Investigation of the electron energy spectrum of low-order acceptor-type intercalation compounds of graphite

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A study has been made of the oscillation and galvanomagnetic effects, and of the electrical conductivity of some low-order acceptor-type intercalation compounds of graphite. The parameters of the energy spectrum were determined as well as the densities, effective masses, and mean free paths of carriers, and the nature of the change in the energy spectrum under hydrostatic pressure. A change in the intercalation order of iodine monochloride in graphite under pressure was detected. Studies were made of the characteristic features of the electrical conductivity of intercalation compounds of graphite near order-disorder phase transitions in intercalant layers. In the case of graphite containing iodine monochloride it was found that a room-temperature "supermetallic" conductivity was associated with a high density of holes and a long mean free path due to the two-dimensional nature of charge transport processes.

INTRODUCTION

Intercalation compounds of graphite (ICG), formed as a result of filling of the interlayer space of the graphite matrix with monatomic or monomolecular intercalant layers, are currently attracting attention because of the extensive practical applications of these materials.

A charcteristic feature of acceptor-type ICG, in which the intercalant acts as an electron acceptor, is a very high "supermetallic" electrical conductivity at room temperature. In view of their very low density (2–3 g/cm^3) and high conductivity [(5–6)×10^5 $\Omega^{-1}\cdot$cm^{-1}] these compounds have potential applications in aviation and space research,[1] and they are also used as electrodes in chemical sources of the electric current.[2] These compounds are good molecular containers of highly active substances with a high energy capacity and catalysts of many chemical reactions occurring in accordance with the cation mechanism.[3–5]

Moreover, ICG are very interesting objects for scientific research. Their physical properties are strongly anisotropic because of the major differences between the forces of the interlayer and intralayer interactions of carbon atoms with one another and with the acceptor molecules. This makes it possible to regard acceptor-type ICG as systems in which the transport of charge, heat, etc., is two-dimensional.

Studies of the properties of ICG make it possible to identify the characteristic features of the processes that occur in monomolecular or monatomic intercalant and carbon layers. In spite of the many investigations of ICG, there is still a whole series of unresolved problems relating to the formation and properties of ICG. They include, in particular, the structure of the Fermi surface, the disperison law of carriers, and the specific features of charge transport in these substances.

We shall describe the formation and investigation of quasi-single-crystal samples of acceptor-type ICG based on well-known oriented pyrolytic graphite and report new experimental data on the electron energy spectrum, changes in the structure under the influence of external factors, phase transitions in intercalated layers, and specific features of the electrical conductivity of graphite compounds with weak acceptors.

SYNTHESIS OF ACCEPTOR-TYPE INTERCALATED COMPOUNDS OF GRAPHITE AND MEASUREMENT METHODS

Acceptor-type ICG containing metal chlorides and bromides, halogens, and interhalides were formed using well-oriented pyrolytic graphite (annealed at ~3300 K) with the misorientation angle of the grains (relative to the c axis) less than 1° (the grain size in the basal plane was ~ 10^3 Å). Before the intercalation reaction the samples of graphite were washed in acetone and then outgassed in vacuum for 20–30 min at ~700 K.

Intercalation of graphite increases the distance between the graphite layers by a factor of 2–3, but alters only slightly the parameters of the crystal lattice in the basal plane.[6,7] Depending on the conditions during synthesis (temperature and intercalant vapor pressure), we can prepare ICG of different orders. The order N is equal to the number of carbon layers located between the two nearest intercalant layers.[8]

We synthesized ICG containing aluminum chloride (AlCl$_3$), copper chloride (CuCl$_2$), aluminum bromide (AlBr$_3$), interhalides [iodine monochloride (ICl) and iodine trichloride (ICl$_3$)] by the vapor method, whereas first-order ICG of bromine (Br$_2$), antimony pentachloride (SbCl$_5$), and iodine monochloride were synthesized by the liquid phase method.[9,10]

Synthesis of iodine monochloride ICG took place in the apparatus shown in Fig. 1. The lower part of the apparatus contained 5–10 g of iodine monochloride, and dry argon was
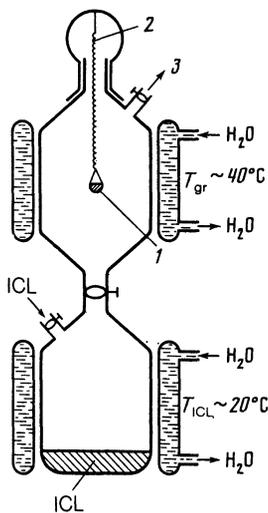
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FIG. 1. Apparatus used in the synthesis of iodine monochloride ICG: 1) graphite; 2) quartz spring; 3) vacuum pump.

driven through the system in order to remove traces of moisture. Then ICl was cooled to liquid nitrogen temperature and a quartz spring (sensitivity 2 mg/mm) was placed in the upper part of the apparatus: this spring supported a tiny glass dish containing graphite. The system was then evacuated and a KM-6 cathetometer was used to determine the initial position of the dish containing graphite. In all cases the iodine monochloride was next heated to 20 °C, and this temperature was maintained to within ± 0.05 °C using a thermostat throughout the experiment. A second thermostat was used to heat the upper part of the system in the temperature range 20–100 °C. Variation of the temperature gradient between ICl and graphite yielded iodine monochloride ICG of different stoichiometric compositions. At the end of the reaction (when the length of the quartz spring ceased to vary), a sample was taken out from the system and subjected to gravimetric, x-ray phase, and chemical analyses of the compounds. An x-ray phase analysis was carried out by placing an ICG plate in a cell made of Plexiglas or quartz, which was covered by a thin x-ray amorphous film in order to avoid decomposition and hydrolysis of samples. X-ray phase analysis was carried out using DRON-1 ($Co K_\alpha$ radiation of $\lambda = 1.790\ 85$ Å wavelength) and DRON-2 ($Cu K_\alpha$ radiation with $\lambda = 1.542\ 42$ Å) diffractometers.

