

Investigation of the galvanomagnetic properties of graphite in magnetic fields up to 500 kOe at low temperatures

N. B. Brandt, G. A. Kapustin, V. G. Karavaev, A. S. Kotosonov, and E. A. Svistova

Moscow State University

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Measurements are made of the Hall coefficient and electrical resistivity of graphite in magnetic fields up to 500 kOe at 4.2 K. It is shown that because of the smallness of the Hall angle the Hall coefficient cannot be used to explain the galvanomagnetic properties or to calculate the kinetic coefficients in graphite. Measurements in fields to 200 Oe show that the minority carriers in the samples studied are high-mobility electrons. The concentrations and mobilities of the majority and minority carriers are calculated by computer on the basis of a three-band model. In the magnetic-field region 300-500 kOe a sharp decrease is observed in the electron and hole decompensation, which may be ascribed to magnetic freeze-out of the impurity carriers.

INTRODUCTION

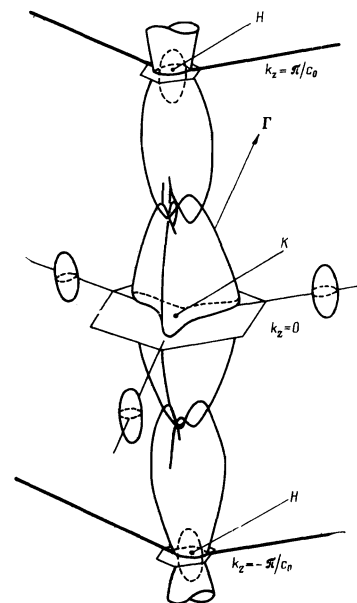
One of the typical representatives of the semimetal group is graphite. The electrical, magnetic, and galvanomagnetic properties of graphite have been the subject of many experimental studies, and comparison of these results with those of theoretical calculations of the spectrum of graphite have permitted quantitative data to be obtained on all of the parameters entering into the theory.

Graphite has a layered hexagonal structure. In a layer the carbon atoms are arranged at the points of a hexagon with an edge of 1.42 Å and are bound together by very strong covalent bonds; the elementary translation in the plane of the layers is $a_0 = 2.46$ Å. In the neighboring layers the atoms are displaced in such a way that the centers of the hexagons of one layer come under (over) the atoms of the other. The period in the direction of the hexagonal axis is $c_0 = 6.7$ Å, so that the layers are weakly bound together. The reduced Brillouin zone is a six-faced prism of height $2\pi/c_0$ and with a base edge $4\pi/a_0\sqrt{3}$. The current carriers occupy a narrow region near the edge of the Brillouin zone. The transverse dimensions of this region amount to $\sim 1\%$ of the prism base edge.

Using group theory and perturbation theory, Slonczewski and Weiss^[1] and McClure^[2] have completely described the band structure of graphite by means of parameters determining the interaction of the atoms in a layer and between layers. The Fermi surface of graphite, constructed from the experimentally measured areas of the extremal sections,^[3] is shown in Fig. 1 (the scale on the k_z axis has been increased five times for convenience). It has a complex trigonal corrugation which is greatest at $k_z = 0$ and decreases as $k_z \rightarrow \pm\pi/c_0$. For $k_z = \pm\pi/c_0$ the sections of the Fermi surface by planes $k_z = \text{constant}$ are circles, i.e., there is no corrugation. Near the point $k_z = 0$ on the edge of the Brillouin zone is located the electron part of the Fermi surface, and on the sides are two hole surfaces. The electron part of the surface touches each of the hole surfaces at four points. One of them, located at the edge of the Brillouin zone, is located further from the point $k_z = 0$ than the three remaining points, which are located symmetrically relative to the edge. The points of contact of the hole and electron parts are conical points.

In pure graphite in the region of fields $H \gtrsim 1$ kOe these holes and electrons with similar concentrations and mobilities provide the main contribution to the con-

FIG. 1. Fermi surface of graphite.



ductivity σ_{xx} . It has been established^[4-8] that in this region the resistivity $\rho_{xx} = \sigma_{xx}^{-1}$ depends on H according to a law close to quadratic.

