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Energy spectrum of binary graphite intercalation compound acceptor-acceptor type $C_{12}FeCl_3(ICI)_{0.75}$

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Abstract. — Here we report the results of a study on the Shubnikov-de Haas effect (SdH) in the first synthesize binary graphite intercalation compound (GIC) $C_{12}FeCl_3(ICI)_{0.75}$ of the first stage acceptor-acceptor type and of the second stage GIC $C_{12}FeCl_3$ and $C_{16}ICI$. The structure and the phase transition order-disorder type also have been investigated.

Introduction.

The widespread interest in the study of graphite intercalation compounds was stimulated by the possibility of studying charge transport in quasitwo-dimensional structures. The high degree of perfection of the GICs presently produced allows one to use quantum oscillatory effects to study their energy spectrum and derive information on the shape and dimensions of the Fermi surface, concentration of carriers and effective masses. New possibilities for understanding the physical properties of the GIC are opened by a complex intercalation in which there are sequential layers of graphite, an intercalate 1, and an intercalate 2. Such compounds referred to as heterointercalated or binary [1-9] can be divided into some classes: those with acceptor-acceptor, acceptor donor or donor-donor intercalate sequences. Here we report the results of a study on the Hall effect, Shubnikov-de Haas effect, phase transitions in the first synthesized acceptor-acceptor type hetero-GIC of the first stage and the second stages of ICl GIC, FeCl$_3$-GIC. The chemical formulas of the compounds investigated are $C_{12}FeCl_3(ICI)_{0.75}$, $C_{12}FeCl_3$ and $C_{16}ICI$.

Experimental.

Highly oriented pyrolitic graphite annealed at $T > 3300$ K with an angle of disorientation less than 1° along C-axis in the form of quasi single crystals plates was used. Ferric trichloride (FeCl$_3$) and iodine monochloride (ICI) were synthesized from elements and refined by multiple distillation in a dry chlorine flow or multiple recrystallisation correspondingly.

FeCl$_3$-GIC and $C_{16}ICI$-GIC were synthesized from gaseous phases as was described in [9].
The compound C_{12}FeCl_{3}(ICl)_{0.75} was synthesized in two steps. To begin with the second stage C_{12}FeCl_{3} was produced. The introduction of the iodine monochloride resulted in the filling of all free interlayer spaces and the formulation of a first-stage GIC with alternating layers of different intercalates and graphite. The sequence of layers in C_{12}FeCl_{3}(ICl)_{0.75} are C-FeCl_{3}-C-ICl-C-FeCl_{3}-C-ICl- etc.

Chemical compositions of GICs were determined by gravimetric analysis and chemical analysis. X-ray analysis was carried out on a diffractometer URD-6 (Germany) Cu Kα irradiation, Ni filter. The families of 001 lines were obtained. The second stage GIC C_{12}FeCl_{3} samples of equal geometric dimensions, weights and compositions were placed into melted ICl in thermostat and every 24 hours X-ray analysis was carried out on one sample. Some diffractograms are shown in figure 1. When the time of synthesis was about 70 hours, a mono phase sample of hetero-GIC C_{12}FeCl_{3}(ICl)_{0.75} containing layers of FeCl_{3} and ICl was produced (fig. 1, curve 3). Under exposition of more than 150 hours the first stage of C_{8}ICl

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Fig. 1. — Diffractograms of a second stage C_{12}FeCl_{3} in ICl at different time of synthesis t, hours: 1) 24; 2) 48; 3) 72; 4) 120; 5) 172. Open circles correspond to peaks of the second stage C_{12}FeCl_{3} and full circles correspond to peaks of the second stage of C_{8}ICl.
may be obtained. The single-phase samples had a repeat period of 10.47 Å for C_{10}ICl, 12.75 Å for C_{12}FeCl_{3} and 16.53 Å for C_{12}FeCl_{3}(ICl)_{0.75}.

