the Introduction, the recent work by Hoare and Matthews[5] suggests that, for a given chemical composition, a simple crystal structure may be expected to correspond to a lower electronic specific heat coefficient than a complex one. The present results appear to support this conclusion.

The reason for the large difference between the electronic specific heat coefficients for two face-centered-cubic alloys, one consisting of Fe+11% Mn+0.5% C[6] and the other the Fe+45% Mn alloy used in the present work, is not very clear. According to Goldman,[14] it is possible that the density of state *vs* energy curve has a very irregular shape in the region concerned, and that the difference is largely due to the increased filling up of the *3d* shell with increased Mn content. A possible alternative explanation might be that the very high value observed for their alloy by Goldman and Guthrie[6] is somehow connected with the carbon content of their alloy. No definite conclusions may be drawn at the present time as to these alternative interpretations.

[14] J. E. Goldman (private communication).

ACKNOWLEDGMENTS

The authors wish to thank Professor Dillon E. Mapother and Mr. F. A. Otto of the Department of Physics, University of Illinois, and Dr. J. K. Hulm of the Westinghouse Research Laboratories and Dr. N. Pearlman of the Department of Physics, Purdue University for their very valuable advice regarding the design of the calorimetric equipment and of the cryostat. Dr. Yuan-Shin Chow, of the University of Illinois, has kindly worked out the program for the necessary calculations with the Illiac Digital Computer.

PHYSICAL REVIEW VOLUME 112, NUMBER 3 NOVEMBER 1, 1958

Magnetic Field Dependence of the Hall Effect and Magnetoresistance in Graphite Single Crystals

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(Received June 30, 1958)

The Hall coefficient and magnetoresistance in purified (99.995%) natural graphite single crystals have been measured from 25 to 25 000 gauss at 298°, 77°, and 4.2°K with the field oriented parallel to the hexagonal axis. Special care was taken in the micromanipulation and strain-free mounting of these small soft crystals. Fast minority carriers due to Fermi-surface warping were discovered by their effect on the low-field Hall coefficient behavior. The compensating effect between the majority electron and hole densities [$(5-2)\times10^{18}$ cm^{-3} with $n_e/n_h=1.0-1.15$ over the above temperature range] and mobilities [$(1.5-130)\times10^4$ cm^2/v sec with $\mu_e/\mu_h=1.10-0.79$] makes the Hall coefficient very sensitive to the temperature, impurities, and field where it even changes sign. A quadratic low-field room-temperature magnetoresistance dependence progresses at higher fields to an impurity-insensitive $H^{1.78}$ behavior. The large magnetoresistance ratio of graphite ($\sim10^5$ at 4.2°K and 23 kilogauss), along with the appearance of de Haas-van Alphen type oscillations in these properties, demonstrates the small effective masses ($0.03m_0$, $0.06m_0$) and long relaxation times (2.5×10^{-11} sec at 4.2°K). The mobility follows a $T^{-1.2}$ law in the lattice-scattering region $\gtrsim$50°K. Low-temperature results, showing carrier density differences and mobilities to be most sensitive to impurities, substantiate the relatively high purity of these crystals.

I. INTRODUCTION

KINCHIN'S pioneering work[1] revealed a remarkable field dependence of the Hall effect in the semimetal graphite. The strong variation in the Hall coefficient, R, included a change in sign at 77°K in addition to showing a sharp minimum in the region of liquid hydrogen and below. Such a variation is partly due to the close balance of electron and hole concentrations and mobilities, producing a small R that is very sensitive to a slight shift of the Fermi level. Accompanying effects are caused by the very large mobilities in the basal plane of this essentially two-dimensional highly anisotropic material. Its tremendous magnetoresistance[1,2] is consistent with the extreme anisotropy in its zero-field resistivity.[3–5] Verification of the small effective masses for carriers travelling in the basal plane has been substantiated by the observation of de Haas–van Alphen type galvanomagnetic oscillations by Berlincourt and Steele[2] which they have correlated with those found in the susceptibility.[6]

