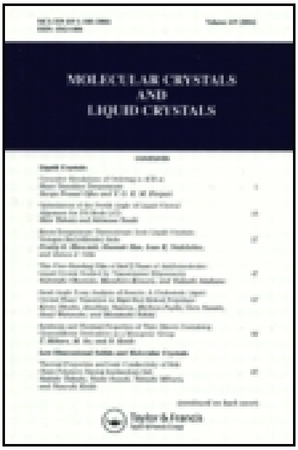

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

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Version of record first published: 23 Oct 2006.

To cite this article: V. A. Kulbachinskii, S. G. Ionov, S. A. Lapin, V. V. Avdeev, E. A. Kamenskaya & A. de Visser (1994): ShubnikoV-De Haas Effect in Low Stage Acceptor Type Graphite Intercalation Compounds, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 245:1, 31-36

To link to this article: http://dx.doi.org/10.1080/10587259408051662

Mol. Cryst. Liq. Cryst. 1994, Vol. 245, pp. 31–36
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Printed in the United States of America

SHUBNIKOV-DE HAAS EFFECT IN LOW STAGE ACCEPTOR TYPE GRAPHITE INTERCALATION COMPOUNDS

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Abstract Quantum oscillation of the magnetoresistance have been investigated in synthesized high quality quasi-single crystals of low stage graphite intercalation compounds (GIC) of the acceptor type for temperatures $1.4<T<4.2K$ and magnetic fields up to 35 tesla. For some compounds frequency beats are seen. One of the reason for the observation of nodes in the oscillations of the magnetoresistance may be interaction between carbon atoms in neighboring layers separated by an intercalate layer. The parameters of the energy spectrum were determined from experimental data for GIC with $AlCl_3$, ICl, $CuCl_2$, ICl_3, H_2SO_4 and $FeCl_3$.

INTRODUCTION

A characteristic feature of acceptor type GIC is a very high electrical conductivity at room temperature. Conductivity and physical properties of GIC depend on many factors: the nature of the intercalant, the stage number N, the method of synthesis, etc. Knowledge of the energy spectrum of GIC is of great significance for the explanation of the origin of the high conductivity and is of importance for any organized search for a new GIC with suitable physical properties. The most complete information about the nature of the electronic structure, the features of the Fermi surface, the effective masses, and the concentration of carriers is given by investigation of quantum oscillations in strong magnetic fields at low temperatures. For such investigations sufficiently perfect single crystals of macroscopic dimensions must be available. In the present paper we report on an investigation of the conductivity, the Shubnikov-de Haas (SdH) effect and the Hall effect in synthesized high quality quasi-single crystals of low stage acceptor type GIC for temperatures $1.4<T<4.2K$ in magnetic fields up to 35 tesla.

SYNTHESIS AND EXPERIMENTAL METHODS

GIC samples of the acceptor type were obtained by intercalation of highly oriented pyrolitic graphite annealed at T=3300K. The misorientation angle of the grains relative to the c-axis was less than 1°, the grain size in the basal plane equalled $\approx 10^5$Å and the repeat distance was d_o=3.356Å. Before the intercalation reaction the graphite samples were washed in acetone and then outgassed in vacuum for 20 min at T=700K. We synthesized GIC containing $AlCl_3$, $CuCl_2$, ICl, ICl_3 and $FeCl_3$ by the vapor method, whereas first order GIC of $SbCl_5$, H_2SO_4 and Br_2 were synthesized by the liquid phase method. The analysis methods made it possible to determine the chemical composition and the stage number N of the GIC, but gave no information on the defects in the crystals. A good criterion for the degree of perfection of GIC is provided by observations of quantum oscillations at low temperatures.

The samples of GIC were prepared as rectangular plates with dimensions 5x1x0.5 mm^3. Thin copper wires were attached to the sample by silver paint in order to measure the electrical resistivity and Hall effect. Many of the compounds were sensitive to air moisture, therefore, the samples were mounted in a hermetically sealed chamber filled with dried argon. During measurements the current was always directed in the basal plane of the sample (ab-plane) and the magnetic field B was oriented perpendicular to the current along the c-axis.

Magnetic fields up to 6.5 tesla were created by a superconducting solenoid. The measurements in high magnetic fields up to 35 tesla have been performed using the facility of the University of Amsterdam.

