Energy spectrum of implanted heterointercalation compounds in acceptor graphite

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A model is constructed for the energy spectrum of first-step implanted compounds in graphite. The interaction of the carbon layers is taken into account. The model predicts that there will be several frequencies in the Shubnikov–de Haas effect in heterointercalation implanted compounds in graphite.

In this letter we report a study of the Shubnikov–de Haas effect in some first-step implanted graphite compounds which have been synthesized for the first time, $C_{10}CuCl_2 \cdot 0.6ICl$ and $C_{15}CuCl_2 \cdot 1.2ICl$ (the "step" is the number of graphite layers which lie between two layers of the intercalant). We will also construct a model for the electronic energy spectrum of these compounds.

The carbon atoms in graphite lie in layers which run parallel to the basal plane and which are separated from each other by a distance $d_0 = 3.35$ Å at room temperature. In the ideal crystal the atoms of each layer lie exactly above the centers of the hexagons of the lower layer, so that one makes a distinction between two types of atoms in graphite: *A* atoms and *B* atoms. The distance to the nearest neighbor along the *C* axis, which runs perpendicular to the basal plane, is d_0 (for the *A* atoms) or $2d_0$ (for the *B* atoms). The order in which the layers are packed is the alternation *ABABAB*...(Fig. 1a).

The compound $C_{10}CuCl_2 \cdot 0.6ICl$ was synthesized through the successive implantation of (first) copper chloride ($CuCl_2$), to the point of the formation of the first step, and then iodine monochloride (ICl) in highly oriented pyrolytic graphite, into the free spaces between two graphite layers. The order of the layers in the resulting compound is graphite-$CuCl_2$-graphite-ICl-graphite-$CuCl_2$-... (Fig. 1b). According to x-ray phase analysis, the repetition period is 16.56 Å (the thicknesses of the intercalant layers of the second-step graphite implantation compounds $C_{10}CuCl_2$ and $C_{16}ICl$ are 9.4 Å and 7.12 Å, respectively).

The compound $C_{15}CuCl_2 \cdot 1.2ICl$ was synthesized from the third-step graphite implantation compound of copper chloride, $C_{15}CuCl_2$, by implanting iodine monochloride in the free spaces remaining between the graphite layers. The repetition period is 23.70 Å; the order of the layers is graphite-$CuCl_2$-graphite-ICl-graphite-ICl-graphite-$CuCl_2$-graphite-ICl-...(Fig. 1c). Gravimetric and chemical analyses confirmed the attainment of the first step and the composition of the samples.

At liquid-helium temperatures, all of the samples studied (five samples of $C_{10}CuCl_2 \cdot 0.6ICl$ and four of $C_{15}CuCl_2 \cdot 1.2ICl$) exhibit a Shubnikov–de Haas effect. Figure 1 illustrates the results with a plot of the resistivity in the basal plane, ρ_a, versus the magnetic field (which is parallel to the C axis) for one of the $C_{15}CuCl_2 \cdot 1.2ICl$ samples. The oscillation amplitude is about 10% of the total resistivity (that for the compound $C_{10}CuCl_2 \cdot 0.6ICl$ is 30%) of the sample. Three frequencies are observed, corresponding to extremal cross sections of the Fermi surface: $S_1 = (1000\text{–}1100) \times 10^{-42}$ $(g \cdot cm/s)^2$, $S_2 = (60\text{–}90) \times 10^{-42}$ $(g \cdot cm/s)^2$, and $S_3 = (270\text{–}300) \times 10^{-42}$ $(g \cdot cm/s)^2$. The cyclotron mass is $m_3^* = (0.20 \pm 0.05) m_0$. The cross sections vary slightly from sample to sample. For the compound $C_{10}CuCl_2 \cdot 0.6ICl$ we observe two frequencies, which correspond to the values $S_1 = (1100\text{–}1120) \cdot 10^{-42}$ $(g \cdot cm/s)^2$ and $S_2 = (64\text{–}70) \cdot 10^{-42}$ $(g \cdot cm/s)^2$ with cyclotron masses $m_1^* = (0.38 \pm 0.05) m_0$ and $m_2^* = (0.100 \pm 0.005) m_0$. The cyclotron masses were determined from the temperature dependence of the oscillation amplitude $A(T,H)$ at temperature $T_1 = 2.1$ K and $T_2 = 4.2$ K, from the expression

$$m^* = (e\hbar H_n / 4\pi^2 k_B T_1) \mathrm{Ar\,cosh}\,[A(T_1, H_n)/A(2T_1, H_n)],$$

where H_n is the value of the magnetic field which corresponds to the emergence of the Landau level with quantum number n. The presence of several frequencies in the Shubnikov–de Haas effect contradicts the existing theory for the energy spectrum of first-step implanted graphite compounds of the acceptor type,[1] according to which there would be only one branch in the energy spectrum of a first-step compound. Our interpretation of the results is based on the dispersion of the current carriers along the C axis, whose existence is implied by the fact that the electrical conductivity in a magnetic field parallel to the basal plane, σ_c, differs from σ_0. According to the measurements, the the relative conductivity $(\sigma_c - \sigma_0)/\sigma_c$ corresponds to about a fourth of the relative conductivity in a magnetic field perpendicular to the basal plane (σ_0 is the conductivity in the absence of a magnetic field).

