GALVANOMAGNETIC EFFECTS IN GRAPHITE AND THE DEFORMATION OF THE ELECTRON SPECTRUM OF GRAPHITE UNDER PRESSURE

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A theory of the galvanomagnetic properties of graphite is developed and formulas are derived for the limiting case of high temperatures using the relaxation-time approximation and the energy spectrum of graphite obtained by Slonczewski and Weiss. An analysis of the experimental data on the temperature dependence of the resistance, Hall coefficient and magnetoresistance, ranging from room temperature to 150°C, yields a simple dependence of the relaxation time on temperature and on quasi-momentum. The combined quantity Q of Eq. (6.1) is independent of temperature and depends only on the energy spectrum parameters. Up to pressures of 10,000 atm Q remains independent of temperature, and this can be used to find the dependence of the energy spectrum parameters on the distance between the layers, using measurements of the resistance and galvanomagnetic coefficients as functions of pressure and temperature. Hence the deformation of the energy spectrum of graphite under pressure can be determined. At 10,000 atm the total number of carriers in graphite increases by 23%. At this pressure the relaxation time increases by 3%.

1. INTRODUCTION

USING the methods of group theory and perturbation theory, Slonczewski and Weiss[1] (see also [2]) described the band structure of graphite completely by means of a model with few parameters. Graphite is the only metal for which the band structure has been analyzed completely on the basis of general principles, and the experimental data are used not for empirical establishment of the energy spectrum (the Fermi surface) but only for the determination of its parameters.

On the assumption that a relaxation time exists, a theory of galvanomagnetic effects in graphite is developed in the present work. Comparison with the experimental data gives the form of the dependence of the relaxation time on temperature and quasi-momentum. The formulas obtained allow us to form combined quantities from the expressions for the galvanomagnetic effects, which depend only on the electron spectrum parameters. Investigation of the dependence of such quantities on hydrostatic pressure allows us to find the variation of these parameters with pressure.

2. ENERGY SPECTRUM OF GRAPHITE

Graphite has a layered hexagonal structure. Within a layer the atoms are distributed in hexagonal sites and are bound to one another by very strong covalent bonds. The distance between the atoms in a layer is 1.42 Å, and the lattice parameter is $a_0 = 2.46$ Å (elementary translation).[3] The layers are weakly bound to one another and the distance between them is 3.35 Å. In the adjacent layer the atoms are displaced so that the center of a hexagon lies above an atom of the lower layer. The period along the hexagonal axis c_0 is 6.70 Å.

The Brillouin zone of graphite is a six-sided prism with a base of side $2\pi/a_0$ and a height (edge) $2\pi/c_0$. Charge carriers occupy a narrow region near the Brillouin zone edges. The transverse dimensions of this region amount to about 1% of $2\pi/a_0$.

In the limit of vanishingly weak interaction between the layers the Fermi surface degenerates into a system of lines coinciding with the edges referred to above. The dependence of the energy on the quasi-momentum with components k_z and κ, which is the distance from an edge of the Brillouin zone, was given by Slonczewski and Weiss[1] by formulas which have sufficient accuracy for our purpose (see below):

$$E_1 = \Delta + 2\gamma_1 \cos\varphi + \hbar^2\varkappa^2/2m^*(\varphi), \quad (2.1)$$

$$E_2 = \Delta - 2\gamma_1 \cos\varphi - \hbar\varkappa^2/2m^*(\varphi), \quad (2.2)$$

$$E_{31} = 2\gamma_2 \cos^2\varphi + \hbar^2\varkappa^2/2m^*(\varphi), \quad (2.3)$$

$$E_{32} = 2\gamma_2 \cos^2\varphi - \hbar^2\varkappa^2/2m^*(\varphi), \qquad (2.4)$$

where $\varphi = k_z c_0/2$ and the effective mass is

$$m^*(\varphi) = {}^4/_3 (\hbar/a_0)^2 (\gamma_1/\gamma_0^2) \cos\varphi. \qquad (2.5)$$

