed at sufficently low temperatures the intercalate layer is ordered in a lattice either commensurate or incommensurate with the graphite lattice[3] [4]. The compensating charge localized on the intercalate ions produces a perturbing potential which has the symmetry of the intercalate layer and which is seen by the delocalized holes in the graphite layers.This potential will produce additionnal gaps in the bands at the Bragg diffraction planes associated with the intercalate lattice.This will modify the topology of the Fermi Surface (FS).IN the case where the intercalate and the graphite layers are commensurate this is equivalent to the folding of the FS computed in the graphite BZ into the new BZ of the GAC which is smaller. The new orbits resulting from the folding are close one to the other in the BZ. So that in the high magnetic field needed for quantum oscillatory effects magnetic breakdown (MB) will occur.This is seen in the experimental results.

III. Results

We have studied quantum oscillatory effects in several low stage GAC.We have used magnetothermal oscillations (MTO) and in-situ de Haas-van Alphen (dHvA) effect.The following low stage GAC were investigated: $C_{8s}(NO_3H)$ s=2,3,4 of the low interplanar distance variety, $C_{7s}(SO_3HF)$ s=2,3 and $C_{4s}Br$ s=2.

The observed dHvA frequencies lay between 40 and 1500 tesla and the associated effective cyclotron masses range between 0.05 and 1.0 m_o.
The numerical results are different in every case but the general features are the same:
1-dHvA frequencies are different for different stages of the same GAC.Here we must notice that in 'diluted' GAC the frequencies are independent of the stage [5].
2- The angular variation of the dHvA frequencies fits the equation:

$$F(\theta) = F(0)/\cos\theta \quad , \qquad (2)$$

where θ is the angle of the magnetic field relative to the hexagonal axis.That correspond to a cylindrical (i.e. a 2-D) FS along this axis.But the quality of the samples which limits the experimental range of angular variation ($\theta<40°$) allows also the fitting of our results by an elongated ellipsoid.
3- There are combinations of frequencies and also combinations of the associated cyclotron masses.This implies a FS made of elementary orbits coupled by MB.From the analysis of these combinations we get the elementary orbits and their relative character (electron or hole).A set of orbits is made of all the orbits coupled one with the other.The elementary orbits are those which have the lowest cyclotron masses.

To illustrate these results we choose the case of second stage nitric-acid GAC: $C_{16}(NO_3H)$.

label	frequencies in tesla	cyclotron masses m/m_o
α	235	0.15 ± 0.02
$\beta-3\alpha$	335	$0.8\ \pm0.3$
$\beta-2\alpha$	570	$0.5\ \pm0.2$
γ	630	---
$\beta-\alpha$	805	$0.3\ \pm0.3$
β	1040	----

Table 1. $C_{16}(NO_3H)$

Frequencies and cyclotron masses are given in table 1.The labelling takes into account the magnetic breakdown effects which allows the determination of the elementary orbits and their characters.In this stage the elementary orbits are α;β and γ .γ is an isolated orbit and α ,β and $\beta-n\alpha$ where n=1,2 or 3 make a set of orbits.The cyclotron masses of $\beta-n\alpha$ is $m_\beta+n\cdot m_\alpha$ as the theory of MB predicts.
We shall interpret these results with the proposed model but we need

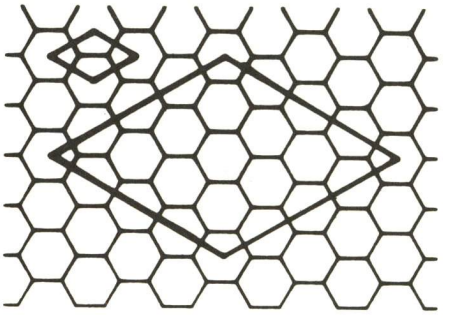

Figure 1 The unit cell of graphite and that of $C_{16}(NO_3H)$ drawn in the graphite lattice

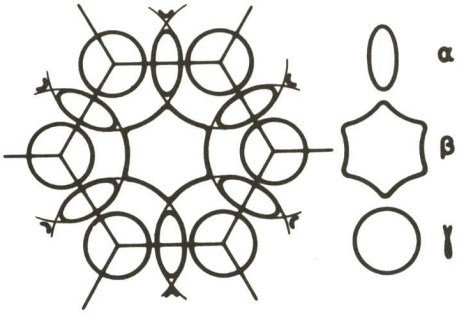

Figure 2 Fermi surface of $C_{16}(NO_3H)$ with the elementary orbits α, β and γ aside

the inplane structure of the intercalate layers. This structure is ill-known and we take a unit cell of the GAC (4ax4a) which contains four acid molecules and is sixteen times larger that of pure graphite as the figure 1 shows. This cell seems to be confirmed by recent X-ray results [6]. The side of the hexagonal BZ will then be G=0.426 Å .

The model of Blinowski & al. gives for the FS two circles centered at the U and U' points of the graphite BZ. If we fold the graphite BZ into that of the GAC this points will correspond to the U and U' points of the GAC BZ. The experimental results coupled with this model allow us to determine the two Fermi wave vectors which are the radii of the two Fermi circles as the figure 2 shows:

$k_1 = 0.265$ Å^{-1} and $k_2 = 0.138$ Å^{-1}

The first circle gives the two elementary orbits α and β and the second one the isolated orbit γ.

Once the Fermi radii are known we obtain the charge tranfer ratio :

$$f = (6\sqrt{3}/\pi)\, b^2(k_1^2 + k_2^2) = 0.60. \quad (3)$$

We can also calculate all the other physical quantities (shift of the Fermi energy or band masses...) if we take into account the dispersion relations where the γ values must be well choosen. Actually in the frame of the model of Blinowski & al. we cannot explain our results. We need to introduce two supplementary parameters γ_3 and γ_4 with the same meaning as in pristine graphite. We also must take into account the trigonal warping resulting from the symmetry of the cell which is usually neglected in pristine graphite [7].

In eq. (1) far from the crossover the bands are linear in k and the slope is proportional to γ_0. For $\gamma_3 = 0$ the slope is proportionnal to $\gamma_0 - \gamma_4$ for v_1 and to $\gamma_0 + \gamma_4$ for v_2. γ_3 introduces a trigonal warping in the FS. If we take $\gamma_0 = 2.40$ eV and for the other band parameters their usual values in pristine graphite [8] we explain our results and the energy of the optical transition between the valence bands observed in the reflectivity spectrum at $\Delta E_v = 0.37$ eV [2].

In conclusion our experimental results show the basic validity of the model of Blinowski et al. which must however be improved by introducing the γ_3 and γ_4 parameters and the folding of the Fermi surface into the Brillouin zone of the graphite acceptor compound.

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