The electronic spectrum of graphite with an *ABABAB*... alternation of layers is described[2,3] by the seven parameters $(\Delta, \gamma_i, i = 0,...,5)$. The parameters γ_1, γ_3, and γ_4 are determined by the overlap of the wave functions of electrons of carbon atoms of the type *AA*, *BB*, and *AB* in neighboring layers; γ_2 and γ_5 are associated with the

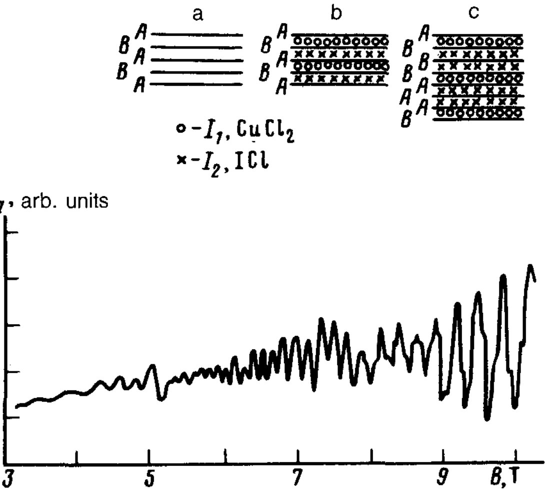

FIG. 1. Oscillatory part of the magnetoresistance ρ_a in the basal plane of $C_{15}CuCl_2 \cdot 1.2ICl$ versus the magnetic field. Shown at the top are schematic drawings of the structure of (a) graphite, (b) the compound $C_{10}CuCl_2 \cdot 0.6ICl$, and (c) the compound $C_{15}CuCl_2 \cdot 1.2ICl$.

interaction of B or A atoms across a layer; and the parameter Δ is a measure of the nonequivalence of atoms A and B in a layer. We are assuming that the crystal structure of heterointercalation implanted graphite compounds can in general contain both AIB and AIA units (I is the intercalant). In the case of a structure with an AIB alternation of layers (Fig. 1b) the electronic spectrum of first-step heterointercalation implanted graphite compounds of the acceptor type is described by only five parameters (in contrast with Refs. 2 and 3), since the parameters γ_2 and γ_5, which represent the interaction across a layer, essentially vanish at an intercalant thickness $d_I > 2d_0$. The dispersion relation for the current carries in the graphite layers in this case is

$$\epsilon_{1,2} = \frac{\Delta}{2} \pm \gamma_1 \cos\phi - \left[\left(\frac{\Delta}{2} \pm \gamma_1 \cos\phi\right)^2 + \eta^2 (1 \mp \nu)^2 k_\rho^2\right]^{1/2}, \qquad (1)$$

where $\eta = (\sqrt{3}/2)\gamma_0 a_0$, $a_0 = 2.46$ Å, $\nu = (2\gamma/\gamma_0)\cos\phi$, $\phi = k_z I_c/2$, I_c is the repetition period of the implanted graphite compound along the C axis, and $\mathbf{k}_\rho$ is the plane of wave vectors with the components $(k_x, k_y, 0)$. In (1) we have ignored the parameter representing the trigonal deformation in the basal plane, γ_3; that parameter complicates the analysis but makes only small corrections, on the order of $(\gamma_3/\gamma_0)^2 \ll 1$ to the spectrum.

The two spectral branches in (1) adequately describe the periods observed experimentally for the Shubnikov–de Haas oscillations in the compound $C_{10}CuCl_2 \cdot 0.6ICl$. According to (1), the Fermi surface of this compound has two extremal cross sections at $\phi = 0$ (Fig. 2). In this case the parameters Δ and γ_4 are $\Delta = -0.008$ eV and $\gamma_4 = 0.044$ eV, i.e., the same as those of graphite.[4] Using the experimental values of $S_{1\,\mathrm{extrem}}$, we find $\epsilon_F = -0.56$ eV, $\gamma_0 = 2$ eV, and $\gamma_1 = 0.24$ eV from (1). Using the relation $m^* = (2\pi)^{-1} \partial S(\epsilon_F, \phi)/\partial \epsilon_F$, and the value calculated for the cross section of the Fermi surface from (1) for the case $\phi = 0$, $S(\epsilon_F, 0) = (\pi/\eta^2)(1 \mp \nu)^{-2} |\epsilon_F| (|\epsilon_F| + \Delta \pm 2\gamma_1)$, we find the effective masses of the