Synthesis of iodine trichloride ICG of the $C_{27.5\pm0.5}ICl_{3.0\pm0.1}$ composition took place in a one-section glass ampoule in a chlorine atmosphere (chlorine pressure ~ 2 atm) at 20 °C applied for 40 h.

Aluminum chloride ICG samples were prepared in two-section ampoules made of Pyrex or molybdenum glass. The ampoules were filled with graphite and $AlCl_3$ in a hermetically sealed chamber filled with dry nitrogen. One section contained aluminum chloride (of the chemically pure grade with a nominal purity 99.99%) and the other a sample of well-oriented pyrolytic graphite. The ampoule was then filled with gaseous chlorine at atmospheric pressure, sealed, and placed in a tubular electric furnace. The use of a two-section method made it possible to intercalate $AlCl_3$ only from the vapor phase and to prevent interaction of molten $AlCl_3$ with graphite. The section containing molten $AlCl_3$ was always at a lower temperature than ICG. Chemical analysis was carried out on some of the samples cut from the internal part of an ICG plate. When $AlCl_3$ was intercalated in a bromine atmosphere, aluminum chloride ICG with different bromine concentrations were formed.

Copper chloride and aluminum bromide ICG were prepared by the same method as aluminuim chloride ICG. Synthesis of first-order bromine, antimony pentachloride and iodine monochloride ICG was carried out by the liquid phase method: graphite samples were placed in a solution or melt of the intercalant and were kept there for the necessary time at a specified temperature.

The conditions and duration of synthesis, as well as the results of x-ray phase and chemical analyses of all the ICG on which physical measurements were carried out, are listed in Table I, where N is the order of ICG: d_i is the thickness of a layer filled with the intercalant; I_c is identity period in the direction of the trigonal axis, $I_c = d_i + (N-1)d_0$; $d_0 = 3.35$ Å; T_{gr} is the temperature of graphite during synthesis; T_{int} is the temperature of the intercalant during synthesis; and t is the duration of synthesis. The analysis methods made it possible to determine the chemical composition and the order of the ICG, but gave no information on the defects in the crystals. A good criterion of the degree of perfection of ICG is provided by observations of the quantum oscillation effects at low temperatures. One of the conditions for the appearance of oscillations in a magnetic field **B** is the inequality

$$\Lambda \geqslant 2\pi v_F m^*/e|\mathbf{B}|, \tag{1}$$

TABLE I. Conditions and duration of synthesis, and results of x-ray phase and chemical analyses of investigated intercalated compounds of graphite.

Chemical formula	N	d_i, Å	I_c, Å	T_{gr}, °C	T_{int}, °C	t, h
$C_{9.3\pm0.1}AlCl_{3.4\pm0.1}$	1	9,54	9,54	250	240	24
$C_{18.6\pm0.2}AlCl_{3.3\pm0.05}$	2	9,48	12,83	400	300	5
$C_{9.8\pm0.1}CuCl_{2.05\pm0.02}$	2	9,40	12,75	610	600	360
$C_{21.0\pm0.5}AlBr_{3.5\pm0.1}$	2	9,97	13,32	220	210	24
$C_{9.5\pm0.2}AlCl_3Br_{0.6\pm0.05}$	1	9,77	9,77	205	180	30
$C_{8.31\pm0.14}ICl_{1.07\pm0.03}$	1	7,13	7,13	21	20	350
$C_{16.5\pm0.5}ICl_{1.07\pm0.03}$	2	7,12	10,47	40	20	24
$C_{24.8\pm0.5}ICl_{1.06\pm0.05}$	3	7,12	13,82	53	20	24
$C_{32.8\pm0.5}ICl_{1.06\pm0.05}$	4	7,12	17,17	64	20	8
$C_{27.5\pm0.5}ICl_{3.0\pm0.1}$	2	6,89	10,24	20	20	48
$C_{24.5\pm0.5}SbCl_{5.0\pm0.1}$	2	9,36	12,71	160	160	24
$C_{16.2\pm0.2}Br_{2.0\pm0.1}$	2	7,03	10,38	20	20	720

where m^* is the effective mass of carriers moving along a cyclotron orbit at the Fermi velocity v_F and Λ is the mean free path representing the low-temperature distance between the scattering centers. In graphite and in its intercalation compounds the scattering centers are mainly defects of the crystal lattice. The value of the magnetic induction $|B_{min}|$ in which the oscillations become distinguishable allows us to estimate the relative degree of perfection of these samples.

Inercalation compounds of graphite with the same stoichiometric composition (and of the same order) synthesized by the gaseous method can be obtained in a range of synthesis conditions. A change in these conditions alters the occupancy of the interlayer spaces of the graphite matrix and this clearly determines the degree of regularity of the resultant structure. For example, the compound $C_{16.3}ICl$ was obtained when the iodine monochloride temperature was kept constant at 20 ± 0.2 °C and the graphite temperature was varied from 30 to 40 °C. When the graphite temperature was below 34 °C, it was found that the Shubnikov-de Haas (SdH) quantum oscillations were not observed for these samples at 4.2 K even when the magnetic induction was up to 6 T. When the temperature of graphite was increased during synthesis, the value of $|B_{min}|$ first decreased, reaching its minimum at ~ 3 T for $t_{gr} = 40 \pm 0.5$ °C, and then began to rise. In this way by varying t_{gr} in steps of 0.5 °C, we determined the near-optimal conditions for the synthesis of "perfect" quasisingle-crystal samples of the compound $C_{16.5}ICl_{1.1}$ based on graphite of the UPV-IT MO grade.

Using this approach, we synthesized also samples of some low-order (including the first) acceptor-type ICG which had not exhibited quantum oscillations before and for which reliable information on the Fermi surface was lacking.