For $H \lesssim 1$ kOe a large deviation is observed from the quadratic law, which can be explained^[8] by the presence of minority carriers, for which the location of the equal-energy surface and the sign of the charge have not been finally established. The Fermi surface of the minority holes may be located^[9] near the points H ($k_z = \pm\pi/c_0$) and probably has a shape close to an ellipsoid strongly elongated along the edge of the Brillouin zone and with a ratio^[10, 11] of the extremal sections ≈ 13 . Nozières^[12] and McClure^[13] have demonstrated the possibility of existence of minority electrons whose equal-energy surface has sections close to the sections of the Fermi surface of the minority holes and is located near the points K ($k_z = 0$).

Study of the galvanomagnetic properties of graphite in magnetic fields up to 160 kOe at 4.2 K has shown^[14] that from 80 to 140 kOe σ_{xx} and σ_{xy} vary proportionally to $1/H$, the resistivity changes linearly with the field, and the Hall coefficient saturates in fields above 90 kOe. For the case of scattering by ionized impurities, with use of a screening potential in the Fermi-Thomas ap-

proximation and the assumption that the screening radius depends on the magnetic field, it has been possible to explain the linear dependence of the magnetoresistance on the field and to obtain an expression for σ_{xx} related to the number of scattering centers^[14] n_S :

$$\sigma_{xx} = \pi (\Delta Z)^2 n_S c / 16 H; \quad (1)$$

$\Delta Z = Z - 4$ is the impurity valence minus the carbon valence. From the linear dependence of the magnetoresistance and the constancy of the Hall coefficient the conclusion is drawn^[14] that in graphite in fields up to 160 kOe no freeze-out of carriers is observed, i.e., there are no bound states whose degree of ionization depends on the magnetic field.

It should be noted that all of the results set forth were obtained by different workers in samples of different quality and obtained by different means in narrow regions of magnetic field not above 160 kOe. It is of interest to carry out studies on the same samples over a wide range of fields where we can expect effects due to restructuring of the energy spectrum of graphite.

EXPERIMENTAL METHOD

In the present work we have studied the galvanomagnetic properties of graphite over a wide range of magnetic fields from a few oersteds up to 520 kOe. To obtain magnetic fields up to 300 Oe we used a solenoid wound of copper wire and placed in liquid nitrogen. Magnetic fields from 200 Oe to 40 kOe were produced by means of a superconducting solenoid. To obtain magnetic fields up to 520 kOe we used a pulsed apparatus.^[15] All of the measurements were made in a field perpendicular to the basal plane of the crystals, for which the magnetoresistance is greatest. To avoid contribution of thermal emfs and magnetoresistance to the Hall effect, the signal from each setup was recorded for two current directions through the sample (in the pulsed apparatus this is necessary also for compensation of induction) and for two directions of magnetic field.

The graphite samples were obtained by crystallization from a solution of carbon in iron, and then purified and annealed at 2000°C in a flux of chlorine. The perfection of the samples was monitored by x-ray structural analysis. Usually the samples had the form of plates of thickness $\sim 100 \mu$ and length several millimeters. The samples were cut with a razor to obtain the necessary dimensions. Particular difficulty was presented by the obtaining of sufficiently firm and electrically reliable contacts between the potential and current leads and the sample, which would withstand repeated cooling to helium temperatures and the mechanical stresses arising in the pulsed field.

The contacts were obtained by successive electrolytic deposition of layers of nickel and copper of thickness 0.5–1 μ , after which the potential and current leads were soldered to the upper copper layer with Wood's metal. To remove effects associated with the proximity of the current and potential electrodes, the current electrodes were soldered to the entire end surface of the samples. This means was used for samples of thickness 0.4 mm or greater. With smaller thicknesses such contacts are inadequately attached. In this case the contacts were simply covered with silver paste. With the first method the contacts obtained were significantly more durable and have less boundary resistance. The size of the sample and also the ratio of their resistances at 4.2 and 300 K are given in Table I.

TABLE I

Sample	Dimensions, mm				$\rho_{300 K} / \rho_{4.2 K}$	$\rho_{4.2 K} \cdot 10^4$ ohm-cm
	a	b	c	t		
№ 2–8	2.4	1.9	0.3	1.1	5.0	31.1
№ 2–9	2.26	2.24	9.0	—	—	—
№ 3–5	2.4	1.75	0.125	0.8	15.1	2.57
№ 4–8	2.3	1.65	0.11	0.9	16.9	2.17
№ 4–7	2.35	1.6	0.065	0.95	18.2	1.82

Note: a, b, and c are respectively the length, width, and height of the samples; t is the distance between the potential electrodes.