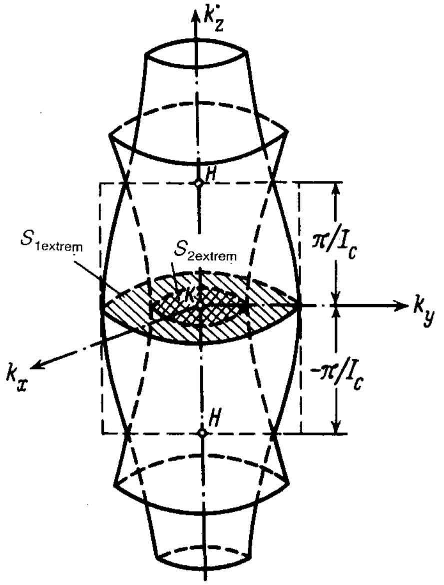

FIG. 2. The Fermi surface in the first Brillouin zone $(\pi/I_c) < k_z < (\pi/I_c)$ for the heterointercalation compound $C_{10}CuCl_2 \cdot 0.6ICl$ with an alternation of layers *AIB* at $\phi = 0$. The extremal cross sections of the Fermi surface (at $\phi = 0$), $S_{1\text{extrem}}$ and $S_{2\text{extrem}}$, are shown by the hatching.

current carriers at $\phi = 0$

$$m^*_{1,2} = (4\hbar^2/3a_0^2\gamma_0^2)(1 \mp 2\gamma_4/\gamma_0)^{-2}\left(|\epsilon_F| + \frac{\Delta}{2} \pm \gamma_1\right). \tag{2}$$

The effective masses calculated from (2), $m_1^* = 0.30m_0$ and $m_2^* = 0.1m_0$ (m_0 is the mass of a free electron), agree well with the values found from the temperature dependence of the oscillation amplitudes.

For the compound $C_{15}CuCl_2 \cdot 1.2ICl$, the appearance of a third frequency of Shubnikov–de Haas oscillations can be attributed to *AIA* units. For *AIA* units we assume that the parameters associated with the interaction of carbon atoms in adjacent layers (γ_1, γ_3, and γ_4) are zero. As a result, we find an additional branch in the electron energy spectrum (Fig. 3),

$$\epsilon_3 = \frac{\Delta}{2} + (\gamma_2 + \gamma_5)\cos^2\phi - \left[\left(\frac{\Delta}{2} + (\gamma_5 - \gamma_2)\cos^2\phi\right)^2 + \eta^2 k_\rho^2\right]^{1/2}, \tag{3}$$

with an effective mass

$$m^*_3 = (4\hbar^2/3a_0^2\gamma_0^2)\left(|\epsilon_F| + \frac{\Delta}{2} + \gamma_2 + \gamma_5\right), \tag{4}$$

which corresponds to the extremal cross section of the Fermi surface at $\phi = 0$.

It can be seen from (3) that since the parameter γ_2 determines the width of the third energy band, which arises during the intrecalation, γ_2 may be quite different from its value in graphite. The extremal cross sections of the fermi surface which we calculate from (1) and (3) correspond to the values found experimentally for the

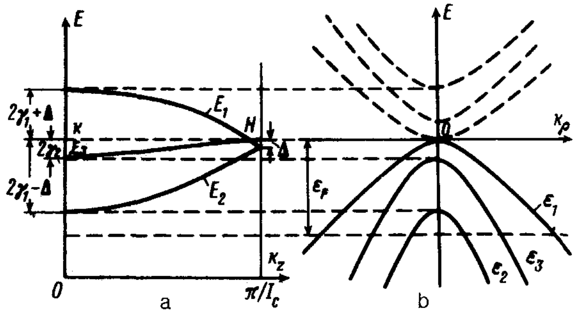

FIG. 3. Energy spectrum of the implanted graphite compound $C_{15}CuCl_2 \cdot 1.2ICl$. a—Energy levels near line *KH* in the Brillouin zone, $E_{1,2} = \Delta \pm 2\gamma_1 \cos \phi$, $E_3 = 2\gamma_2 \cos^2 \phi$; b—energy versus the wave vector k_ρ at $\phi = 0$.

implanted graphite compound $C_{15}CuCl_2 \cdot 1.2ICl$ with the parameter values $\Delta = -0.008$ eV, $\gamma_0 = 2.4$ eV, $\gamma_1 = 0.28$ eV, $\gamma_2 + \gamma_5 = -0.15$ eV, and $\gamma_4 = 0.44$ eV. For these parameter values we have $\epsilon_F = -0.685$ eV, and the effective mass calculated from (4) is $m_3^* = 0.13 m_0$.

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