The C-axis charge density \( \rho_{z} \) may be calculated from the Fourier transform of the structure factors \( F_{00l}^{0} \) as it was done in [10]. The experimental structure factors \( F_{00l}^{e} \) are related to the integrated intensities \( I_{00l}^{e} \) of the X-rays diffracted from atomic planes perpendicular to the graphitic c-axis by the well known expression

\[
|F_{00l}^{0}| = (I_{00l}^{e}/KLPA)^{1/2}
\]

where \( K \) is a scale factor, \( L \), \( P \) and \( A \) are the angle-dependent Lorentz factor, polarization factor and the absorption factor, respectively. The theoretical structure factor \( F_{00l}^{1} \) in equation (1) depends on the position \( (z_{j}) \) and the atomic density \( (n_{j}) \) of the atomic layers according to the well known expression

\[
F_{00l}^{1} = \sum_{j=1}^{M} n_{j} f_{j} [\cos (2 \pi l z_{j}) + i \sin (2 \pi l z_{j})] D_{j}
\]

where the sum extends over the \( M \) planes in the cell, \( f_{j} \) and \( D_{j} \) represent the atomic scattering factor and the Debye-Waller temperature factor for the \( j \)-th layer. The integrated intensity data has been analyzed by comparing the experimentally derived structure factors \( F_{00l}^{e} \) (Eq. (1)) with structure factors calculated according to equation (2) which we will henceforth refer to as \( F_{00l}^{t} \). The layer parameters \( n_{j}, z_{j} \), in equations are simultaneously adjusted in computer program to minimize the weighted residual function \( R \), were \( R \) is given by

\[
R = \left| \sum_{l=0}^{M} \left( |F_{00l}^{e}| - |F_{00l}^{t}| \right)^{2} w_{l} \right|^{1/2} / \sum_{l=0}^{M} |F_{00l}^{t}|^{2} w_{l}
\]

The sum in equation (3) extends over all the observed diffraction peaks and \( w_{l} \) is the statistical weight of the \( l \)-th experimental structure factor. The statistical weight, \( w_{l} \), is inversely proportional to the square of the standard deviation in the structure factor. A C-axis charge density, \( \rho_{z} \), can be calculated from the Fourier transform of the structure factors. In the case of a centrosymmetric structural model for the intercalate layer which has a central Fe layer localised at \( z = 0 \) Å, the expression for \( \rho_{z} \) takes the form

\[
\rho_{z} = \frac{1}{d_{c}} \sum_{l=0}^{M} F_{00l}^{e} \cos \left( \frac{2 \pi l z}{d_{c}} \right)
\]

where \( d_{c} \) is the repeat distance for the c-axis charge distribution. Other atomic layers appear as pairs of layers in the unit cell positioned with mirror symmetry about \( z = 0 \) Å. We found non-centrosymmetric layer models to be in poor agreement with experimental data. The function was constructed from the measured set \( \{ |F_{00l}^{e}| \} \) of structure factors. In this case, the magnitude \( |F_{00l}^{e}| \) is determined directly from the data \( \{ I_{00l}^{e} \} \), but the phase (sign) must still be extracted from a structural analysis.

In figure 2 we plot the results of the Fourier synthesis (Eq. (4)) as a function of \( z \) for the stage 1 hetero-GIC C_{12}FeCl_{3}(ICl)_{0.75}. The width of figure 2 corresponds to one repeat distance for the c-axis charge density. Peaks in the function \( \rho_{z} \) seen in figure 2 correspond to the atomic layers of C, Fe, ICl, Cl which lie perpendicular to the graphitic c-axis. Our analysis indicate that the ferrum chloride molecular species in the intercalate layer of the
compound are oriented in such a way as to generate Cl\(^-\) layers that contact the bounding carbon layers. The Fe has been found to be located in a central layer (\(z = 0\)).

We studied the Shubnikov-de Haas (SdH) effect in the second stages \(\text{C}_{12}\text{FeCl}_3\), \(\text{C}_{16}\text{ICl}\) and the first stage \(\text{C}_{12}\text{FeCl}_3(\text{ICl})_{0.75}\). The SdH oscillations of the second stages \(\text{C}_{12}\text{FeCl}_3\), \(\text{C}_{16}\text{ICl}\) are shown in figure 3. Only one oscillation frequency is observed for every compound. The angular dependence of the oscillation frequency and, hence, the angular dependence of the extremal cross-section of the Fermi-surface \(S\) corresponds to the formula \(S(\theta) = S(0) \cos^{-1}(\theta)\). Here \(\theta\) is the angle between \(C\)-axis and the magnetic field \(B\). Thus, the \(\text{C}_{12}\text{FeCl}_3\), \(\text{C}_{16}\text{ICl}\) Fermi-surfaces are a smooth (or slightly undulating) cylinder. The Hall coefficient \(R\) does not depend on the magnetic field up to \(B = 10\) tesla. The concentration of

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**Fig. 2.** — \(C\)-axis charge density \(\rho_z\) vs. \(z\) for the stage 1 GIC \(\text{C}_{12}\text{FeCl}_3(\text{ICl})_{0.75}\). Peaks in the function \(\rho_z(z)\) seen in the figure correspond to the atomic layers of \(C\), \(Fe\) and \(\text{Cl}^-\) which lie perpendicular to the graphitic \(C\)-axis.