Here γ_0 (2.8 eV) is a parameter of the two-dimensional model and represents the interaction of conduction electrons in the plane of the layer; γ_1 (0.27 eV) represents overlapping of the wave functions of neighboring nonequivalent layers, separated by a distance $c_0/2$ from one another; and γ_2 (0.02 eV) represents the interaction of equivalent layers, separated by a distance c_0 from one another. The quantity Δ is of the order of γ_2 and will not be included in our calculations. The quantity γ_0 is determined from the diamagnetic susceptibility, γ_1 from cyclotron resonance and the product $\gamma_1\gamma_2$ from the de Haas–van Alphen effect. (We shall use throughout the numerical values of the parameters given by McClure.[2])

The Fermi level (at nonzero temperatures, the chemical potential) η of graphite free of donor or acceptor impurities is found from the condition of electrical neutrality: the number of electrons N_- is equal to the number of holes N_+.

We shall consider in greater detail the calculation of integrals which determine the number of carriers, since the expressions given later for the galvanomagnetic properties have similar structure. The number of electrons and holes per unit volume, with allowance for the two spin orientations, is given by the formulas

$$N_- = \frac{1}{4\pi^3}\int f_0 d^3k, \qquad N_+ = \frac{1}{4\pi^3}\int (1 - f_0)\, d^3k. \qquad (2.6)$$

Here

$$f_0 = [\exp((E - \eta)/kT) + 1]^{-1}$$

is the Fermi distribution function, and $d^3k = dk_x dk_y dk_z$ is an element of volume in wave vector space.

Integration should be carried out for four branches of the energy spectrum (E_1, E_2, E_{31}, E_{32}). Essentially the energy branches E_1 and E_2 make an exponentially small contribution to the integrals in Eq. (2.6) when $\gamma_2 \ll \gamma_1$ and $\gamma_1 \gg kT$. Only in the region of the points $k_z = \pm\pi/c_0$, where $E_1 \approx E_2 \approx E_3$, are the effects of all the spectrum branches comparable; however, this region extends over a distance of the order of γ_2/γ_1; its contribution to the integral should be neglected within the accuracy accepted here.

In integrating along the branches E_{31} and E_{32} with allowance for the axial symmetry of our problem it is convenient to make the replacement

$$dk_x\, dk_y = 2\pi\varkappa d\varkappa = \pi d|\chi|,$$

where $\chi = \kappa^2$ in defined by Eq. (2.4):

$$\chi = \frac{8\gamma_1 \cos\varphi}{3a_0^2\gamma_0^2}(E - 2\gamma_2\cos^2\varphi), \qquad (2.7)$$

so that χ is positive for electrons (branch E_{31}) and negative for holes (branch E_{32}). Integrating Eq. (2.6) once by parts we obtain

$$N_{-,+} = -\frac{1}{4\pi^3}\int \chi \frac{\partial E}{\partial\chi}\frac{\partial f_0}{\partial E} d^3k, \qquad (2.8)$$

and the condition of electrical neutrality is written in the form

$$\int \chi \frac{\partial E}{\partial\chi}\frac{\partial f_0}{\partial E} d^3k = 0. \qquad (2.9)$$

Introducing the variable $\varphi = k_z c_0/2$, going over from integration with respect to χ to integration with respect to E, and extending the integration limits to infinity, we obtain in place of Eq. (2.9)

$$\int_0^{\pi/2} d\varphi \int_{-\infty}^{+\infty} \chi \frac{\partial f_0}{\partial E} dE = 0 \qquad (2.9a)$$

or, finally,

$$\int_0^{\pi/2} \cos\varphi\, d\varphi \int_{-\infty}^{+\infty} (E - 2\gamma_2\cos^2\varphi)\frac{\partial f_0}{\partial E} dE = \int_0^{\pi/2} \cos\varphi\,(\eta - 2\gamma_2\cos^2\varphi)\, d\varphi = 0. \qquad (2.9b)$$