RESULTS

A common feature of the SdH oscillations in low magnetic fields of the compounds $C_{9.3}AlCl_{3.4}$, $C_{9.5}AlCl_3Br_{0.6}$, $C_{16.3}ICl_{1.1}$, $C_{12}FeCl_3$, $C_{27.5}ICl_3$ and $C_8H_2SO_4$ is the monochromatic nature of the oscillations. The angular dependence of the extremal cross-section of the Fermi surface for an increase of the angle θ between the direction of the magnetic field and the c-axis of the sample obeys the relation $S(\theta)=S(0)\cos^{-1}\theta$, which confirms that the Fermi surface is nearly cylindrical. The amplitude of the oscillations decreases rapidly with increasing θ, which limited the range of θ-values at which it was possible to observe the SdH effect. In the compound $C_{9.5}AlCl_3Br_{0.6}$ the presence of Br leads to a substantial increase of the concentration of carriers (by a factor of ≈ 30). Here the SdH oscillations for $B<6T$ preserve their monochromaticity. In high-magnetic fields up to 35 tesla we measured the SdH effect only in the samples of the second stage $C_{18.6}AlCl_{3.4}$, $C_{9.8}CuCl_2$ and $C_{16}ICl_{0.8}$. The following characteristics of the SdH oscillations were observed (see fig. 1). In high magnetic fields spin splitting is observed. The ratio γ of spin splitting to the orbital splitting equals ≈ 0.37 for $C_{9.8}CuCl_2$ while $\gamma \approx 0.45$ for $C_{18.6}AlCl_{3.4}$. In the SdH oscillations of $C_{18.6}AlCl_{3.4}$ and $C_{16}ICl_{0.8}$ GIC frequency beats are seen, evidence for two closed frequencies of different amplitude in each harmonic (fig. 1).

DISCUSSION

The effective masses m^* of the carriers of the investigated GIC as determined from the temperature dependence of the amplitudes of the SdH oscillations are presented in table 1. The effective masses of the holes are connected with the parameters of the energy spectrum[1]. The parameter γ_0 of the energy spectrum which describes the interaction of carbon atoms in a layer may be estimated from the experimental values of m^* and the extremal cross-sectional area of the Fermi surface S (Table 1). The Hall coefficient of the investigated GIC samples does not depend on the magnetic field at liquid helium temperatures. The values of the hole concentrations