Samples of ICG were planar rectangular plates of $5 \times 1 \times 0.1$ mm dimensions to which gold or copper contacts were attached by a silver paste in order to determine the electrical resistivity or the Hall emf. Many of the compounds were sensitive to moisture present in atmospheric air. Therefore, samples were mounted in a hermetically sealed chamber filled with dried nitrogen. Samples mounted on a bone holder were placed in a hermetically sealed cell or were encapsulated in dehydrated wax.

Magnetic fields up to 6.5 T intensity were created by a superconducting solenoid. The temperature dependences were recorded using an evacuated ampoule with a heater placed inside a helium cryostat. Temperatures in the range 4.2–300 K were measured using copper-Constantan and gold-iron thermocouples. Temperatures below 4.2 K were deduced from the helium vapor pressure.

Hydrostatic pressures were created in constant-pressure chambers made of beryllium bronze filled with a kerosene-oil mixture.[11] At helium temperatures the pressure was determined from a change in the temperature of the superconducting transition of a tin sensor placed in the working channel of the chamber in the direct vicinity of a sample. The degree of homogeneity of the hydrostatic pressure at low temperatures was improved by heating a sample and simultaneously cooling the chamber.[12]

The electrical conductivity of ICG samples was determined by the four-contact method under dc conditions and also by a contactless induction method at a frequency of 100 kHz. Plates of a given compound were located in the space between coils transmitting and detecting an electromagnetic field, and measurements were made of the received signal. The sensitivity of the method was improved by using a pair of compensating coils and an additional electronic compensator.

The SdH oscillations were determined either directly by recording the dependence of the electrical resistance on the magnetic field with a suitable compensation of the monotonic component of the magnetoresistance or by recording the first derivative $\partial\rho(B)/\partial B$ employing the usual modulation method.

ENERGY SPECTRUM OF CHARGED CARRIERS IN LOW-ORDER ACCEPTOR-TYPE INTERCALATION COMPOUNDS OF GRAPHITE

The SdH oscillations in sufficiently "perfect" acceptor-type ICG samples prepared as described were of amplitude comparable with the monotonic component of the transverse magnetoresistance, indicating a high quality of the intercalated samples.

2. Compounds formed by intercalation of graphite with metal chlorides and interhalides

A common feature of the compounds $C_{9.3}AlCl_{3.3}$, $C_{16.3}ICl_{1.1}$, $C_{28}ICl_3$, and $C_{9.8}CuCl_2$ was the monochromatic nature of the oscillations throughout the range of magnetic fields investigated (Figs. 2 and 3). The angular dependence of the extremal cross sections of the Fermi surface obeyed the relationship

$$S_{extr}(\theta) = S_{extr}(0)\cos^{-1}\theta, \tag{2}$$

where θ is the angle between the direction of the magnetic field and the c axis of the sample, which indicated that the Fermi surface was nearly cylindrical (Fig. 4).

The Dingle temperature T_D calculated from the magnetic-field dependence of the oscillation magnitude was 15–19 K for the samples investigated and did not vary in the temperature range 2–4.2 K. The effective masses of the carriers m^* deduced from the temperature dependences of the
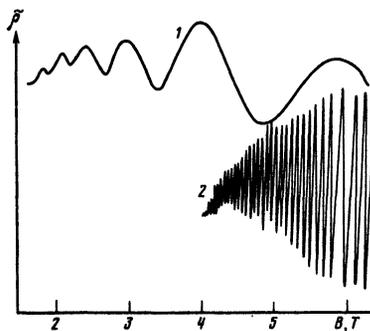

FIG. 2. Oscillations of the transverse magnetoresistance exhibited at 4.2 K in $C_{9.3}AlCl_{3.4}$ (curve 1) and in $C_{9.3}AlCl_3Br_{0.6}$ (curve 2).
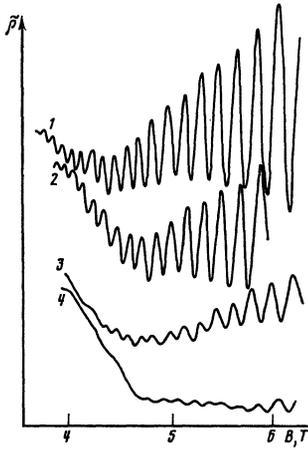
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FIG. 3. Oscillatory components of the transverse magnetoresistances observed in $C_{9.8}CuCl_2$ at 4.2 K for different values of the angle θ: 1) $0°$; 2) $11°$; 3) $22°$; 4) $25°$.

amplitudes of the oscillation extrema at temperatures 2–4.2 K are listed in Table II. The Hall coefficient R_B of the investigated ICG samples was independent of the magnetic field at helium temperatures and was positive.

The monochromatic nature of the oscillations and the constancy of the Hall coefficient in magnetic fields indicated that only one type of charge carrier (hole) was present in first- and second-order compounds ($C_{9.3}AlCl_{3.3}$, $C_{16.3}ICl_{1.1}$, $C_{28}ICl_3$, $C_{9.8}CuCl_2$).

The energy spectrum of carriers in low-order acceptor-type ICG can be described by a model proposed in Ref. 13. In this mode, ICG are regarded as spatially modulated electron structures in which π electrons of the carbon atoms are partly localized in the intercalant layers and carriers in the carbon planes are holes. In the case of first-order ICG the dispersion law is the same as for an isolated graphite layer:

$$\varepsilon_{c,v} = \pm {}^3/_2 b_0 \gamma_0 k, \qquad (3)$$

where k is the wave vector; γ_0 is the resonance overlap integral of the wave functions of the π electrons in the basal plane; and the subscripts "c" and "v" refer to the conduction and valence bands, respectively.

In first-order perturbation theory we can describe second-order ICG by introducing a parameter γ_1 which represents (as in the case of graphite) the interaction between the nearest graphite layers not separated by an intercalant. In this case the dispersion law for two valence bands can be written in the form

$$\varepsilon_v^{1,2} = {}^1/_2 [\pm \gamma_1 - (\gamma_1{}^2 + 9b_0{}^2\gamma_0{}^2 k^2)^{1/2}]. \qquad (4)$$

In the case of higher-order ICG the numbers of the valance and conduction bands increase correspondingly.