Hence it follows that the chemical potential η is independent of temperature and equal to[1)]

$$\eta = {}^4/_3\gamma_2. \qquad (2.10)$$

Allowing for spatial degeneracy (two regions of carriers per unit cell of the reciprocal lattice) the total carrier density, $N = N_+ + N_-$, is found to be

$$N = -\frac{2}{\pi^2 c_0}\int_0^{\pi/2} d\varphi \int_{-\infty}^{+\infty} |\chi| \frac{\partial f_0}{\partial E} dE = -\frac{16\gamma_1}{3\pi^2 c_0 a_0^2 \gamma_0^2}\int_0^{\pi/2} \cos\varphi d\varphi \int_{-\infty}^{+\infty} |E - 2\gamma_2\cos^2\varphi| \frac{\partial f_0}{\partial E} dE. \qquad (2.8a)$$

The result for N can be conveniently represented as

$$N = N_0 w\left(\frac{T}{\gamma^2}\right), \qquad N_0 = \frac{128\,\gamma_1\gamma_2}{27\sqrt{3}\,\pi^2 c_0 a_0^2 \gamma_0^2} = 4.6\cdot 10^{18}\ \text{cm}^{-3}$$

where N_0 is the total carrier density at T = 0.

A plot of the function $w(T/\gamma_2)$ is given in Fig. 1. It is easy to obtain the asymptotic expansions for

[1)] If we use the nonapproximate electron spectrum, then terms of order γ_2^2/γ_1, $\gamma_2 kT/\gamma_1$, $(kT)^2/\gamma_1$ are added to Eq. (2.10).

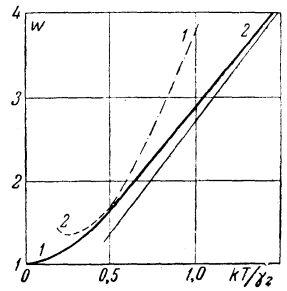

FIG. 1. Plot of the dependence of the quantity $w = (N_- + N_+)/(N_-^0 + N_+^0)$ on kT/γ_2. The thick line represents the function w(T); the dash-dot and dashed curves give its asymptotic expansions: 1) at low temperatures; 2) at high temperatures. The thin continuous line shows the dependence $2.70\ kT/\gamma_2$.

w(T) in the limits $T \to 0$ and $T \to \infty$ [2]:

$$w\,(T/\gamma_2)_{T\to 0} \to 1 + 2.77\,(kT/\gamma_2)^2,$$
$$w\,(T/\gamma_2)_{T\to\infty} \to 2.70\,kT/\gamma_2 + 0.173\,\gamma_2/kT.$$

Figure 1 shows that the asymptotic expressions do indeed determine the dependence w(T) for the whole range of temperatures. In particular at T = 300°K the total number of carriers is found to be $N = 16.8 \times 10^{18}\ cm^{-3}$. Figure 1 shows that the temperatures beginning from 150°K can be regarded as "high."

The Fermi surface shown in Fig. 2 has complex trigonal structure in the region of self-intersection.

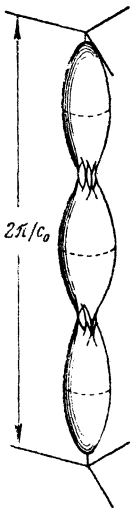

FIG. 2. Fermi surface of pure graphite. The central region contains holes, the two outer ones contain electrons.

Slonczewski and Weiss, by analyzing the complete spectrum which is more complex than that given by Eqs. (2.1)—(2.4), showed that this trigonal structure is governed by the parameter $\gamma_3 \approx 0.1$ eV. The corresponding correction $H_{33} \sim \gamma_1 \times (\gamma_3/\gamma_0)^2$ should be referred to the energy $\sim\gamma_2$. At the end of the present paper it is shown that $\gamma_2 \sim \gamma_1^2/\gamma_0$. Since $\gamma_3 \sim \gamma_1$, we obtain $H_{33}/\gamma_2 \sim \gamma_1/\gamma_0$. The contribution of this region to the integrated effects which are of interest to us will be neglected.

Here and later we shall also neglect the ratios γ_1/γ_0, γ_2/γ_1, kT/γ_1. They are all of the order of 10%. This is the error committed in replacing the exact energy spectrum with the expressions (2.1)—(2.4).