The graphite crystals heretofore investigated were all of a natural origin being, in general, quite impure and

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highly twinned. They are usually found in the form of small soft platelets that are difficult to handle without introducing strains. Measurements have been restricted to natural crystals due to the formidable problem of growing good reasonably-sized single crystals. This is partially due to the fact that graphite liquefies only under pressures greater than 100 atmos at temperatures of the order of 4000°C. As a result, very little work has been done on single crystals of this material. Consequently, the first major problem of the present work has been to improve and maintain crystal quality. This has been accomplished by first selecting the best of natural crystals, by careful handling, by purification, and finally by developing an essentially strain-free mounting for measurements.

This investigation was undertaken to extend the limited range of previous measurements on both the Hall effect and the magnetoresistance. In particular, a second point of emphasis is made here on the low-field behavior, magnetoresistance measurements having been taken down to 100 gauss and Hall measurements to 25 gauss where evidence of new, highly mobile minority carriers was discovered.[7] It is interesting to note that an analogous situation has been reported for p-type germanium,[8,9] and recently for p-type InSb[10] where fast holes cause a similar behavior in the Hall coefficient. In addition, the low-field magnetoresistance and zero-field resistivity have been employed to give average mobility temperature dependencies in the lattice and impurity scattering ranges. Finally, a correlation between several of these results has been made as a function of residual impurity content to determine the effect upon relative mobility and carrier density behaviors. Also, some information was obtained about the impurities themselves.

A third principal aim of this investigation has been to study low-temperature, relatively high-field behavior. A correlation of the results determined from the extremes can thereby be made. Accordingly, measurements were extended to 25 kilogauss over the temperature range down to 4.2°K. For purposes a clarity in discussion, the subject will be treated in two parts: the present paper covering low-field and general non-oscillatory behavior dominant primarily at the higher temperatures and the following paper[11] giving an analysis of the de Haas–van Alphen type oscillations, a low-temperature, essentially high-field effect.

II. SAMPLE PREPARATION AND MOUNTING

The graphite crystals used in these experiments came from Essex County, New York. These were chosen after inspecting crystals from many sources. In the natural form, they were embedded in a calcite matrix that was subsequently dissolved away with hydrochloric acid. Out of many hundreds of crystals so isolated, a few almost perfect ones were found, as determined by visual observations and x-ray analysis. These were small platelets ranging from 1 to 3 mm in diameter by 0.1 to 0.2 mm in thickness. Since the utmost care had to be exercised in their handling, tweezers could not be used; but rather, the crystals were transported and manipulated by adhesion to a fine damp camel-hair brush. Most of the work involved microtechniques that were developed utilizing micromanipulators in conjunction with a stereoscopic microscope.

The crystals were purified and annealed by heating to 3000°C in a stream of chlorine. This process reduced the impurity concentration producing a resultant crystal purity of better than 99.995%.

In order to cut a crystal into an appropriate shape for measurements, it was first potted in an epoxy resin that had essentially negligible linear shrinkage, $<0.05\%$, upon hardening. A steel mask having the desired shape of the crystal was embedded in the resin slightly above the sample. The exposed portions of the crystal were then slowly etched away by means of a small dental sand-blast unit.

Orientation of a sample was accomplished by making use of the (111) double-twin striations that appeared on the surface of the crystal which are oriented perpendicular to the a axes. A crystal would be picked where these striations appeared only near the edges so that they could serve as a means of orientation and still not be included in the final cut crystal. The twin planes were originally identified by a measurement of the angles between striations on the basal plane and angle of tilt of the striation planes up from the basal plane. The angles measured on many samples were $60.0\pm0.8°$ for the former and $20.3\pm1.2°$ for the latter compared to those calculated for a (111) twin of 60° and 20.8°, respectively. This identification is in agreement with that reported by Palache.[12] In most cases the crystals were oriented so that the current passed along the a axis, though it turned out that this had no apparent effect on the present measurements. There was perfect orientation of the plane of the sample with that of the basal plane, of course, due to the natural morphology of the crystal.