MAGNETORESISTANCE OF GRAPHITE AND HALL EFFECT

In Fig. 2 we have shown the resistivity $\Delta\rho/\rho_0$ of graphite as a function of magnetic field for a current directed along the basal plane of the sample. In fields up to several kilo-oersteds there are two quadratic dependences of $\Delta\rho/\rho_0$ on H, corresponding to the horizontal portions in the curves $\Delta\rho/\rho_0 H^2 = f(H)$ (Fig. 3), one of which (in fields up to 20 Oe) is due to the presence of minority carriers of small mass and high mobility, and the second is due to majority carriers.

In fields above several kilo-oersteds the quadratic dependence of the magnetoresistance goes over to a linear dependence which is preserved up to ≈ 150 kOe, which has been explained^[14] by a change in the screening radius of the scattering ionized impurity centers in the magnetic field. An estimate of the concentration n_S of impurity centers by means of Eq. (1) gives for the samples studied the following results: $n_S = 1.60 \times 10^{18} \text{ cm}^{-3}$ for sample No. 3–5, $n = 1.16 \times 10^{18} \text{ cm}^{-3}$ for sample No. 4–8, and $n_S = 0.96 \times 10^{18} \text{ cm}^{-3}$ for sample No. 4–7.

Above 150 kOe a strong deviation of the magnetoresistance from a linear law in the direction of saturation is observed, which can be explained by a rise in the concentration of current carriers in the ultraquantum limit

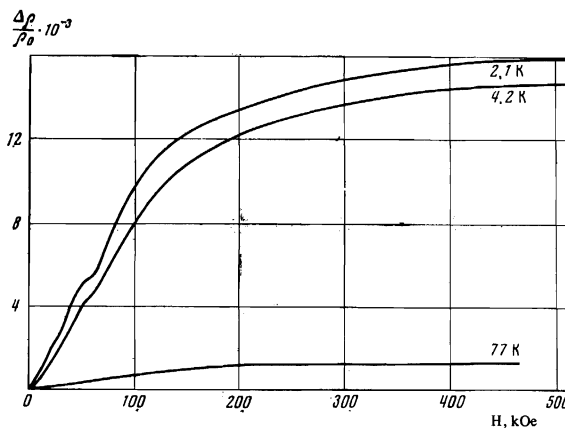


FIG. 2. Variation of resistivity of graphite in a magnetic field (sample No. 3-5).

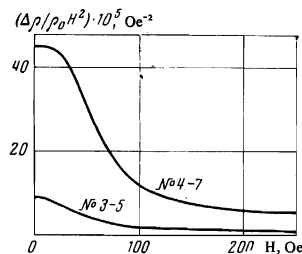


FIG. 3. Transverse magnetoresistance coefficient in graphite (samples No. 3-5 and 4-7) as a function of magnetic field. T = 4.2 K.

of the fields, due to an increase in the degree of degeneracy of levels with $n = 0$. Here it is necessary to take into account, however, that at the same time there occurs in the field a decrease in the overlap of the majority-carrier bands,^[16] which slows down the rise in concentration. Thus, for example, according to the data of McClure and Spry,^[14] in a field $H \approx 100$ kOe the concentration of electrons and holes rises by a factor of 2.3 in comparison with zero field. Such a large increase in concentration of carriers can result in a significant deviation of the function $\rho_{xx}(H)$ from linearity, in the direction of saturation.