3. FORMULAS FOR THE GALVANOMAGNETIC EFFECTS

We shall use the solution of the carrier transport equation in the τ-approximation, assuming that it is possible to introduce an effective relaxation time which describes the interaction between carriers. As is known, the principal mechanism which determines the resistance at high temperatures is the scattering by phonons. At not too low temperatures the wave vector of the great majority of phonons is of the order of the reciprocal lattice period. Carriers which in the reciprocal lattice space occupy a narrow region with a cross section of $\sim 1\%$ of the distance between two separate carrier regions are removed from such a region by every collision with a phonon.

Qualitatively the situation is similar to that considered by Azbel' and Kaner [4] for the anomalous skin effect in a metal. Then the main contribution to the collision integral comes from the part related to the loss of carriers from a given point in phase space. In that case we can introduce a relaxation time depending on quasi-momentum and temperature [3]: $\tau = \tau(T, \mathbf{k})$. In general, the relaxation time thus introduced is a function of all three components of the wave vector. However, in graphite the carriers occupy only very narrow regions in phase space near the edges of the Brillouin zone. This makes it possible to expand the function τ near these edges and to confine the expansion to the first term with an accuracy $\sim \gamma_1\gamma_2/\gamma_0^2$. At sufficiently low carrier densities we can expect the converse effect of carriers on the phonon spectrum to be small and we can seek a function of the form $\tau = \tau(T, k_z) \equiv \tau(T, \varphi)$; the experimental data will be used below to consider the absence of singularities or zeros of κ in the function τ.

In the limit of a weak magnetic field (directed along the trigonal z axis) the following relationships apply to the conductivity tensor components:

[2] Here and later the expansion is taken actually in terms of the parameter $(2\gamma_2/3kT)^2$; at room temperature $(2\gamma_2/3kT)^2 \approx 0.25$.

[3] A more rigorous analysis of the collision integral is being carried out at present.

$$\sigma_{xx} = \sigma_0 - \beta H^2, \qquad \sigma_{xy} = \alpha H, \tag{3.1}$$

where

$$\sigma_0 = -\frac{e^2}{4\pi^3\hbar^2}\int \tau \left(\frac{\partial E}{\partial k_x}\right)^2 \frac{\partial f_0}{\partial E}\, d^3k,$$

$$\alpha = -\frac{e^3}{4\pi^3\hbar^4 c}\int \tau \frac{\partial E}{\partial k_x}\Omega_z\left(\tau \frac{\partial E}{\partial k_y}\right)\frac{\partial f_0}{\partial E}\, d^3k,$$

$$\beta = \frac{e^4}{4\pi^3\hbar^6 c^2}\int \tau \frac{\partial E}{\partial k_x}\Omega_z\left\{\tau\Omega_z\left(\tau \frac{\partial E}{\partial k_x}\right)\right\}\frac{\partial f_0}{\partial E}\, d^3k$$

$$= -\frac{e^4}{4\pi^3\hbar^6 c^2}\int \tau\left\{\Omega_z\left(\tau \frac{\partial E}{\partial k_x}\right)\right\}^2 \frac{\partial f_0}{\partial E}\, d^3k. \tag{3.2}$$

Here and later the z axis is directed along the trigonal axis, the x-axis coincides with the direction of the current, and the component of the operator Ω_z of interest to us is

$$\Omega_z = \frac{\partial E}{\partial k_x}\frac{\partial}{\partial k_y} - \frac{\partial E}{\partial k_y}\frac{\partial}{\partial k_x}. \tag{3.3}$$

The experimentally determined resistivity ρ_0, Hall coefficient R and magnetoresistance $\Delta\rho_H/\rho_0 = -\Delta\sigma_H/\sigma_H$, is in the limit of weak fields related to the components σ_{xx} and σ_{xy} by the relationships

$$\sigma = \frac{\sigma_{xx}^2 + \sigma_{xy}^2}{\sigma_{xx}} \approx \sigma_{xx} \approx \sigma_0, \qquad \rho_0 = \frac{1}{\sigma_0},$$

$$R \approx \frac{1}{H}\frac{\sigma_{xy}}{\sigma_{xx}^2} = \frac{\alpha}{\sigma_0^2}, \qquad \frac{\Delta\rho_H}{\rho_0 H^2} \approx \frac{(\beta\sigma_0 - \alpha^2)}{\sigma_0^2}. \tag{3.4}$$