A sample mounting consisted initially of 0.003-in. phosphor-bronze lead wires anchored to a fused-quartz plate. These were soldered simultaneously to the five copper-plated tips of the crystal "ears" with Cerralow (117°F) solder using a small hot stage. The result was that the crystal was entirely supported by the lead wires. Consequently, there was negligible strain on the sample throughout the temperature range from room temperature down to 4.2°K. A typical sample mounting

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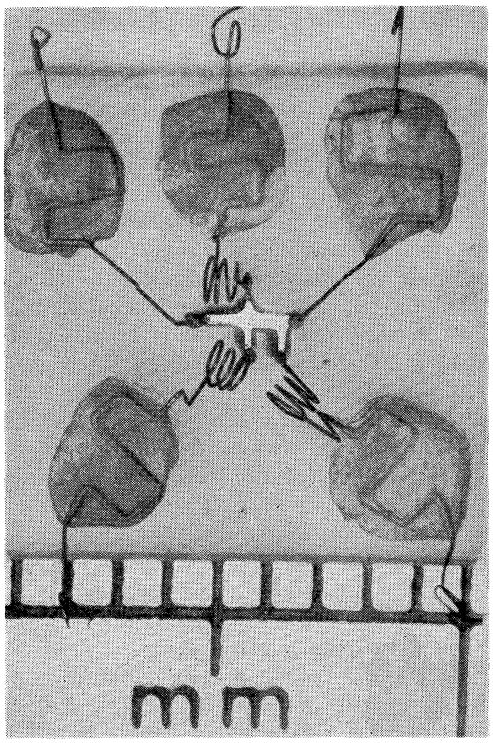

FIG. 1. Mounting of graphite single crystal, EP-14, for galvanomagnetic measurements. Auxiliary lighting shows the high metallic reflectivity of the basal plane.

(EP-14) is shown in Fig. 1. Note that only the noncurrent carrying probes (potentiometric method of measurement) could be coiled to minimize mechanical strain. The current electrodes, on the other hand, were not coiled so as to avoid strain due to interacting magnetic fields.

III. EXPERIMENTAL PROCEDURE

Conventional dc methods utilizing both directions of the electric and magnetic fields were used to measure the Hall voltage and the voltage drop due to the magnetoresistance. A Leeds and Northrup K-2 potentiometer was generally employed, though at the higher magnetic fields the Leeds and Northrup indicating microvolt dc amplifier could alternatively be used. A constant current technique was employed using a current usually of 10 ma as determined to within 0.5%. All samples were ohmic.

The magnetic field, which was homogeneous within 0.006% over the length of a sample ($\lesssim$3 mm), was supplied by a Varian 12-in. electromagnet. The orientation of the sample in the magnetic field was accomplished by employing its magnetoresistance maximum as the criterion for alignment. All measurements were made with the hexagonal c axis parallel to H. A modified Rawson rotating-coil fluxmeter, used in conjunction with a Ballantine 300 vacuum-tube voltmeter and calibrated against a proton resonance standard, was employed to monitor the field. With this arrangement a magnetic field measurement could be made with an accuracy within 1% and with a precision within 0.3% throughout the field range of 25 gauss to 26 000 gauss. At the lowest fields, however, the contribution of the earth's field ($\lesssim$0.8 gauss) produced an additional error of $\lesssim$3%.

The samples were maintained isothermal by direct immersion in the coolant. This condition combined with the projecting Hall "ears" of the sample and the high thermal conductivity along the basal planes of graphite made any possible contribution of the Ettinghausen effect negligible. Stray thermal emf's were minimized by employing lead wires made of copper thermocouple wire which extended in single continuous lengths from the sample to the measuring apparatus. On the potentiometer side of the circuit, thermocouple wire was used with adjacent cut ends connected at a given terminal pair. This in turn was maintained approximately isothermal by means of Styrofoam covers. A thermal-free reversing switch was also used. With this arrangement, the total measured thermal emf could be kept to $\lesssim$0.2 microvolt.