We note that the existence of uncompensated carriers apparently cannot be the cause of saturation of the magnetoresistance. To estimate the effect of decompensation Δn we can use the equation^[17]

$$\rho = \rho_0 \left(\frac{H}{H_1} \right)^2 / \left[1 + \left(\frac{\Delta n}{n} \frac{H}{H_1} \right)^2 \right], \quad (2)$$

where $H_1 = m^*c/e\tau$, τ is the relaxation time, and n is the concentration of electrons or holes. It follows from Eq. (2) that $\rho_{\text{sat}} = \rho_0(n/\Delta n)^2$. As was pointed out above, in the ultraquantum region of fields the carrier concentration n increases. At the same time Δn , as will be shown below, begins to decrease rapidly in fields above 200 kOe as the result of the effect of magnetic freeze-out of the current carriers (see below, Figs. 7 and 9). Both of these effects lead to the result that in the region of fields greater than 100 kOe the factor $(n/\Delta n)^2$ decreases as a minimum by several hundred times, while the resistivity $\Delta\rho/\rho_0 \sim \rho/\rho_0$ in this region rises only by $\sim 50\%$.

In the monotonic portion of the magnetoresistance and Hall coefficient (Figs. 3 and 4) in fields up to 70 kOe, Shubnikov-de Haas quantum oscillations are observed, which are the superposition of oscillations of the two periods (majority holes and electrons). At 4.2 K the amplitude of the oscillations for $H \approx 30$ kOe is about 20% of the value of the magnetoresistance. When the temperature is reduced to 2.1 K, the amplitude rises by several tens of percent, which permits estimation of the mass of the majority carriers (Table II). The calculated periods and masses are in good agreement with the data of other studies.^[6, 8]

In investigation of the oscillations of magnetic susceptibility (the de Haas-van Alphen effect) an additional period is observed: $\Delta(H^{-1}) = (3.0 \pm 0.3) \times 10^{-4} \text{ Oe}^{-1}$, which is close to that found by Woollam^[10] and Soule^[11]. Further investigation showed that this period belongs to a section of the Fermi surface of minority electrons.

The Hall coefficient R in very weak magnetic fields (< 100 Oe) has a small positive value and rises rapidly with increasing field (Figs. 4 and 5). After a maximum at a field ≈ 100 Oe the Hall coefficient drops, and at a field $H_0 \approx 500$ Oe it goes to zero and then becomes negative and approaches saturation in fields of ≈ 50 kOe. Above 100 kOe a sharp drop in $|R|$ sets in, which continues over the entire range of fields.

TABLE II

Sample	Majority electrons		Majority holes		Minority carriers Period 10^{-4} Oe^{-1}
	Period 10^{-4} Oe^{-1}	m^*/m_0	Period 10^{-4} Oe^{-1}	m^*/m_0	
№ 3-5	0.147 ± 0.007	0.051 ± 0.005	0.224 ± 0.010	0.029 ± 0.005	—
№ 4-7	0.154 ± 0.007		0.223 ± 0.01		—
№ 2-8			0.230 ± 0.012		3.0 ± 0.3
№ 2-9	0.15		0.214		2.99 ± 0.3
[6, 8]	0.16	0.057	0.219	0.039	2.24

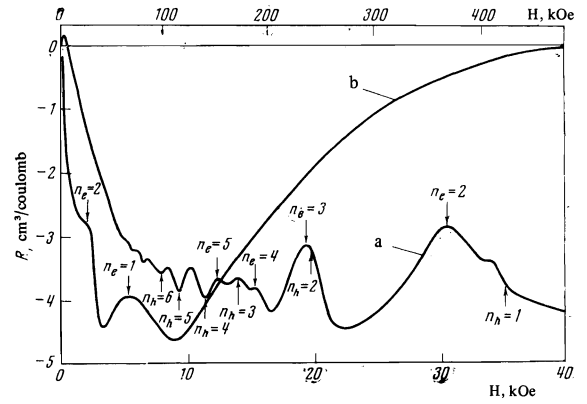


FIG. 4. Hall coefficient in graphite (sample 3-5) as a function of magnetic field at $T = 4.2$ K: a—up to 40 kOe; b—up to 500 kOe.

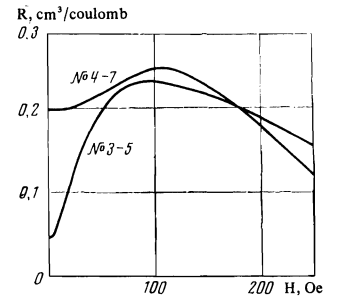


FIG. 5. Hall coefficient in graphite for two samples as a function of magnetic field, $T = 4.2$ K.