The Fermi level of acceptor-type ICG is located below the top of the upper valance band and its position depends on the order of the compound and the oxidizing power of the intercalant. The results obtained indicated that in the case of second-order compounds $C_{16.3}ICl_{1.1}$, $C_{26}ICl_3$, and $C_{9.8}CuCl_2$ the Fermi level intersects only the upper valence band and $|\varepsilon_F| < \gamma_1$.

The carrier density for the group of carriers characterized by a cylindrical Fermi surface can be calculated from

$$P_{osc} = \frac{4S_{extr(2)}}{(2\pi\hbar)^3 [d_0 + d_i]} \quad \text{and} \quad P_{Hall} = \frac{1}{|e|R_B}, \qquad (5)$$

where d_i is the thickness of the intercalant layer and the index (2) of S_{extr} refers to the Fermi surface of the second-order ICG. The good agreement between P_{osc} and P_{Hall} (Table II) is additional evidence that these compounds contain only one group of carriers.

The value of γ_1 for some second-order ICG was determined from the optical reflection data and it amounted to 0.377 eV, which was close to the corresponding parameter of graphite.[13,14] An increase in the number of carriers in ICG compared with graphite, in which the density of electrons and holes was about 10^{-4} per carbon atom, should enhance the screening of the atomic potentials and reduce the parameter γ_0. We could determine the degree to which the value of γ_0 decreased as a result of intercalation by employing the following formula deduced from the model of Ref. 13:

$$m_z^* = \frac{1}{2\pi} \frac{dS_{extr(2)}}{d\varepsilon} = \frac{\hbar^2(\gamma_1 + 9b_2^0\gamma_0^2 S_{extr(2)}/\pi\hbar^2)^{1/2}}{9b_2^0\gamma_0^2}. \qquad (6)$$

In this formula the quantities m_2^* and $S_{extr(2)}$ were determined experimentally. The value of γ_1 could be regarded to be the same as that of graphite, i.e., equal to 0.377 eV. Having found γ_0 in this way, we used the formula

$$\varepsilon_F = -\frac{1}{2} \left[\gamma_1 - \left(\gamma_1{}^2 + 9b_0{}^2\gamma_0{}^2 \frac{S_{extr(2)}}{\pi\hbar^2} \right)^{1/2} \right] \qquad (7)$$

to calculate the Fermi energy ε_F.

The values of S_{extr}, m_2^*, and γ_0 calculated from Eq. (5), as well as P_{osc}, P_{Hall}, and the corresponding values of ε_F are listed in Table II. Clearly, the parameter γ_0 decreased as P increased, and for $P = 2.8 \times 10^{26}$ cm^{-3} the change in γ_0, compared with its value for graphite, was $\sim 25\%$. The Fermi energy ε_F of $C_{16.3}ICl_{1.1}$, $C_{28}ICl_3$, and $C_{9.8}CuCl_2$ calculated from Eq. (7) was less than γ_1 (Table II), confirming the above hypothesis that the Fermi level intersected only the upper valence band, since $|\varepsilon_v^1 - \varepsilon_v^2| = \gamma_1$ [see Eq. (4)].
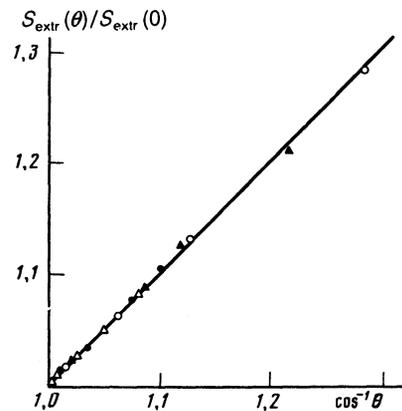

FIG. 4. Dependence of the ratio $S_{extr}(\theta)/S_{extr}(0)$ on $\cos^{-1}\theta$ for $C_{9.3}AlCl_{3.4}$ (O), $C_{9.8}CuCl_2$ (●), $C_{16.3}ICl_{1.1}$ (△), and for graphite (▲).

TABLE II. Parameters of energy spectrum of carriers in investigated intercalated compounds of graphite.

Chemical formula	N	S_{extr}, 10^{-42} $g^2 \cdot cm^2 \cdot sec^{-2}$	m^*/m_0	γ_0, eV
$C_{9.3}AlCl_{3.3}$	1	11.6±0.3	0.056±0.003	3.2
$C_{9.5}AlCl_3Br_{0.6}$	1	362±3	—	—
$C_{9.8}CuCl_2$	2	180±2	0.091±0.005	2.7±0.2
$C_{16.3}ICl_{1.1}$	2	287±3	0.132±0.007	2.5±0.2
$C_{28}ICl_3$	2	319±3	0.148±0.008	2.4±0.2

ε_F, eV	P_{osc}, 10^{26} m^{-3}	P_{Hall}, 10^{26} m^{-3}	R_B, 10^{-7} m^3/C
−0.12±0.01	0.11±0.01	0.12±0.01	5.0±0.5
−	3.38±0.07	3.6±0.4	0.17±0.02
−0.25±0.02	1.29±0.02	1.3±0.1	0.47±0.05
−0.34±0.03	2.50±0.05	2.6±0.2	0.24±0.02
−0.34±0.03	2.84±0.06	2.8±0.3	0.22±0.02

A characteristic feature of some of the investigated metal chloride and interhalide ICG was a reduction in the frequency of the SdH oscillations for the same sample in the course of its "aging," which was clearly due to a change in the chemical composition of the intercalated layers because, for example, of hydrolysis of the intercalant. Particularly large changes in the oscillation frequency (by a factor of ~4) were observed for samples of the compound $C_{9.3}AlCl_{3.3}$ in which the intercalated layers had an excess of chlorine, some of which formed negatively charged $AlCl_4^{\delta-}$ complexes. The degree of dissociation of these complexes had a strong influence on the density of holes in the graphite layers which appeared because of a redistribution of the electron density during intercalation. The processes of loss of excess chlorine and partial hydrolysis had not been observed also for other ICG (Ref. 15). The time dependence of the density of holes was the reason for the changes in the SdH frequencies in various ICG samples of this type.