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**Fig. 3.** — Dependence of the oscillatory part of the transverse magnetoresistance \(\rho_\perp\) on magnetic field:
1) graphite, 2) \(\text{C}_{16}\text{ICl}\), 3) \(\text{C}_{12}\text{FeCl}_3\).
holes was determined from Hall effect \( (P_H) \) and from SdH effect \( (P_{SdH}) \) data independently by using formulas

\[
P_H = \frac{1}{R|e|}; \quad P_{SdH} = \frac{4S}{(2\pi h)^2 \left[ d_i + (N - 1) d_o \right]}
\]

were \( d_o = 3.35 \text{ Å} \), \( N \) is a stage number, \( d_i \) is the width of the intercalate layer, \( d_i + (N - 1) d_o \) being the repeat period of GIC investigated. In C\(_{12}\)FeCl\(_3\), C\(_{16}\)ICl the value of \( P_H = P_{SdH} = 2.6 \times 10^{26} \text{ m}^{-3} \) and \( 2.1 \times 10^{26} \text{ m}^{-3} \) correspondingly and hence they have only one group of holes. The extremal Fermi surface cross-section in C\(_{12}\)FeCl\(_3\) is \( S = (295-310) \times 10^{12} \text{ (sm)}^{-2} \) and in GIC C\(_{16}\)ICl is \( S = (260-290) \times 10^{12} \text{ (sm)}^{-2} \).

Compared to the original C\(_{12}\)FeCl\(_3\) compound in which only one oscillation frequency is observed, the energy spectrum of the C\(_{12}\)FeCl\(_3\)(ICl)\(_{0.75}\) is much more complicated. The SdH oscillation of the first stage compound are a superposition of three frequencies in all of which beats are seen, evidence of two close frequencies in each harmonic (Fig. 4a). In the Fourier spectra of SdH oscillations three modulated frequencies dominate (Fig. 4b). The extremal

![Graph](https://via.placeholder.com/150)

**Fig. 4.** — Dependence of the oscillatory part of the transverse magnetoresistance \( \rho_x \) on magnetic field of hetero-GIC C\(_{12}\)FeCl\(_3\)(ICl)\(_{0.75}\) (a) and the Fourier transform of the oscillations (b).

Fermi surface cross-section in GIC $C_{12}FeCl_3(ICI)_{0.75}$ are $S_1 = (60-80) \times 10^{12} \text{ (sm)}^{-2}$ $S_2 = (860-920) \times 10^{12} \text{ (sm)}^{-2}$ and $S_3 = (280-300) \times 10^{12} \text{ (sm)}^{-2}$ The extremal Fermi-surface cross-sections correspond undulating coaxial cylinders oriented along the C-axis. The reason for the appearance of several isoenergetic surfaces in the form of undulating cylinders in the binary GIC is an additional indirect interaction between carbon atoms in neighboring layers of carbon separated by an intercalate layer, according to the model of energy spectrum of hetero-GIC, proposed in [4, 9]. Assuming a layer sequence ABAB... for the GIC $C_{12}FeCl_3(ICI)_{0.75}$ we get [4, 9] a dispersion relation for two bands:

$$ E_{1, 2} = \pm \gamma_1^* \cos \Phi - (\gamma_1^* \cos^2 \Phi + \eta^* k_p^2)^{1/2} \quad (6) $$

where $\Phi = k_z l_c / 2$, $l_c$ is the repeat period of the GIC along the C-axis, $\eta^* = 3^{1/2} a_0 \gamma_0^* \gamma_0^2 / 2$, $k_p$ is the in-plane wave vector. The value of the extremal cross sections in $k$-space $S_{1, 2} = \pi k_p^2$ in the $k = 0$ plane perpendicular to the C-axis is equal to

$$ S_{1, 2} = \frac{\pi \times |E_F| \times (|E_F| \pm 2 \gamma_1^*)}{\eta^* 2} \quad (7) $$

An expression for the carrier effective masses $m_{1, 2}^*$ is equal to

$$ m_{1, 2}^* = \frac{4 \hbar^2 (|E_F| \pm \gamma_1^*)}{3 a_0 \gamma_0^* \gamma_0^2} \quad (8) $$

The energy spectrum (6) thus leads to a Fermi surface in the shape of two undulating coaxial cylinders oriented along the C-axis. Using the experimental values for the Fermi surface cross section and the cyclotron mass, one can find using equations (6-8) the parameters of the energy spectrum of GIC which are shown in the table I.