The positive sign of R in fields less than H_0 is explained by the higher mobility of the majority holes in comparison with the mobility of the majority electrons, and the transition to the negative region indicates an excess concentration of electrons, which follows from the equations of the two-band model in the limit of weak magnetic fields,

$$R = (n_h \mu_h^2 - n_e \mu_e^2) / c |e|.$$

CALCULATION OF CONCENTRATIONS AND MOBILITIES OF CARRIERS IN GRAPHITE

By solving the Boltzmann equation on the assumption that $\omega_i \tau_i$ is independent of energy (ω_i is the cyclotron frequency and τ_i is the relaxation time), it is possible to obtain^[4] expressions for the components of the magnetoconductivity tensor for N groups of carriers with charge e_i for a magnetic-field orientation $H \parallel z$:

$$\sigma_{xx} = \sum_{i=1}^N \frac{\sigma_{0i}}{1 + (H/H_i)^2}, \quad (3)$$

$$\sigma_{xy} = \sum_{i=1}^N \frac{\alpha_i n_i e_i c H / H_i^2}{1 + (H/H_i)^2}, \quad (4)$$

$$\sigma_{0i} = n_i e_i \mu_i = n_i e c / H_i, \quad (5)$$

$$H/H_i = \omega_i \tau_i; \quad (6)$$

here σ_{0i} is the conductivity in zero field associated with the i -th type of carrier; n_i and μ_i are the concentration and mobility of carriers of the i -th type; c is the velocity of light. The coefficient $\alpha_i \approx 1$ takes into account the difference between the mobilities entering into the conductivity σ and the Hall coefficient R .

Conversion from the experimentally determined quan-

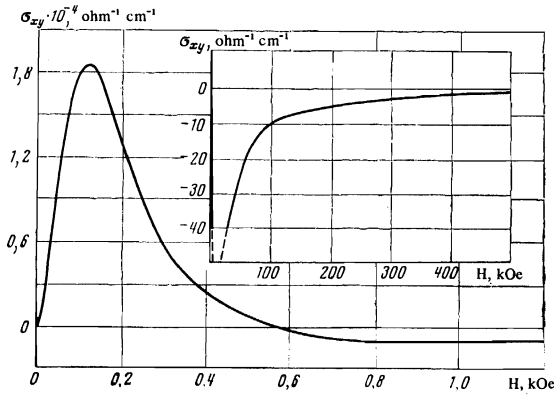


FIG. 6. Conductivity σ_{xy} in graphite (sample No. 3-5) as a function of magnetic field ($T = 4.2$ K), calculated from Eq. 8.

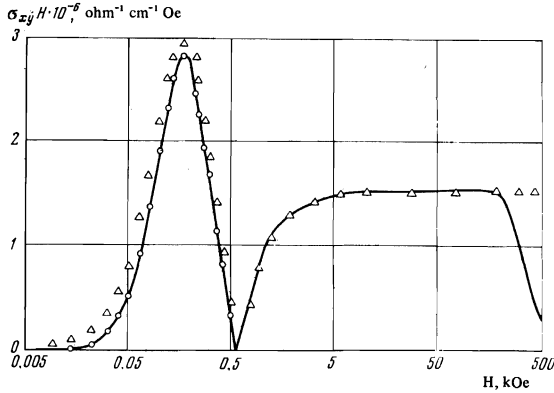


FIG. 7. The quantity $\sigma_{xy}H$ in graphite (sample No. 3-5) as a function of magnetic field; $T = 4.2$ K. Points: Δ —values of $\sigma_{xy}H$ calculated by computer according to the two-band model; \circ —according to the three-band model.

ties R and σ to the conductivity tensor components is given by the formulas ($H \parallel z$)

$$\sigma_{xx} = \sigma / [1 + (R\sigma H)^2], \quad \sigma_{xy} = \sigma R\sigma H / [1 + (R\sigma H)^2]. \quad (7)$$

Since the Hall coefficient in graphite is small and the tangent of the Hall angle is $R\sigma H < 0.2$ over the entire range of fields, Eq. (7) for $(R\sigma H)^2 \ll 1$ goes over to

$$\sigma_{xx} \approx \sigma, \quad \sigma_{xy} \approx \sigma R\sigma H. \quad (8)$$

In weak magnetic fields (Fig. 6) the conductivity $\sigma_{xy} > 0$ rises and then decreases, changes sign, passes through a minimum, and then in magnetic fields up to ~ 200 kOe $|\sigma_{xy}|$ decreases in proportion to $1/H$ (with an accuracy to several percent), which is easily visible in Fig. 7.