At low magnetic fields (25 to $\sim$2000 gauss) a technique was used in which, in addition to the above precautions, measurements were taken as a function of current (10 to 120 ma) at each magnetic field point to resolve zero errors. With this method, the error in R could be kept to $\leq$1% in general, except at the very lowest fields where the value might be off by as much as 5% due to the earth's field.

It was difficult to measure the absolute value of the zero-field resistivity, ρ_0, to better than 5% due to the sample shape and width of the probes. It was measured by making a potential distribution determination from conducting paper cut to the sample shape. Another check was made by probing a sample itself using electrolytically etched tungsten probes operated by micromanipulators. This method, however, was used only after all other measurements were taken because of possible damage to the sample produced by the probes.

Because of the "bridge cut" sample shape shown in Fig. 1, it was feared that the probe nearest to the current electrode might distort the equipotential lines to give an inaccurate magnetoresistance measurement. This was checked by noting upon reversal of the magnetic field that in all cases the measured voltages were not significantly different.

IV. RESULTS AND DISCUSSION

A. General Hall Effect Field Dependence

The general behavior of the Hall coefficient, R, with respect to the magnetic field up to 25 kilogauss at the temperatures 298°, 77°, and 4.2°K is shown in Fig. 2. At large H, R is always negative showing that $n_e > n_h$ throughout the measured temperature range. For small

H, R is positive at 77° and 4.2°K resulting from the fact that $\mu_e<\mu_h$. It is negative at room temperature in the field region where it would normally go positive due to majority holes if the above inequality were operative, thus indicating that the mobility ratio has reversed changing to $\mu_e>\mu_h$.

The field dependence of R is approximately linear for larger fields at $T\gtrsim 77$°K and for $H<10$ kilogauss at 4.2°K. Its temperature variation in this linear region is also linear as determined between 8 to 10 kilogauss. This behavior is entirely different from that observed previously by Kinchin and by Berlincourt and Steele where $|-R|$ decreased with H in the high-field region producing a minimum at about 1 to 2 kilogauss.

A study of the above behavior can be made by considering R as a function of the appropriate components of the magnetoconductivity tensor[13,14] which for the case of the electric field in the X direction and H in the Z direction is

$$R=\frac{1}{H}\left(\frac{\sigma_{xy}}{\sigma_{xx}^2+\sigma_{xy}^2}\right), \tag{1}$$

where σ_{xx} and σ_{xy} are the tensor components of the conductivity and are given by

$$\sigma_{xx}=\sum_{i=1}^{N}\frac{\sigma_{0_i}}{1+(H/H_{si})^2}=\frac{\sigma}{1+(R\sigma H)^2}, \tag{2}$$

$$\sigma_{xy}=\sum_{i=1}^{N}\frac{n_i e_i cH/H_{si}^2}{1+(H/H_{si})^2}=\frac{\sigma(R\sigma H)}{1+(R\sigma H)^2}; \tag{3}$$

the latter forms are evaluated directly from the measurements, σ being the conductivity. The summation is taken over N different types of carrier, n_i and e_i are their respective number densities and electronic charges, and σ_{0_i} are the zero-field conductivities. The saturation fields, H_{si}, are related to the mobilities, μ_i', as defined by

$$H_{si}\equiv cm_i^*/e\tau_i\equiv c/\mu_i', \tag{4}$$

where the effective masses, m_i^*, and the relaxation times, τ_i, are averages appropriate to the condition $\omega_i\tau_i=1$, ω_i being the cyclotron frequencies. It is to be understood that H_s represents the effective saturation field since there is actually a distribution of relaxation times and effective masses. The relation of μ' to the Hall mobility, μ_H, and the conductivity mobility, μ_c, is given by

$$\mu'=(\mu_H\mu_c)^{\frac{1}{2}}. \tag{5}$$

In Eqs. (2) and (3), only the first term of a summation over the Fourier harmonics that account for the anisotropy has been used in the present special case. For this particular orientation of H, parallel to the hexagonal axis, the carrier path lies in the basal plane which for graphite has effectively two-dimensional isotropy.