Working as in the calculation of the number of carriers, we find for Eq. (3.2)

$$\sigma_0 = -\frac{3e^2 a_0^2 \gamma_0^2}{2c_0\pi^2\hbar^2\gamma_1}\int_0^{\pi/2}\int_{-\infty}^{+\infty}\frac{\tau}{\cos\varphi}|\chi|\frac{\partial f_0}{\partial E}\, dE\, d\varphi,$$

$$\alpha = \frac{9e^3 a_0^4 \gamma_0^4}{8c_0\pi^2\hbar^4 c\gamma_1^2}\int_0^{\pi/2}\int_{-\infty}^{+\infty}\left(\frac{\tau}{\cos\varphi}\right)^2 \chi\frac{\partial f_0}{\partial E}\, dE\, d\varphi,$$

$$\beta = -\frac{27\, e^4 a_0^6 \gamma_0^6}{32c_0\pi^2\hbar^6 c^2\gamma_1^3}\int_0^{\pi/2}\int_{-\infty}^{+\infty}\left(\frac{\tau}{\cos\varphi}\right)^3|\chi|\frac{\partial f_0}{\partial E}\, dE\, d\varphi. \tag{3.5}$$

4. RELAXATION TIME

Further specification of the form of the function τ can be obtained by using the experimental data on the galvanomagnetic effects. We seek τ in the form of the series

$$\tau = \sum_{n=0}^{\infty}\Theta_n(T)\Phi_n(\varphi), \tag{4.1}$$

where $\{\Phi_n(\varphi)\}$ is any complete system of functions with a period π in the interval $\varphi = \pm\pi/2$. Any term of this series substituted into Eq. (3.5) gives the following temperature dependence for high temperatures $kT \gg \gamma_2$:

$$\sigma_0 \sim \Theta_n(T)\, T\langle\Phi_n\rangle_\varphi, \qquad \beta \sim \Theta_n^3(T)\, T\langle\Phi_n^3\rangle_\varphi, \tag{4.2}$$

where $\langle\ \rangle_\varphi$ denotes averaging over $\varphi = k_z c_0/2$. Let us form a combined quantity

$$\Delta\rho_H/\rho_0 H^2\sigma_H^2 = (\beta\sigma_0 - \alpha^2)/\sigma_0^4 \approx \beta/\sigma_0^3. \tag{4.3}$$

Since the experimental data show that $\beta\sigma_0 \gg \alpha^2$, the substitution of Eq. (4.2) into Eq. (4.3) leads to a temperature dependence of the type $1/T^2$.

Figure 3 shows the quantity $Q = T\rho_0(\Delta\rho_H/\rho_0 H^2)^{1/2}_{H\to 0}$ as a function of temperature for different samples of natural graphite. The constancy of Q shows that the $1/T^2$ law is obeyed very accurately in rather a wide range of temperatures. If we take at least two terms from the expansion (4.1), for example the n-th and m-th terms, we arrive at the expression

$$\Delta\rho_H/\rho_0 H^2\sigma_H^2 = T\langle(\Theta_n\Phi_n + \Theta_m\Phi_m)^3\rangle/T^3\langle\Theta_n\Phi_n + \Theta_m\Phi_m\rangle^3. \tag{4.4}$$

It is easily seen that the coefficient of $1/T^2$ is constant only in the case when the functions $\Theta_n(T)$ and $\Theta_m(T)$ are proportional to each other.

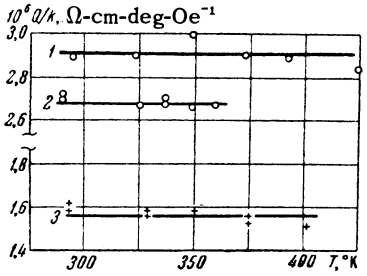

FIG. 3. Temperature dependence of the quantity Q: 1) sample Ts-12; 2) sample Z-11; 3) sample Z-6.