In the limit of strong fields $H_1 \gg c/\mu_1 \approx 0.2$ kOe, Eq. (4) takes the form

$$\sigma_{xy} = (n_h - n_e)ec/H, \quad (9)$$

so that the quantity $\sigma_{xy}H$ in fields above several kilosterds is determined only by the difference in concentrations $\Delta n = n_e - n_h$ of electrons and holes, which in the range of fields from 5 to 200 kOe remains constant (Fig. 7).

By means of Eqs. (3)–(5) and with experimental values of R and σ in the region of fields from 1 to 5 kOe (in which $\sigma \propto H^{-2}$), it is possible to calculate the concentrations and mobilities of the majority holes and electrons.

FIG. 8. Conductivity σ_{xy} in graphite (sample No. 3-5) as a function of magnetic field, $T = 4.2$ K. Points: Δ —values of σ_{xy} calculated by computer according to the two-band model, \circ —according to the three-band model.

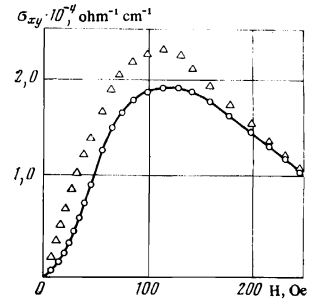


TABLE III

Characteristic	Samples				
	№ 3—5	№ 4—8	№ 4—7	Data of refs. 8, 11, and 12	
				$T = 77$ K	$T = 4.2$ K
$n_e \cdot 10^{-18} \text{ cm}^{-3}$	2.42	1.72	1.48	2.46	2.14
$n_h \cdot 10^{-18} \text{ cm}^{-3}$	2.32	1.68	1.46	2.39	2.08
$\mu_e \cdot 10^{-5} \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{sec}^{-1}$	4.61	8.24	9.1	0.49	5.91
$\mu_h \cdot 10^{-5} \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{sec}^{-1}$	5.66	8.64	10.2	0.65	6.45
$n_e' \cdot 10^{-16} \text{ cm}^{-3}$	2.25	—	1.73	0.87	—
$\mu_e' \cdot 10^{-5} \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{sec}^{-1}$	28.8	—	30.0	20.0	—
$n_e'' \cdot 10^{-18} \text{ cm}^{-3}$	0.85	0.60	0.49	—	—
$n_h'' \cdot 10^{-18} \text{ cm}^{-3}$	0.75	0.56	0.47	—	—

By introducing the ratios $a = n_h/n_e$ and $b = \mu_e/\mu_h$ and using the condition $\sigma_{xy} = 0$ at a field H_0 , the system of Eqs. (3)–(5) can be reduced to a single equation with two unknowns a and b :

$$\frac{\sigma_{xy}}{\sigma_0} = \frac{Hb(a-b^2)^{1/2}(1-a)^{1/2}(1-H^2/H_0^2)}{H_0(a+b)[b^2(1-a) + (a-b^2)H^2/H_0^2][(1-a) + (a-b^2)H^2/H_0^2]} \quad (10)$$

which was solved by the method of least squares in a computer. The concentrations and mobilities of electrons and holes are determined by the formulas

$$\mu_e = \frac{1}{H_0} \left(\frac{a-b^2}{1-a} \right)^{1/2}, \quad n_e = \frac{\sigma_0}{e\mu_h(a+b)}, \quad n_h = an_e, \quad \mu_h = \frac{\mu_e}{b}. \quad (11)$$

In Figs. 7 and 8 the triangles denote values of σ_{xy} and $\sigma_{xy}H$ corresponding to values of n_e , n_h , μ_e , and μ_h calculated on the basis of Eq. (11) by computer. The deviation of the points from the experimental curve in fields from 0.2 to 200 kOe does not exceed 5%, which is within the experimental error.