For very high magnetic fields where $R\sigma H\gg 1$, Eq. (3) for the majority carriers reduces to

$$R=1/c|e|\,(n_h-n_e), \tag{6}$$

where n_e and n_h are the majority electron and hole densities, respectively. For a two-carrier system like graphite, this approximation turns out to be a stringent one since $n_e\mu_e\simeq n_h\mu_h$ causing R to remain small even out to high fields. For EP-14 at 4.2°K, $R\sigma H$ goes only to a value of -0.44 at 24 kilogauss.

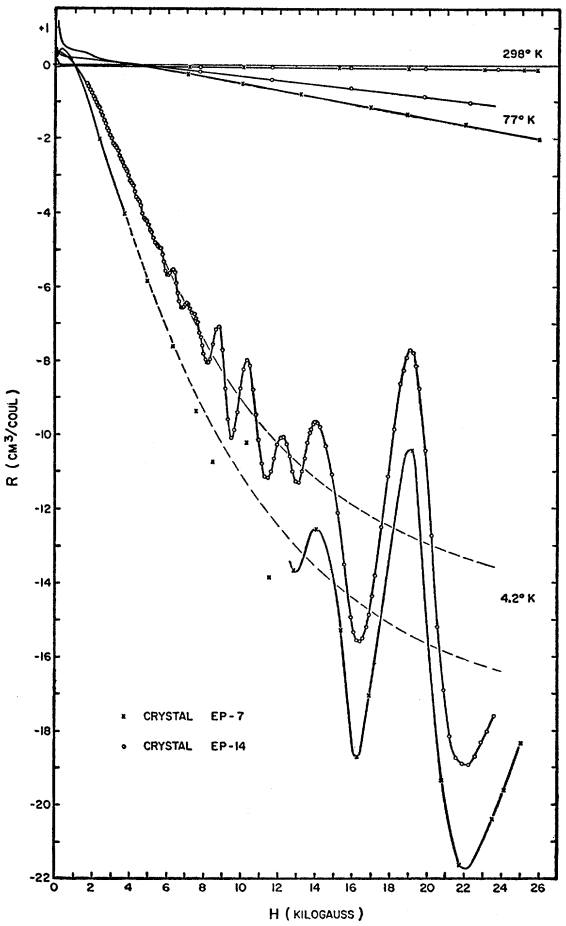

FIG. 2. Hall coefficient magnetic-field dependence of EP-7 and EP-14 at 298°, 77°, and 4.2°K. The low-field points have been omitted for clarity (see Fig. 3). The dashed curves are empirical midlines.

TABLE I. Carrier concentrations in EP-14 and EP-7 at 4.2°K.

	$n_e\times10^{-18}$ (cm^{-3})	$n_h\times10^{-18}$ (cm^{-3})
EP-14	3.1	2.7
EP-7	2.3	2.0

[13] For a discussion, see, A. H. Wilson, *Theory of Metals* (Cambridge University Press, Cambridge, 1953), second edition, pp. 212–218.

[14] An analysis has been carried out by McClure where he fits these data to the components of the magnetoconductivity tensor over wide magnetic field ranges as discussed in an accompanying paper by J. W. McClure [Phys. Rev. **112**, 715 (1958)].