The relaxation time can thus be represented in the form

$$\tau = \Theta(T)\,\Phi(\varphi). \tag{4.5}$$

The formula for the Hall coefficient (3.5), with allowance for (4.5), leads to the dependence $R \sim 1/T^2$. However, the measured temperature dependence shown in Fig. 4 indicates that at high temperatures the Hall coefficient is almost independent of temperature and its absolute value is consider-

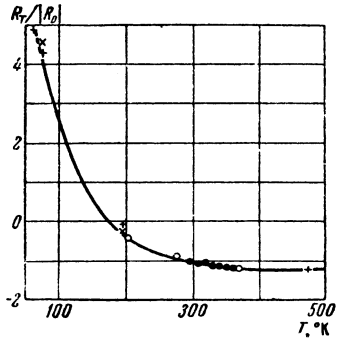

FIG. 4. Temperature dependence of the relative Hall coefficient: +, × – Kinchin's results,[7] ○, ● – our samples.

ably smaller than the value at low temperatures. This forces us to assume that in the approximation considered the Hall coefficient is in general zero and its nonzero value is related to the influence of the rejected terms of order kT/γ_1 and γ_2/γ_1. At present it is not possible to allow for these terms since their calculation would require consideration of the contribution of the energy spectrum branches E_1 and E_2 and consideration of the dependence of τ on κ.

The zero value of the Hall coefficient in our approximation means that the integral in the expression of Eq. (3.5) for α should vanish. The integrand in that integral is the integrand of Eq. (2.9a) multiplied by $(\tau/\cos\varphi)^2$. We can therefore assume that $\tau/\cos\varphi$ is a constant and the anomalously small value of the Hall coefficient is due to the specific relation

$$\tau = \Theta(T)\cos(k_z c_0/2). \qquad (4.6)$$

5. FORMULAS FOR THE GALVANOMAGNETIC EFFECTS

The relaxation time obtained in the form of Eq. (4.6) for the one-phonon interaction allows us in principle to expand the general formulas (3.4)—(3.5).

In the limit of high temperatures $kT \gg \gamma_2$ we obtain the following asymptotic formulas:

$$\sigma_0 = \frac{8\ln 2\cdot e^2\Theta(T)\,kT}{c_0\hbar^2\pi^2}\left\{1 + O\left(\frac{\gamma_2}{\gamma_1}, \left(\frac{\gamma_2}{kT}\right)^2\right)\right\}, \qquad (5.1)$$

$$\alpha \approx O\left(\frac{\gamma_2}{\gamma_1}, \left(\frac{\gamma_2}{kT}\right)^2\right), \qquad (5.2)$$

$$\beta = \frac{9\ln 2\cdot e^4 a_0^4\gamma_0^4\Theta^3(T)\,kT}{2c_0c^2\pi^2\hbar^6\gamma_1^2}\left\{1 + O\left(\frac{\gamma_2}{\gamma_1}, \left(\frac{\gamma_2}{kT}\right)^2\right)\right\}. \qquad (5.3)$$

In fact the expansion is in terms of $(\gamma_2/kT)^2$ with numerical coefficients. Thus for example for σ_0 the quantity $O(\gamma_2/kT)^2 \approx \gamma_2^2/15(kT)^2$.

The corresponding correction is smaller than the expected inaccuracy of the formulas ($\approx 10\%$). In the temperature region of the order of (and much less than) the degeneracy temperature the one-phonon process is obviously not the only one. As shown by studies at high pressure, considerable hysteresis occurs in the region of nitrogen temperatures. This indicates the considerable importance of scattering by crystal structure defects. Consequently when $kT \ll \gamma_2$ the mechanism of scattering by defects may be the main one. The theoretical formulas obtained for low temperatures will be published later by the present authors, together with the experimental data.

6. RESULTS OF MEASUREMENTS

Measurements of the galvanomagnetic coefficients of graphite under pressures of up to 10,000 atm and at temperatures up to +90°C were carried out using a method similar to that described earlier.[5] At the same time the temperature dependence of the coefficients was obtained up to +150°C at atmospheric pressure.

Since it is not possible to obtain good single crystals of graphite (whether natural or synthetic), we used flakes (platelets) of Ceylon graphite and of graphite from the Zaval'ev deposit in the Ukraine. X-ray investigation of these flakes showed that they consist of crystallites whose hexagonal axes make a small angle with the normal to the plane of the sample. Since the properties of graphite samples (or at any rate the properties governed by the majority carriers) depend only on the direction with respect to the hexagonal axis, measurements in the plane of the flakes give values of the resistance, Hall emf and magnetoresistance which do not differ from the values for single crystals.