In fields $H < 200$ Oe a large deviation of the theoretical points from the experimental curve is observed, which is due to the presence of minority electrons not taken into account in the calculation. To determine their concentration n_e' and mobility μ_e' we made computer calculations for the case of three types of carriers:

$$\sigma_{xy} = \frac{n_e\mu_h^2H}{1+\mu_h^2H^2} - \frac{n_e'e\mu_e^2H}{1+\mu_e^2H^2} - \frac{n_e'e(\mu_e')^2H}{1+(\mu_e')^2H^2}. \quad (12)$$

This equation with two unknowns n_e' and μ_e' was solved also by the method of least squares. The values of the conductivity σ_{xy} calculated according to the three-band model are in good agreement with the experimental curve (Fig. 8, circles). In Table III we have given the concentrations and mobilities of majority and minority carriers calculated by computer from Eqs. (10)–(12) for the three samples, and also the concentrations of scattering ionized donors n_e^S and acceptors n_h^S which are easily determined from the total number of scattering centers $n_S = n_e^S + n_h^S$ and the decompensation $\Delta n = n_e - n_h = n_e^S - n_h^S$.

The results obtained in the different samples agree qualitatively, but it is of interest to compare them with

the degree of perfection of the samples studied. In Table I the three samples are arranged in order of increasing quality, as can be seen from the resistance values $\rho_{4.2K}$ at a field $H = 0$, the ratio $\rho_{300K}/\rho_{4.2K}$, the decompensation value Δn , and the concentration of scattering centers n_S . With increasing degree of imperfection of the sample, i.e., with increase of n_S , the concentrations of majority and minority electrons increase and the mobilities decrease. Here the values of the magnetoresistance coefficient $\Delta\rho/\rho_0 H^2$ and the Hall coefficient R behave as a function of field as follows: $\Delta\rho/\rho_0 H^2$ and R (for $H \rightarrow 0$) decrease (figs. 3 and 5), and the field H_0 increases. The maximum value of $R(H)$ (fig. 5) and the magnetic-field value corresponding to it decrease with increase of n_S , in agreement with the results of Hishiyama et al.^[8]

THE EFFECT OF A RAPID DECREASE IN THE COMPONENT σ_{xy} IN STRONG FIELDS

In magnetic fields $H > 200$ kOe the value of σ_{xy} and consequently also of $\Delta n \sim \sigma_{xy} H$ of the carrier decompensation (Fig. 9) begin to decrease sharply, which apparently can be explained by the effect of magnetic freezing of the current carriers. The phenomenon of magnetic freeze-out is well known to consist of the following: In a magnetic field, as the result of the increase in the binding energy E_B of the electron with the donor, the distance between the impurity level and the bottom of the conduction band increases, and consequently at temperatures $T \lesssim E_B$ the concentration n_e of electrons in the conduction band decreases as $\exp(-E_B/T)$. The theory of this phenomenon for semiconductors with an isotropic energy spectrum for the model of a hydrogen-like impurity center has been developed by Yafet et al.^[18] and von Ortenberg^[18] (the YKA theory) and has been generalized to the case of anisotropic isoenergy surfaces by Beneslavskiĭ et al.^[20]

In the effective-mass approximation at $H = 0$ for the isotropic model, the energy of the first level Ry^* and the first Bohr radius a_B^* are determined by the expressions

$$Ry^* = E_B(0) = \frac{m^* e^4}{2\kappa \hbar^2} = \frac{m^*}{m_0 \kappa^2} Ry, \quad (13)$$

$$a_B^* = \hbar^2 \kappa / m^* e^2 = (m_0 / m^*) \kappa a_B, \quad (14)$$

where m_0 and m^* are respectively the free-electron mass and the effective mass of the carriers in the conduction band, κ is the dielectric permittivity, $Ry = 13.6$ eV is the ground-state energy of the hydrogen atom, and $a_B = 5.29 \times 10^{-9}$ cm is the first Bohr radius of the hydrogen atom.

The YKA theory can be used in the presence of discrete impurity levels whose existence is defined by the condition $a_B^* \lesssim n_S^{-1/3}$ (n_S is the number of impurity centers per unit volume). In graphite for $H = 0$ the radius $a_B^* \approx 50$ – 100 Å and $n_S^{-1/3}$ ($n_S \approx 10^{18}$ cm $^{-3}$) are of the same order (in the optical region^[21] $\kappa = 4.1$ and in the infrared region^[22] $\kappa = 9$); $E_B(0) \approx 100$ K.

