# Pressure-induced change in the intercalation step in the graphite compound C₁₆ICl

N. B. Brandt, S. V. Kuvshinnikov, and S. G. Ionov
*Moscow State University*

A change in the intercalation step in the acceptor-type compound C₁₆ICl, formed by intercalation into graphite under hydrostatic pressure, is observed for the first time. The accompanying changes in the parameters of the energy spectrum of the current carriers are determined.

PACS numbers: 72.20.Jv

When acids, salts, and alkali metals are intercalated into graphite, the electronic density between the carbon atoms and the intercalating substance is redistributed. In the compounds formed by intercalation into graphite (GIC), the number of free carriers increases by several orders of magnitude (when the intercalate is a "hole" acceptor), which is one of the reasons for the appearance of "supermetallic" conductivity in acceptor-type compounds.[1]

The energy spectrum of current carriers in ICG is determined by the intercalation step (the number of steps is equal to the number of atomic carbon layers situated between the nearest layers of the intercalating substance) and by the properties of the intercalate: its composition, packing density, and mutual arrangement of molecules. In acceptor-type graphite compounds, the Fermi surface consists of several cylinders, oriented along the "$C$" axis. In first-step GIC, six such cylinders are situated at the vertices of a hexagonal Brillouin zone. This type of Fermi surface also occurs in second-step compounds C₁₆ICl, the only difference being that the radius of each of the cylinders increases. For third-step GIC C₂₄ICl, each of the vertices of the Brillouin zone contains two coaxial cylinders (in the case of oxidizers that are stronger than iodine monochloride, the number of such cylinders can increase to three).[1,2] Since the compressibility of GIC along the "$C$" axis is very high (the anisotropy of the compressibility is $\sim 10^2$), we can expect that the pressure must have a strong effect on the properties of these compounds. As far as we know, this problem has not yet been studied for acceptor-type compounds.

In this work, we investigate the quantum oscillations of the transverse magnetoresistance (Shubnikow–de Haas effect) in the second-step GIC iodine monochloride C₁₆ICl under pressures up to 12 kbar. The pressure was produced in a chamber with a kerosene-oil medium at room temperature. To conserve the highly hydrostatic nature of the pressure the chamber was cooled by simultaneously heating the specimen using the method proposed in Ref. 3. A peculiarity of low-temperature $e$ studies in chambers of this type is that due to the difference in the thermal coefficient of expansion of the medium transmitting the pressure and of the material forming the housing of the chamber, the pressure at room temperature is $\sim 3$ kbar higher than at liquid-helium temperature.[3] This correction must be taken into account if the pressure-induced
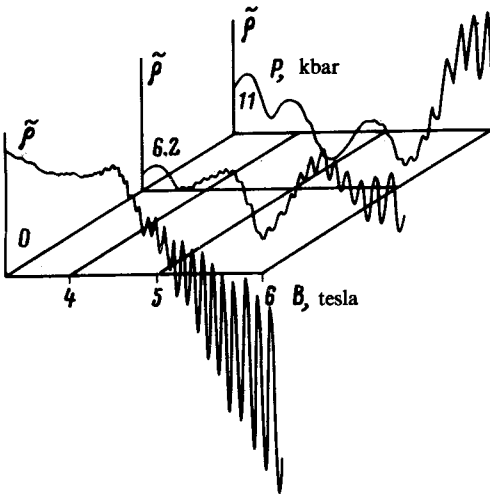
FIG. 1. Dependence of the oscillating part of the transverse magnetoresistance on the magnetic field in the GIC iodine monochloride under different pressures.

changes in the specimen occur at room temperature and are then "frozen." In these experiments the pressure at liquid-helium temperatures was determined from the change in the temperature of the transition of the tin sensor to the superconducting state.

At atmospheric pressure, monochromatic SdH oscillations are observed in the compound $C_{16}ICl$, corresponding to the extreme value of the cross section $S_{2\,ext}$ $= (287 \pm 2) \times 10^{-42}\, \Gamma \cdot cm^2 \cdot s^{-2}$ and of the effective mass $m_2^* = (0.132$
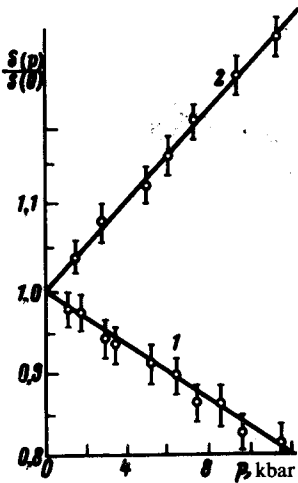


FIG. 2. Relative change in the areas of extremal cross sections under compression. 1) $S_{2\,ext}$; 2) $S_{3\,ext}$.

$\pm\,0.010)m_0$. Using these data and the model of the energy spectrum proposed in Ref. 2, the Fermi energy can be calaculated using the equation

$$\epsilon_F = \frac{1}{2}\left\{\gamma_1 - \sqrt{\gamma_1^2 + 9\gamma_0^2\,b_0^2\,\frac{p_F^2}{\hbar^2}}\right\}, \tag{1}$$

where $\gamma_0$ and $\gamma_1$ are the resonant overlap integrals of the wave functions of the carbon atoms in the layer ($\gamma_0$) and in the neighboring layers ($\gamma_1$) $b_0 = 1.42$ Å is the distance between the nearest carbon atoms in the basal plane, and $p_F = \sqrt{S_{ext}/\pi}$ is the limiting Fermi momentum. According to the optical reflection data,[2] for the compound $C_{16}ICl$, $\gamma_1 = 0.377$ eV. To determine the parameter $\gamma_0$ for the compound $C_{16}ICl$ we can use the equation

$$m_2^* = 2h\,\sqrt{\gamma_1^2 + 9\gamma_0^2\,b_0^2\,\frac{p_F^2}{\hbar^2}}\,/9\gamma_0^2\,b_0^2\,, \tag{2}$$

in which the value of $m_2^*$ is known. The value $\gamma_0 = 2.5$ eV calculated in this manner agrees well with the magnitude of this parameter for graphite, for which, according to different references, it varies from 2.4 to 3.2 eV.