The purity of the samples was judged from their resistivity at room temperature ρ_0. This criterion was used to select the flakes. In the case of flakes available to the authors ρ_0 ranged from 6×10^{-5} to 12×10^{-5} Ω-cm and only one flake of the Zaval'ev graphite (sample Z-6) had $\rho_0 = 3.8 \times 10^{-5}$ Ω-cm, which is in agreement with the ρ_0 values of the best single crystals of Soule.[6] The other flakes investigated Ts-12 and Z-11 had ρ values of 7.8×10^{-5} and 6.7×10^{-5} Ω-cm, respectively. In spite of the differences of ρ_0, the temperature dependence of the resistance, of the Hall emf and of the magnetoresistance was the same for all the flakes. In our analysis we also used the data of Kinchin[7] on the temperature dependence of the Hall coefficient of single-crystal graphite and the very good results of Soule[6] on the galvanomagnetic effects in graphite at 300, 77.3, and 4.2°K.

A. Results of Measurements at Atmospheric Pressure. The resistance in a magnetic field was measured in fields up to 5000 Oe, and the value of the coefficient $\Delta\rho_H/\rho_0 H^2$ was extrapolated to $H = 0$. Then for each sample we calculated the quantity

$$Q = T\rho_0\left(\frac{\Delta\rho_H}{\rho_0 H^2}\right)^{1/2}_{H\to 0} = \frac{3c_0\pi^2\,a_0^2\gamma_0^2}{32\ln 2\cdot ec\gamma_1}. \qquad (6.1)$$

As pointed out earlier (Fig. 3), at atmospheric pressure the quantity Q is indeed independent of temperature.

From the value for the best graphite sample (Z-6) we find the ratio $\gamma_0^2/\gamma_1 = 36$ eV. If McClure's parameters[2] are used we obtain 29 eV. The difference amounts to about 20%, which is within the limits of the expected error in the theory developed here. The latest results of an analysis of the data on cyclotron resonance[8] give $\gamma_0^2/\gamma_1 = 31$ eV. This agreement indicates the absence of marked singularities of κ in the function $\tau(\mathbf{k})$. The presence of a singularity in the form of κ^S would have led to quite a different numerical coefficient without altering the temperature dependence Q(T).

The temperature dependence of Θ is determined from the temperature dependence of the quantity $(\Delta\rho_H/\rho_0 H^2)_{H\to 0}$. Figure 5 shows the dependence on a double logarithmic scale for the sample Ts-12 at atmospheric pressure (curve 1). It follows the empirical law that $\Theta \sim T^{-3/2}$. The same temperature dependence is obtained, with a slightly different value of the numerical coefficient, from the temperature dependence of the electrical resistance of the test samples of graphite. Thus for sample Z-6 at room temperature we find that $\Theta = 3.2 \times 10^{-13}$ sec from the electrical resistance data and 4.1×10^{-13} sec from the magnetoresistance.

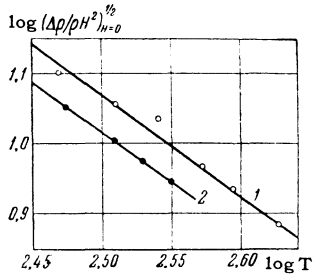

FIG. 5. Temperature dependence of the quantity $(\Delta\rho_H/\rho_0 H^2)^{1/2}_{H\to 0}$ in logarithmic coordinates: 1) p = 1 atm; 2) p = 8800 atm.

B. Results of Measurements Under Hydrostatic Pressure. Figure 6 shows the temperature dependence of the Hall coefficient at 1500 and 8800 atm. The nature of the temperature dependence of the Hall coefficient is not altered by pressure and the coefficient remains small.

Under high pressure the quantity Q is also independent of the temperature. Figure 7 shows the dependence of Q on pressure for samples Z-11 and Z-6(b). It is seen that the values of Q for different temperatures lie on the same Q(p) curve within the limits of experimental scatter. The relative change of Q with pressure gives directly the pressure dependence of the combined quantity $c_0 a_0^2 \gamma_0^2/\gamma_1$.