2. Compounds of graphite intercalated with strong acceptors

Introduction of a small amount of bromine into a first-order compound with aluminum chloride, $C_{9.5}AlCl_3Br_{0.6}$, increased the frequency of the SdH quantum oscillations, indicating that the density of holes in the graphite layers increased correspondingly by a factor of more than 30 (Fig. 2).

In the case of second-order compounds $C_{16}Br_2$ and $C_{21}AlBr_{3.4}$ the SdH oscillations were not monochromatic and their frequencies were considerably higher than in the case of compounds with aluminum chloride. This was not only due to an increase in the acceptor strength of the intercalant, but also to low-temperature formation (as deduced from x-ray structure analysis) of a superlattice of charged centers, commensurate with the graphite lattice, in the intercalated layers. Formation of such a superlattice gave rise to new planes of discontinuity of the energy in the momentum space (it altered the dimensions of the Brillouin zone), so that the Fermi surface split into several constant-energy surfaces and new frequencies corresponding to combination orbits of carriers in a magnetic field appeared in the oscillation spectrum. A complex oscillation pattern was also exhibited

by the compound $C_{24}SbCl_5$ and the SdH frequencies observed in the present study were in good agreement with the results reported by other authors for the same compound.[16] In view of these factors, it was necessary to carry out a special study in order to obtain information on the energy spectrum of ICG containing strong acceptors.

3. Angular dependence of amplitudes of Shubnikov-de Haas oscillations in intercalated compounds of graphite

The change in the amplitude of the SdH oscillations in ICG on increase in the angle θ between the direction of the magnetic field $\mathbf{B}$ and the c axis of a sample was unusual and different from that observed for graphite. The amplitude of the oscillation peaks decreased rapidly as the angle θ increased (Fig. 3). This limited the range of angles in which the oscillation effects could be measured. The existence of the maximum angle θ_{max} at which the SdH oscillations were no longer observed in magnetic fields up to 6.5 T was characteristic of each of the investigated ICG samples. The value of θ_{max} decreased with increasing oscillation frequency and increasing identity period of the crystal structure in the direction of the c axis. Figure 5 shows the dependences of the amplitudes of the oscillation extrema on the angle θ for the second-order compound $C_{9.8}CuCl_2$. In the angular range $\theta > \theta_{max} \gtrsim 30°$ the oscillations were not observed even in fields of ~6.5 T.

Since the charge transport processes in low-order acceptor-type ICG are two-dimensional,[17] the carrier orbits in a magnetic field lie in the basal plane for all values of θ, i.e., they lie in the carbon layer planes.

The magnetic induction vector $\mathbf{B}$ can be regarded as a sum of two components: $B_{\parallel}$, which is parallel to the c axis of the sample, and $B_{\perp}$, which is perpendicular to the c axis. The component $B_{\perp}$ gives rise to a Lorentz force $F_L = eB_{\perp}v_F$ directed at right angles to the plane of the cyclotron orbits of the carriers moving at the velocity v_F in the basal plane.

When the angle θ is increased each specific oscillation extremum shifts toward lower magnetic fields and the value of the field in which it is observed varies in accordance with the law $B_M(\theta) = B_M(0)\cos^{-1}\theta$. At the same time there is an increase in the Lorentz force $F_L(\theta) = e|\mathbf{B}|\sin\theta v_F$, which tends to alter the cyclotron orbit plane. Since rotation of the
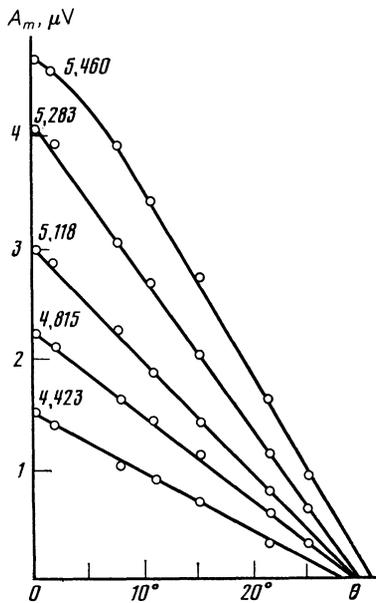
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FIG. 5. Amplitudes of the SdH oscillations extrema for $C_{9.8}CuCl_2$ vs the angle θ. The magnetic field (in teslas) corresponding to the position of these extrema at $\theta = 0$ is given alongside each curve.

orbit is impossible, there is an increase in the probability that carriers are scattered by the intercalant ions, and this reduces the relaxation time and damps the SdH oscillations. In the case of graphite, the amplitude of specific oscillation extrema remains practically constant in the range $\theta \lesssim 60°$.

It therefore follows that the specific two-dimensional nature of the motion of carriers in ICG gives rise to an interesting effect: the application of an additional magnetic field oriented perpendicular to the c axis reduces strongly the oscillation amplitudes, right down to their complete disappearance, and this happens for a constant value of the component of the field directed along the c axis.

"SUPERMETALLIC" ELECTRICAL CONDUCTIVITY OF INTERCALATED COMPOUNDS OF GRAPHITE

Attention has been drawn on many occasions to the extremely high electrical conductivity of low-order acceptor-type ICG and studies have been made of the dependence σ_a on the chemical composition of compounds for different intercalants.[18,19] According to the published data, the highest room-temperature electrical conductivity is exhibited by strong-acceptor ICG. For example, in the case of ICG with the formula AsF_5 the electrical conductivity is $\sigma_a \sim 6.0$

$\times 10^5 \, \Omega^{-1} \cdot cm^{-1}$, which is higher than the conductivity of copper or silver.[20]

However, it has to be remembered that the presence of strong acceptors can distort the planar structure of the carbon atom layers because of deformation of the C–F and C–O bonds[21] which reduces the mean free path of carriers. We can expect that, in spite of the lower acceptor strength of metal chlorides and interhalides (compared with fluorine compounds), the value of σ_a for ICG with acceptors of this type will also be high.