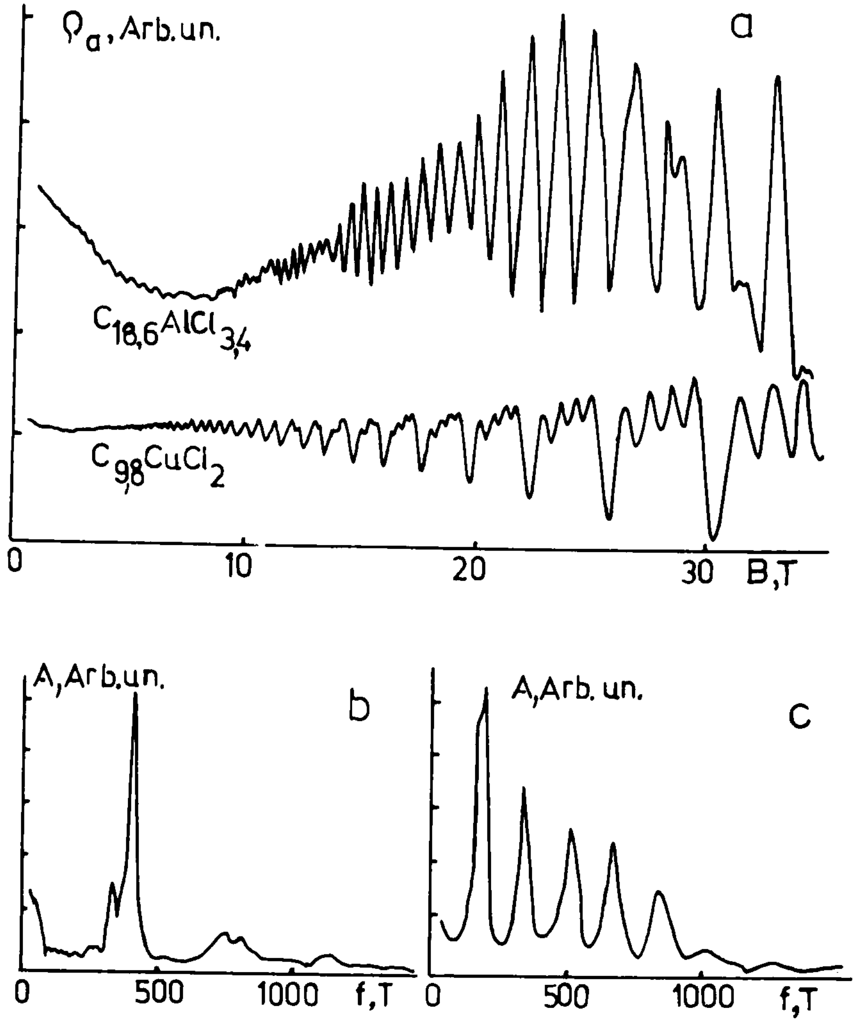

FIGURE 1 a) SdH oscillations for the second stage GIC $C_{18.6}AlCl_{3.4}$ and $C_{9.8}CuCl_2$; b) and c) - the corresponding Fourier transforms for $C_{18.6}AlCl_{3.4}$ (b) and $C_{9.8}CuCl_2$ (c).

Table 1 Parameters of the energy spectrum of GIC.

Compound	N	R_H (cm^3/C)	S (10^{-42}) $(gcm/s)^2$	m^*/m_o	γ_o (eV)	E_F (eV)
$C_{9.3}AlCl_{3.4}$	1	0.5	11.6±0.2	0.065±0.003	3.2	-0.12
$C_{9.5}AlCl_3Br_{0.6}$	1	0.17	362±3	-	3.2	-0.69
$C_{16.0}ICl_{0.8}$	2	0.16	420±3	0.187±0.007	2.5	-0.44
$C_{27.5}ICl_{0.3}$	2	0.022	319±3	0.148±0.008	2.4	-0.34
$C_{9.8}CuCl_2$	2	0.047	180±5	0.091±0.005	2.7	-0.25
$C_8H_2SO_4$	1	0.27	20±0.2	0.070±0.002	3.2	-0.14
$C_{16.3}ICl_{1.1}$	2	0.024	302±3	0.130±0.001	2.5	-0.34
$^*C_{16.3}ICl_{1.1}$	2	0.024	302±3	0.130±0.001	2.7	-0.34
$^*C_{12}FeCl_3$	2	0.025	336±3	0.145±0.007	2.7	-0.33
$^*C_{9.8}CuCl_2$	2	0.047	180±5	0.090±0.010	2.7	-0.25

obtained from Hall effect measurements agree well with the ones obtained from the SdH data. In the SdH oscillations of the second stage GIC $C_{9.8}CuCl_2$ and $C_{9.3}AlCl_{3.4}$ frequency beats are seen in high magnetic fields (fig. 1a) and a frequency splitting in the Fourier transforms (fig. 1b). One of the reason for the observation of nodes in the oscillations is a Fermi surface consisting of an undulating cylinder with two extremal cross-sections -in the center of the Brillouin zone and at the Brillouin zone boundary. One of the reason of the complicated energy spectrum of the GIC may be the interaction between carbon atoms in neighboring layers separated by an intercalate layer[2,3]. It is not possible, strictly speaking, to consider the intercalated graphite compounds as purely 2D system. Taking into account the dispersion relation along the c-axis[2,3] and experimental data on SdH oscillations, we may calculate parameters of the energy spectrum for $C_{9.8}CuCl_2$, $C_{16.3}ICl_{1.1}$ and C_2FeCl_3, which are marked in the table 1 by stars. An increase in the number of holes in acceptor GIC compared with graphite enhances the screening of the atomic potentials and reduces the parameter γ_0 which is equal to 3.2 in graphite. Of course, we cannot fully exclude the possible explanation of beating in SdH effect by the existence of regions in the samples with slightly different concentrations of intercalated molecules, but according to our X-ray data all samples were monophase.

The experimental results indicate that the ratio γ of the spin to orbital splitting is equal to ≈ 0.37 and ≈ 0.45 for $C_{9.8}CuCl_2$ and $C_{18.6}AlCl_{3.4}$ respectively. Since $\gamma = gm^*/2m_0$ the value of the g-factor for holes in GIC is almost the same as for 2D electrons in GaAs-GaAlAs heterostructures[4]. The enhancement of the g-factor was attributed in heterostructures to the exchange interaction of carriers. The same may be done in quasi-two dimensional GIC.

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