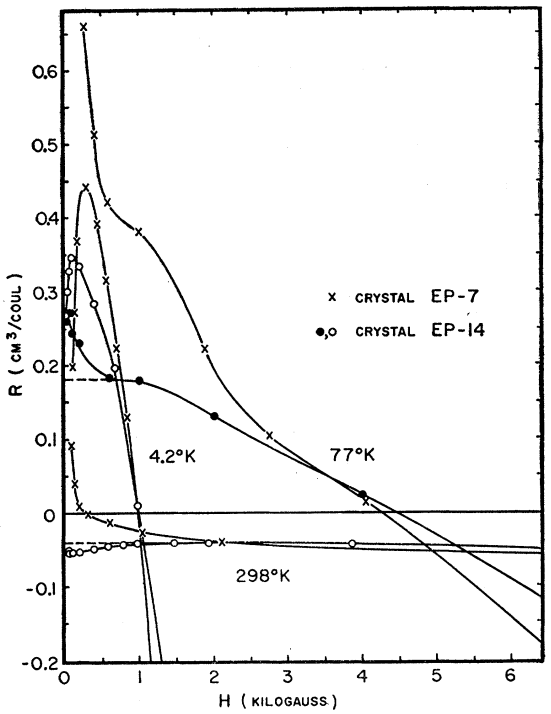

FIG. 3. Low-magnetic-field dependence of the Hall coefficient of EP-7 and EP-14 at 298°, 77°, and 4.2°K. The dashed lines indicate the assumed extrapolations due to the majority carriers alone.

Unfortunately, there is a further complication in that Eq. (6) is not strictly valid in the quantum region where the de Haas–van Alphen oscillations appear ($H \gtrsim 3$ kilogauss). Quantum effects were disregarded, however, in the light of the present development of the theory, and the empirical midline of R, fortunately a straight line on a $1/H$ scale in the high-field range, was extrapolated to infinite H. The value for $n_e - n_h$ so determined is 3.7×10^{17} cm^{-3} for EP-14 and 3.0×10^{17} cm^{-3} for EP-7. The de Haas–van Alphen approximate result[11] for EP-14 is $\sim 6\times10^{17}$ cm^{-3}. A correlation between these values should not be taken too seriously, however, since they are very sensitive to many factors that need further verification. The sum of carrier densities, n_e+n_h, calculated by McClure[14] from the area under the σ_{xx} curve, should be a reliable number when considered over a wide enough field region. The resultant calculated densities at 4.2°K are given in Table I. Only the low-temperature values were calculated. At higher temperatures, the high-field approximation becomes very inaccurate since the saturation fields are much larger being about 1 kilogauss at 77°K and 25 kilogauss at 298°K.

B. Low-Field Hall Effect

A new and unusual type behavior of R was discovered at low fields. An expanded plot of this region is shown in Fig. 3 for EP-7 and EP-14 where measurements were made down to 25 gauss. It will be noted that generally at the higher temperatures for $H \lesssim 500$ gauss, R rises sharply in the positive (or negative) direction.[15] This behavior is believed to be extremely sensitive to the position of the Fermi level and can be thought to indicate that very mobile holes (or electrons) exist in graphite in addition to the normal majority electrons and holes. The effect on R of this new type of carrier can be considered from the low-field approximation of Eq. (1). For three types of carrier, this becomes

$$R=\left[\frac{n_1e_1c}{H_{s1}^2}+\frac{n_2e_2c}{H_{s2}^2}+\frac{n_3e_3c}{H_{s3}^2}\right]\frac{\{1+H^2(A-B-C)\}}{(\sigma_{01}+\sigma_{02}+\sigma_{03})^2}, \quad (7)$$

where

$$A=2\left[\frac{\sigma_{01}}{H_{s1}^2}+\frac{\sigma_{02}}{H_{s2}^2}+\frac{\sigma_{03}}{H_{s3}^2}\right]\Big/(\sigma_{01}+\sigma_{02}+\sigma_{03}),$$

$$B=c^2\left[\frac{n_1e_1}{H_{s1}^2}+\frac{n_2e_2}{H_{s2}^2}+\frac{n_3e_3}{H_{s3}^2}\right]^2\Big/(\sigma_{01}+\sigma_{02}+\sigma_{03})^2,$$

$$C=\left[\frac{n_1e_1}{H_{s1}^4}+\frac{n_2e_2}{H_{s2}^4}+\frac{n_3e_3}{H_{s3}^4}\right]\Big/\left[\frac{n_1e_1}{H_{s1}^2}+\frac{n_2e_2}{H_{s2}^2}+\frac{n_3e_3}{H_{s3}^2}\right],$$

where the subscripts of e identify the signs of the carriers. For a simple one-carrier isotropic system, one has $A=B+C$, and R becomes a constant.