Under hydrostatic compression, a new frequency appears in the SdH oscillations in specimens of the compound $C_{16}ICl$, corresponding to the cross section of the Fermi surface $S_{3\,ext} = (25 \pm 0.5)\times 10^{-42}\,\Gamma^2\cdot cm^2\cdot s^{-2}$. An extremal cross section of the same size is also characteristic for the third-step compound $C_{24}ICl$ (this is the cross section of the inner coaxial cylinder with a shorter radius). Oscillations related to the outer Fermi cylinder are not observed, since its cross section is approximately two times greater than the cross section $S_{2\,ext}$. With an increase in pressure, the quantity $S_{3\,ext}$ increases at a rate $\partial\ln S_{3\,ext}/\partial p = 0.027$ kbar$^{-1}$, while the cross-sectional area $S_{2\,ext}$ decreases at a rate $\partial\ln S_{2\,ext}/\partial p = -0.017$ kbar$^{-1}$. The Fermi energy, calculated from Eq. (1), taking into account the change in the parameter $\gamma_1$ under compression,[4] decreases in absolute magnitude from the value $\epsilon_F = -0.36$ eV at $p = 0$ at a rate $\partial\epsilon_F/\partial p = 6.5$ meV kbar$^{-1}$. The areas of the extremal sections vary linearly with pressure and in a reversible manner in the region $< 12$ kbar. With an increase in pressure, the amplitude of the SdH oscillations, corresponding to the cross section $S_{2\,ext}$ decreases, while the amplitude of the oscillations corresponding to the cross section $S_{3\,ext}$ increases. This indicates an increase in the relative fraction of the phase volume of the third-step compound in the specimen.

The data obtained indicate that a pressure-induced phase transition occurs in the GIC iodine monochloride, accompanied by an aliquant change in the intercalation step: from the second to the third. The characteristic feature of the transition is the monotonic (and, apparently, without a pressure threshold) increase in the content of third-step regions with the composition $C_{24}ICl$ and a decrease in the content of second-step regions with composition $C_{16}ICl$ in the bulk of the specimen. The density of current carriers decreases simultaneously int he second-step regions as a result of the decrease in the interplanar distances. The density of current carriers in the third-step regions increases with increasing pressure. The simultaneous observation of SdH oscil-
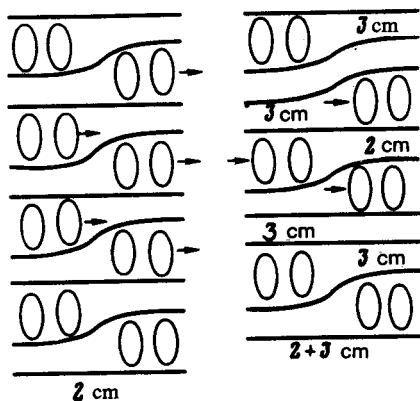
FIG. 3. Model of pressure-induced restructuring of the domain structure of $C_{16}ICl$.

lations, corresponding to sections of the Fermi surface belonging to second- and third-step compounds, indicates that the single-crystal nature of the corresponding regions is conserved, in spite of the $\sim 30\%$ difference in the repeat period of the compounds $C_{16}ICl$ and $C_{24}ICl$. The structure of the specimen arising in the course of the phase transition can be explained on the basis of the domain model of GIC.[5] Since the penetration of the intercalate proceeds from the periphery of the specimen toward the center, domains of a particular step, whose dimensions are smaller than the dimensions of the crystallites, can form with the appearance of interfaces in the form of deformed graphite layers. Under the action of pressure at room temperature, the iodine monochloride molecules diffuse in the basal plane along the graphite layers, accompanied by a corresponding displacement of the domain wall, as shown, for example, in Fig. 3. The excess intercalate is pushed toward the boundaries of the crystallites. When the pressure is removed, the initial structure is partially restored. This is indicated by the increase int he amplitude of the SdH oscillations corresponding to $S_{2\,ext}$ and the decrease in the amplitude of oscillations corresponding to $S_{3\,ext}$.

[1]N. B. Brandt, S. V. Kuvshinnikov, S. G. Ionov, V. A. Mukhanov, V. V. Avdeev, and K. N. Semenenko, Pis'ma Zh. Tekh. Fiz. **8**, 1494 (1982) [Sov. Tech. Phys. Lett. **8**, 641 (1982)].

[2]J. Blinowski, H. H. Nguyen, C. Rigaux, J. P. Vieren, R. LeToullec, G. Furdin, A. Herold, and J. Melin, J. Phys. (Paris) **41**, 47 (1980).

[3]N. B. brandt, S. V. Kuvshinnikov, N. Ya. Minina, and E. P. Skipetrov, Prib. Tekh. Eksp. **6**, 160 (1974).

[4]N. B. Brandt, A. S. Kotosonov, S. V. Kuvshinnikov, and M. V. Semenov, Zh. Eksp. Teor. Fiz. **79**, 937 (1980) [Sov. Phys. JETP **52**, 476 (1980)].

[5]N. Daumas and A. Herold, C. R. Acad. Sci. **268**, 373 (1969).