Our investigations showed that σ_a depends on the composition of the intercalant, on the grade of graphite, and on the order of the compound (Table III).

A determination of the SdH oscillations and of the electrical conductivity of the same "perfect" quasisingle-crystal samples of low-order acceptor-type ICG enabled us to find for the first time how σ_a is affected not only by the order N, but also by the carrier density and mobility (mean free path).

Estimates of the mean free path Λ were made using the Drude-Lorentz formula allowing for the two-dimensional nature of the charge transport processes:

$$\Lambda = \frac{\sigma_a}{e^2} \left[\sum_i \frac{p_i}{p_{F_i}} \right]^{-1} = \frac{\sigma_a (2\pi\hbar)^2}{4e^2} \frac{d_i + (N-1) d_0}{\sum_i \left[\pi S_{extr(i)} \right]^{1/2}}, \quad (8)$$

where the index i labels the group of holes and p_F is the Fermi momentum of these holes. In the calculation of the mean free path Λ in third- and fourth-order iodine monochloride ICG samples containing several groups of holes it was assumed that the value of this quantity was the same for all groups of carriers and was governed primarily by the domain size.

Subject to these assumptions, the mobility and the relaxation time of carriers in ICG samples can be described by the formulas

$$\mu = e\Lambda/p_F, \quad (9)$$

$$\tau = \Lambda m^* (\pi/S_{extr})^{1/2}. \quad (10)$$

The calculated values of Λ, μ, and τ are listed in Table III. It is interesting to note that the room-temperature values of Λ for ICG are $(3-5) \times 10^3$ Å and they exceed the mean free path of carriers in graphite (10^3 Å), which is clearly due to the stronger manifestation of the two-dimensional nature of conduction processes in ICG. However, the room-temperature mobilities of carriers in ICG are of the same order of magnitude as in graphite.

TABLE III. Values of electrical conductivity (σ_a), mean free path (Λ), mobility (μ), and relaxation time (τ) of carriers in some intercalated compounds of graphite.

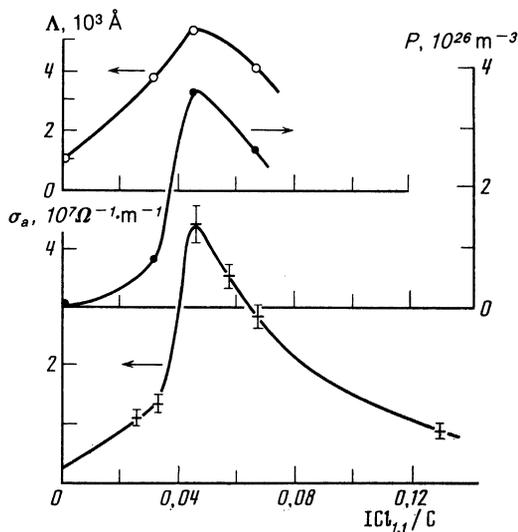| Chemical formula	N	σ_a, 10^7 OM$^{-1} \cdot$M^{-1}	Λ, 10^3 Å	μ, M^2/B$\cdot$c	τ, 10^{-12} c
$C_{16.5\pm0.5}ICl_{1.07\pm0.03}$	2	2.8±0.6	3.7	0.65	0.41
$C_{24.8\pm0.5}ICl_{1.06\pm0.05}$	3	4.4±0.6	5.9	0.74	–
$C_{32.8\pm0.5}ICl_{1.06\pm0.05}$	4	1.3±0.3	3.8	1.16	0.63
$C_{27.5\pm0.5}ICl_{3.0\pm0.1}$	2	2.5±0.3	3.5	0.56	0.47
$C_{9.5\pm0.2}AlCl_3Br_{0.6}$	1	2.7±0.2	3.1	0.47	–
$C_{9.8\pm0.1}CuCl_{2.05\pm0.02}$	2	1.2±0.1	2.7	0.58	0.3

FIG. 6. Dependences of the conductivity σ_a (300 K), of the carrier density P, and of the mean free path Λ for compounds of graphite with iodine monochloride on the ratio $\mathrm{ICl}_{1.1}/\mathrm{C}$ of the intercalated compound to carbon.

The value of σ_a for iodine monochloride ICG reaches its maximum for the third-order compound $\mathrm{C}_{24.5}\,\mathrm{ICl}_{1.1}$ and it exceeds the electrical conductivity of gold under the same conditions. Figure 6 shows how σ_a, P, and Λ depend on the number of ICl molecules per carbon atom in ICG. In the case of ICG of mixed order $\langle N \rangle = 2.3 = 0.7 \times 2 + 0.3 \times 3$, the experimental values of the electrical conductivity are described by

$$\sigma_{a/N=2,3}=\sigma_{a/N=2}\cdot 0.7+0.3\sigma_{a/N=3}.$$

The maximum value of σ_a for $\mathrm{C}_{2.45}\,\mathrm{ICl}_{1.1}$ corresponds to the intercalation order characterized by maximum values of Λ and P. An increase in the conductivity is then mainly due to a strong increase in the density of holes in this compound.

It should be pointed out that the dependences of the electrical conductivity σ_a on the order of acceptor-type ICG obtained by other authors have similar maxima for $N = 2$–3 (Ref. 22).

It follows from these data that the "supermetallic" conductivity of acceptor-type ICG is primarily due to an increase in the carrier density, compared with graphite, whereas the high mobility associated with the two-dimensional nature of the transport processes is still retained.