Table I. — Parameters of the energy spectrum of GIC.

<table>
<thead>
<tr>
<th>Composition</th>
<th>N</th>
<th>$S$, $10^{12} \text{ cm}^{-2}$</th>
<th>$m^* / m_0$</th>
<th>$E_F$, eV</th>
<th>$\gamma_0^*$, eV</th>
<th>$\gamma_1^*$, eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_{16}ICl$</td>
<td>2</td>
<td>270</td>
<td>0.140</td>
<td>0.31</td>
<td>2.7</td>
<td>0.3</td>
</tr>
<tr>
<td>$C_{12}FeCl_3$</td>
<td>2</td>
<td>300</td>
<td>0.145</td>
<td>0.33</td>
<td>2.7</td>
<td>0.3</td>
</tr>
<tr>
<td>$C_{12}FeCl_3(ICI)_{0.75}$</td>
<td>1</td>
<td>880</td>
<td>0.26</td>
<td>0.6</td>
<td>2.3</td>
<td>0.26</td>
</tr>
</tbody>
</table>

Thus, as a result of heterointercalation, the original $C_{12}FeCl_3$ GIC Fermi surface, a smooth (or slightly undulating) cylinder is transformed into a Fermi surface consisting of two undulating coaxial cylinders oriented along the C-axis.

The existence of ABAB... regions leads to the creation of two branches in the energy spectrum, described by equation (6). We find a representation of the spectrum of the AAA.. stack of layers [4, 9]. The new energy sub-band arises from the possible AAA... layer stack in $C_{12}FeCl_3(ICI)_{0.75}$. We find for the third extremal Fermi surface cross-section the expression

$$ S_3 = \frac{\pi \times (|E_F| + 2 \gamma_2^*)^2}{\eta^* 2} \quad (9) $$

The experimental value of $S_3 = (280-300) \times 10^{12} \text{ (sm)}^{-2}$ approximately coincides with the Fermi surface cross-section of the second stage GICs $C_{16}ICl$ and $C_{12}FeCl_3$ and may belong to regions of this GIC in the volume of the sample, but according to the X-ray data all investigated samples were monophasic of $C_{12}FeCl_3(ICI)_{0.75}$.

Thus a composite structure of the type ABAB... and AAAA... may lead to a three-band structure. For such a spectrum the Fermi surface consists of three undulating coaxial cylinders along the $C$-axis.

It is known that when GICs are cooled down to a certain temperature a phase transition occurs due to the solidification of the intercalate layer. In the mono-GICs of iodine monochloride disorder-order transitions occur for $T_0 = 305-315$ K ($T_0$ grows as the GIC stage number increases) and is easily registered by the discontinuity in resistivity along the $C$-axis. In figure 5 the relative change in the $C$-axis resistivity is shown for the hetero-GIC $C_{12}FeCl_3(ICI)_{0.75}$ (curve 1) and for the second stage GIC $C_{12}FeCl_3$ (curve 2). The transition in $C_{12}FeCl_3(ICI)_{0.75}$ occurs at a lower temperature $T_0 = 302$ K than in $C_{16}ICl$ ($T_0 = 312$ K). Note that the resistivity discontinuity for the transition in the hetero-GIC is less by a factor 2. The temperature of the transition $T_0 = 302$ for the hetero-GIC $C_{12}FeCl_3(ICI)_{0.75}$ is slightly less than the temperature of the transition for the first stage of GIC $C_8ICl$. The temperature shift of the transition means that a change of an ICl layer to FeCl$_3$ leads to reduced interaction in the remaining ICl layers.

![Fig. 5. — Relative change in resistivity along the $C$-axis in the first stage GIC $1-C_{12}FeCl_3(ICI)_{0.75}$ (1) and in the second stage $C_{16}ICl$ (2).](image)

In conclusion we would like to direct attention to the following important fact. The presence of intercalate molecules creates the possibility of indirect interaction between carbon atoms separated by intercalate molecules. Therefore, it is not possible, strictly speaking, to neglect interlayer interactions and consider the GIC as purely two-dimensional systems, in spite of the significant increase in interlayer distance.
References