From x-ray measurements of the compressibility of graphite, carried out by Vereshchagin and Kabalkina,[9] it is known that the deformation of

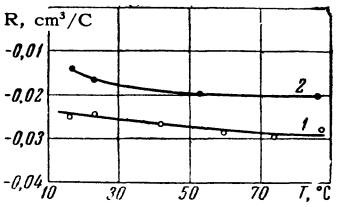

FIG. 6. Temperature dependence of the Hall coefficient: 1) p = 1500 atm; 2) p = 8800 atm.

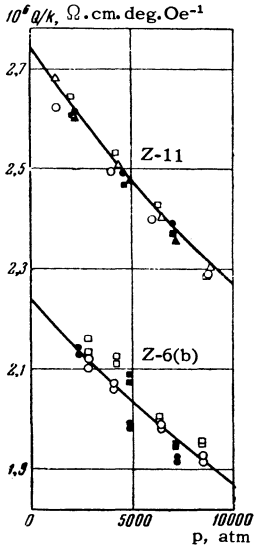

FIG. 7. Pressure dependence of Q. Sample Z-11: ○, ● – T = 292.4°K; △, ▲ – T = 336.1°K; □, ■ – T = 354.9° K. Sample Z-6(b): ■, □ – T = 293.0° K; ●, ○ – T = 353.2°K. The open symbols represent points for rising pressure, the black symbols represent decreasing pressure.

the lattice in the plane of a layer (variation of a_0) is negligible, and the variation of the distance c_0 between the layers is

$$-\Delta c_p/c_0 = 28\cdot 10^{-7} p - 45\cdot 10^{-12} p^2$$

where p is in atm. Therefore, we may assume that a_0 and γ_0 are independent of pressure and we can find the dependence of γ_1 on c_0.

Since the small parameters γ_1 and γ_2 appear as a result of overlapping of the layer functions, which decrease exponentially at large distances, their dependence on the distance between the layers should obey the law

$$\gamma_1 \sim \gamma^* \exp(-c_0/a^*),\ \gamma_2 \sim \gamma^* \exp(-2c_0/a^*)$$

with the same parameter a*, which is of the order of the distance between the carbon atoms in a layer, and a coefficient γ^* of the order of γ_0. The parameter a* is calculated from the pressure dependence of Q (Fig. 7); it is 0.98 Å. Knowing a* we can calculate the pressure dependences of γ_2, the Fermi energy and carrier density. We have

p, atm :	1	10 000
γ_1, eV :	0.27	0,32
γ_2, eV :	0,020	0,028
η, eV :	0,027	0,037
N (at 300°K), cm^{-3}:	$16,8\cdot 10^{18}$	$21\cdot 10^{18}$

According to Eq. (5.1) the electron spectrum parameters disappear from the expression for

the electrical conductivity σ_0 of graphite at "high" temperatures and σ_0 depends only on the relaxation time. From measurements of the pressure dependence of the electrical conductivity of graphite at high temperatures it follows that the relaxation time increases by 3% at a pressure of 10,000 atm. As expected, the change in the phonon spectrum is of the order of the change in the elastic constants and much smaller than the change of the electron spectrum parameters.

7. CONCLUSIONS

On the basis of the theory developed here it has been possible to explain the influence of the electron spectrum parameters on the integrated characteristics of graphite: its galvanomagnetic properties. This made it possible to separate the effects related to the lattice (the relaxation time) and to the conduction electrons. Measurement of the galvanomagnetic effects gives satisfactory accuracy and is technically much simpler than the use of cyclotron resonance, de Haas–van Alphen effect, absorption of ultrasound and other standard methods of determining the energy spectrum. Because of the characteristics of the electron spectrum of graphite the pressure dependence (the dependence on the distance between the layers) of the parameters in the Slonczewski and Weiss model is governed by a single constant a*. Measurement of the galvanomagnetic effects of graphite at low temperatures would make it possible to determine independently the variation with pressure of other energy spectrum parameters apart from γ_1.

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