ORDER-DISORDER PHASE TRANSITIONS IN INTERCALANT LAYERS

Intercalation of molecules in graphite produces monomolecular layers in which the intercalant molecules do not occupy strictly fixed positions, but form a "two-dimensional liquid." Cooling of ICG solidifies these layers which form either a periodic lattice or an amorphous glassy structure. The structure of intercalant layers is governed by the actual form of the intercalants and in some cases may be determined by x-ray structure analysis.[23,24] It should be pointed out that the regular structure of the layer need not be associated with the regular distribution of charged centers, the

number of which can vary quite widely (this is true, for example, of aluminum chloride ICG).

Order-disorder phase transitions in the ICG samples which we investigated were accompanied by a strong reduction (by a factor of 2–3) in the electrical conductivity σ_c along the c axis. Such a change exhibited some hysteresis on the temperature scale, typical of first-order phase transitions. A determination of the conductivity σ_a in the basal plane by a remote induction method revealed that at temperatures corresponding to a change in σ_c there was also an abrupt change in the temperature coefficient of the electrical conductivity. However, the dependence of ρ_a on T did not show any strong anomalies (Fig. 7). Unfortunately, it was not possible to suggest a definite reason for the anomalous behavior of σ_c at the phase transition point.

Investigations of the angular dependences of σ_c in a magnetic field at helium temperatures, carried out on $\mathrm{C}_{16.3}\,\mathrm{ICl}_{1.1}$ and $\mathrm{C}_{9.8}\,\mathrm{CuCl}_2$ compounds, revealed that they were of the same nature as in the case of quasisingle-crystal samples of pyrolytic graphite. This result supported the hypothesis that σ_c of ICG was dominated by a contribution of deformed carbon layers in the regions at domain boundaries.

The abrupt change in the temperature coefficient of the electrical conductivity at the phase transition was most probably due to softening of the phonon spectrum as a result of "melting" of two-dimensional intercalant layers.

INFLUENCE OF HIGH PRESSURES ON THE ELECTRON STRUCTURE OF INTERCALATED COMPOUNDS OF GRAPHITE

The SdH oscillations of the transverse magnetoresistance, of the electrical resistivity, and of the Hall emf of second-order $\mathrm{C}_{16.3}\,\mathrm{ICl}_{1.1}$ and $\mathrm{C}_{9.8}\,\mathrm{CuCl}_2$ ICG were determined at pressures up to 12 kbar. In the case of the low-temperature investigations using chambers in which the pressure was set at room temperature the difference between the thermal expansion coefficients of the casing of the chamber and the medium inside it reduced the presssure at liquid helium temperature by 3 kbar compared with the room-temperature pressure.[25] Therefore, if changes in the structure caused by the pressure occurred at room temperature and were then "frozen-in," it was necessary to include a correction for the
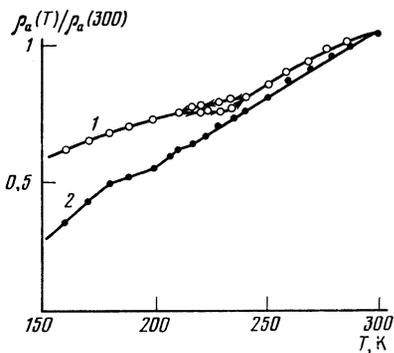

FIG. 7. Temperature dependences of the resistivity ratio $\rho_a (T)\rho_a$ (300 K) measured by an induction method for $\mathrm{C}_{24}\,\mathrm{SbCl}_5$ (curve 1) and $\mathrm{C}_{9.3}\,\mathrm{AlCl}_{3.4}$ (curve 2) compounds.
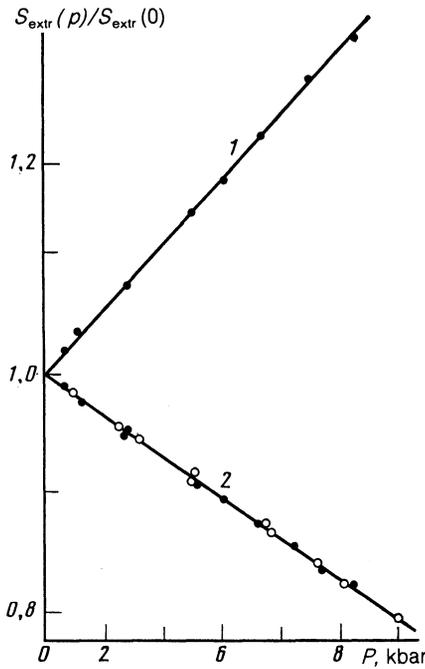
FIG. 8. Dependences of the Fermi surface cross sections $S_{extr(3)}$ (curve 1) and $S_{extr(2)}$ (curve 2) on the pressure applied at 4.2 K to compounds $C_{16.3}ICl_{1.1}$ (●) and $C_{9.8}CuCl_2$ (○).

difference in the pressures as a result of cooling.

It was found that at atmospheric pressures the samples exhibited clear SdH oscillations corresponding to the extremal cross sections of the Fermi surface:

$$S_{extr(2)} = (287 \pm 3) \cdot 10^{-42} \text{ g}^2 \cdot \text{cm}^2 \cdot \text{sec}^{-2} \text{ for } C_{16.3}ICl_{1.1},$$

$$S_{extr(2)} = (180 \pm 2) \cdot 10^{-42} \text{ g}^2 \cdot \text{cm}^2 \cdot \text{sec}^{-2} \text{ for } C_{9.8}CuCl_2.$$