We will now take into account the effect of screening of impurities by current carriers, which was not considered in the YKA theory and which has a substantial value in graphite—a semimetal in which the total number of carriers is significantly greater than the impurity concentration. Screening of charged centers by conduction electrons leads to the result that bound states can be formed only for the condition $a_B^* < r_S$, where r_S is

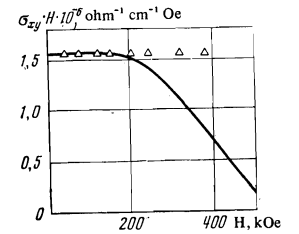


FIG. 9. The quantity $\sigma_{xy} H$ in graphite (sample No. 3-5) as a function of magnetic field; $T = 4.2$ K. Δ —values of $\sigma_{xy} H$ calculated according to the two-band model.

the screening radius determined from the condition

$$r_S = \left[\frac{\kappa \hbar^2}{4m^* e^2} n^{-1/3} \right]^{1/2} = \frac{1}{2} [a_B^* n^{-1/3}]^{1/2}. \quad (15)$$

In graphite $r_S \approx 40$ Å and the condition $a_B^* < r_S$ is not satisfied. Thus, in spite of the large binding energy and low temperatures, bound states apparently are not formed in zero field.

A magnetic field substantially changes the conditions necessary for occurrence of magnetic freeze-out: The effective Bohr radius changes (decreases) and the effective screening radius r_S^H decreases. As H increases the wave function ψ of the electron, which for $H = 0$ occupies a spherical volume of radius a_B^* , begins to be compressed in the plane perpendicular to the direction of H . Here the energy levels are substantially shifted. In strong fields ($\hbar\omega \gg Ry^*$) the transverse dimension of ψ is determined by the magnetic length

$$\lambda = (\hbar c / eH)^{1/2}, \quad (16)$$

and the longitudinal dimension by the quantity $a_B^* \ln^{-1}(a_B^* / \lambda)$, so that the volume occupied in space by the wave function ψ decreases with increasing H as $\lambda^2 a_B^* \ln^{-1}(a_B^* / \lambda)$. This can be interpreted as a decrease in some effective Bohr radius a_B^{eff} and an increase of the binding energy of the electron with the donor.

Allowance for the anisotropy of the Fermi surface^[20] has the result (for orientation of the magnetic field along the direction of prolateness, which occurs in graphite for $H \parallel z$) that a_B^{eff} decreases and E_B^{eff} increases in the field significantly more rapidly than in the isotropic case. Unfortunately, the theory^[20] is applicable only in the range of fields $H_{min} < H < H_{max}$ in which spherization of the wave function occurs. For graphite $H_{min} \approx 10$ Oe and $H_{max} \approx 10^3$ Oe, and the estimates on the basis of the theoretical formulas^[20] are incorrect, although we can suppose that the existence of anisotropy of the Fermi surface in graphite will result in a more rapid decrease of a_B^{eff} in a magnetic field.

The screening radius for a constant concentration n of current carriers decreases in a magnetic field,^[23] but at the present time there are no sufficiently reliable data on the magnitude of this effect. In graphite the dependence of r_S^H on H is weakened as the result of the decrease in carrier concentration (the amount of overlap of the bands in graphite decreases in a magnetic field^[24]), although the increase in r_S^H associated with this should be small (15). Apparently a significant increase in r_S^H can take place only for a very substantial change of n , which occurs only near the critical field value at which the overlap of the bands goes to zero.

Thus, it is at the present not possible to make a quantitative evaluation of the magnetic field at which magnetic freeze-out of electrons should occur in graphite, especially since, as far as we know, no experimental or theoretical studies on magnetic freeze-out in semimetals

exist at the present time. Since a decrease in decompensation of carriers in fields above 300 kOe occurs as the result of the decrease in electron concentration, it is quite likely that in the region of stronger magnetic fields the value of $\sigma_{xy}H$ should change sign (when n_H^S becomes greater than n_e^S). With further increase of field two effects are possible: magnetic freeze-out of holes, and an electronic transition from semimetal to semiconductor. Which of these effects sets in earlier is difficult to say. Preliminary estimates show that both of these effects should be observed in the region of fields up to 10^6 Oe.

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