Under the action of pressure the areas of these cross sections decreased for both compounds at the following rate (Fig. 8):

$$\partial \ln S_{extr(2)}/\partial p = -(0.017 \pm 0.01) \text{ kbar}^{-1}.$$

The change in the density of holes could in this case be found from the formula

$$\frac{\partial \ln P}{\partial p} = \frac{\partial \ln S_{extr(2)}}{\partial p} + \frac{\partial \ln (d_i + d_0)}{\partial p}, \quad (11)$$

where the first term describes the change in the cross section of the Fermi cylinders and the second the change in their height, i.e., the change in the size of the Brillouin zone in the direction of the c axis. The available data on the compressibility of ICG made it possible to assume that

$$\partial \ln [d_i + d_0]/\partial p \approx 2 (\partial \ln d_0/\partial p) = 5.6 \cdot 10^{-3} \text{ kbar}^{-1},$$

where $\partial \ln d_0/\partial p$ is the rate of change of the interlayer separation in graphite as a result of compression.[26] In the case of the compounds investigated, we found that the following condition was obeyed:

$$|\partial \ln S_{extr(2)}/\partial p| > |\partial \ln [d_i + d_0]/\partial p|,$$

which corresponded to a reduction in the carrier density with increasing pressure. The most probable reason for the reduction in $S_{extr(2)}$ and in the carrier density due to compression of ICG was a change in the structure of the interca-

lant layer (in particular, an increase in the density of this layer), as already found for donor-type ICG (Ref. 27). Unfortunately, the nature of the chemical bonds in ICG is at present known only generally and it is therefore impossible to draw any conclusions on the nature of changes in the bonds as the density of the layers increases.

The change in the Fermi energy due to the application of pressures to second-order ICG is given by the expression

$$\frac{\partial \varepsilon_F}{\partial p} = -\frac{1}{2} \left\{ -\frac{\partial \gamma_1}{\partial p} + \frac{\gamma_1 (\partial \gamma_1/\partial p) + (9/\pi \hbar^2) \gamma_0^2 b_0^2 (\partial S_{extr(2)}/\partial p)}{[\gamma_1^2 + 9\gamma_0^2 b_0^2 (S_{extr(2)}/\pi \hbar^2)]^{1/2}} \right\}.$$

The pressure dependence of the parameter γ_1 can be allowed for by assuming that it is the same as in the case of graphite.[28] We then obtain

$$\partial \varepsilon_F/\partial p = 6.5 \pm 0.5 \text{ meV/kbar}^{-1} \text{ for } C_{16.3}ICl_{1.1},$$

$$\partial \varepsilon_F/\partial p = 5.3 \pm 0.5 \text{ meV/kbar}^{-1} \text{ for } C_{9.8}CuCl_2.$$

In the case of iodine monochloride ICG samples under pressure we observed a new SdH oscillation frequency corresponding to the Fermi surface cross section $S_{extr(3)}$ $= (25 \pm 0.5) \times 10^{-42} \text{ g} \cdot \text{cm}^2 \cdot \text{sec}^{-2}$ which is typical of the third-order compound $C_{24}ICl_{1.1}$ (Fig. 9). The cross section applies to the internal coaxial Fermi cylinder. It rises on increase in the pressure at the rate (Fig. 7):

$$\partial \ln S_{extr(3)}/\partial p = (0.027 \pm 0.003) \text{ kbar}^{-1}.$$

It was found that an increase in the pressure reduced the electrical conductivity and the Hall coefficient of iodine monochloride ICG. The amplitude of the oscillations corre-
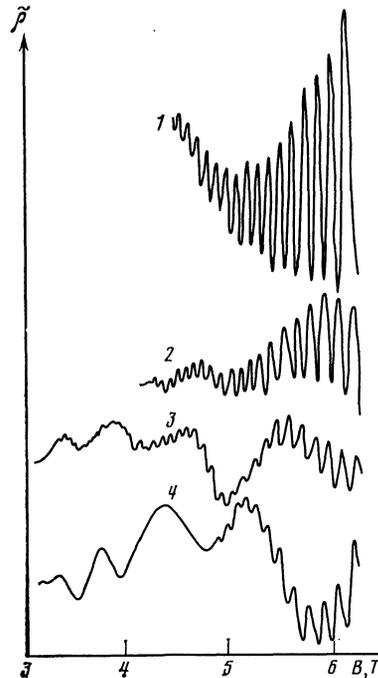

FIG. 9. Oscillations of the transverse magnetoresistance of $C_{16.3}ICl_{1.1}$ at different pressures: 1) 1 bar; 2) 3 kbar; 3) 6.2 kbar; 4) 8.5 kbar.

sponding to $S_{extr(3)}$ increased on increase in the pressure and the amplitude of the oscillations corresponding to $S_{extr(2)}$ decreased. Changes in the values of $S_{extr(2)}$ and $S_{extr(3)}$ under pressure were reversible, but when the pressure was removed the oscillations corresponding to $S_{extr(3)}$ did not disappear completely. In the case of $C_{9.8} CuCl_2$ there was only a reduction in the cross section $S_{extr(2)}$ (Fig. 7) and no new oscillations appeared as a result of compression.

These results demonstrated that application of pressure to second-order iodine monochloride ICG samples created third-order regions. The dimensions of these regions increased under pressure and when the pressure was removed, their size decreased but the regions did not disappear completely.

The mechanism of formation of third-order regions under pressure was clearly as follows. When intercalant was introduced into graphite, a domain structure was established[29] and inside crystallites contact was established between filled interlayer spaces shifted along the direction of the c axis, resulting in the formation of boundary regions which were deformed graphite layers. At room temperature, which was quite close to the phase transition temperature of the iodine monochloride layer (~ 313 K) in ICG, the intercalant molecules had sufficient mobility for motion under the influence of external factors, such as pressure. Changes in the ICG structure occurring at room temperature under pressure were "frozen-in" during cooling and the resultant displaced structure was retained to helium temperatures in spite of a reduction in the pressure. In the case of the copper chloride ICG an order–disorder phase transition in the intercalant layer was not observed, at least for temperatures $T \sim 400$ K. Therefore, we could assume that the mobility of $CuCl_2$ molecules in ICG under the action of pressure applied at room temperature was considerably less than in the case of iodine monochloride molecules.

One should point out that in spite of the 30% change in the crystal lattice parameter as a result of the structural phase transition in iodine monochloride ICG, clear SdH oscillations were still observed. Hence, we concluded that a change in the structure did not alter the single-crystal nature of the domains because of the high stability of the planar structure of the graphite layers.

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