The zero-field extrapolated values of R_0 for EP-14 are -0.056 cm^3/coul at 298°K, $+0.27$ cm^3/coul at 77°K, and $+0.26$ cm^3/coul at 4.2°K. While these values reflect the behavior due to all types of carrier, it is assumed that the dashed extrapolations to zero field shown in Fig. 3 represent the values of R_0 that would result if the third highly mobile type of carrier were not present. These modified values, R_0*, are -0.040 cm^3/coul, $+0.18$ cm^3/coul, and $+0.26$ cm^3/coul, respectively. Then with the minority carriers contributing only about 1% to the σ_0 sum in the denominator of Eq. (7) and under the assumption that $\mu_c/\mu'=1$, the following relation for the majority carriers results:

$$R_0^*=\frac{1}{ec}\left(\frac{a-b^2}{n_e[a+b]^2}\right), \quad (8)$$

where $a=n_h/n_e$ and $b=\mu_e/\mu_h$. Using the best value for a and n_e, the mobility ratio was calculated. It was

TABLE II. Mobility ratio of majority carriers in EP-14.

Temperature (°K)	μ_e/μ_h
298	1.10
77	0.87
4.2	0.79

[15] It should be pointed out that a contribution due to size effects is believed negligible since an estimated average mean free path at 4.2°K is $\sim 17\,\mu$ in the basal plane while the smallest sample dimension in the plane is 247 μ.

found to be a linear function of temperature. The resulting values are given in Table II. They agree with those found from the magnetoconductivity analysis[14] to within 2% at all temperatures. Fortunately, b is very insensitive to the value of n_e, the least accurately known variable involved, varying only by 1.5%, for example, with a 20% change in n_e. It is also rather insensitive to the exact value of a; for example, an 8% change in a produces only a 1.3% change in b.

Upon increasing H, R increases or decreases due to the H^2 terms of Eq. (7) depending on the relative magnitudes of A, B, and C. It is not necessary to have a very large percentage of the fast carriers present with respect to the normal carriers to cause a large effect. For example, in EP-14 at room temperature where about 0.0071% of the carriers[14] are fast electrons, term C dominates, contributing over 99% of the total H^2 term and effectively all of the C term itself is due to the fast electrons. At liquid nitrogen temperature, 0.15% are fast holes and C contributes 73% of the total and the fast holes comprise only about 6% of this. Higher H terms than have been included in Eq. (7) are needed to describe the entire sharp positive rise. For both of the above cases, the sign of C is such that this term causes $|R|$ to decrease as observed. At still lower temperatures, where the H_{si} have become exceedingly small, the effect of these fast minority carriers decreases to the point where at liquid helium temperature it cannot be seen at all from these measurements.

The existence of these fast carriers in graphite has been further substantiated by the cyclotron resonance results of Galt, Yager, and Dail,[16] with a subsequent interpretation due to Lax and Zeiger[17] and to Nozières,[18] where effective masses of $0.028m_0$ and $0.015m_0$ for the minority holes and electrons, respectively, were reported.[17]

It is believed that the origin of these fast carriers is associated with the effect upon dA/dE of warping at the tips of the elongated ellipsoid-like Fermi surfaces, which is related to m^* by

$$m^* = (\hbar^2/2\pi)(dA/dE)_{E_0}, \tag{9}$$

where A is a cross section of the Fermi surface cut by a plane perpendicular to the applied H. These projections, due to Johnston[19] and shown in McClure's paper,[20] take the form of one center and three trigonally symmetric (about k_z) conical points that extend along k_z, the major axis of the ellipsoids. A family of constant energy contours lying in the k_xk_y plane ($\perp H$) at $k_z \simeq \pi/3c_0$ above the center of the Brillouin zone is shown in Nozières' paper. The configuration of these contours is quite similar to that produced by contours of a particular Fermi energy lying in k_xk_y planes cut at intervals along the k_z axis outlining the shape of the conical projections. The middle crossover contour[18] represents the energy where A given in Eq. (9) transforms from one area into four smaller areas. Nozières finds that dA/dE goes through a sharp discontinuity at this point, transforming from a distribution of values representing the majority carriers to one for values of the minority carriers.

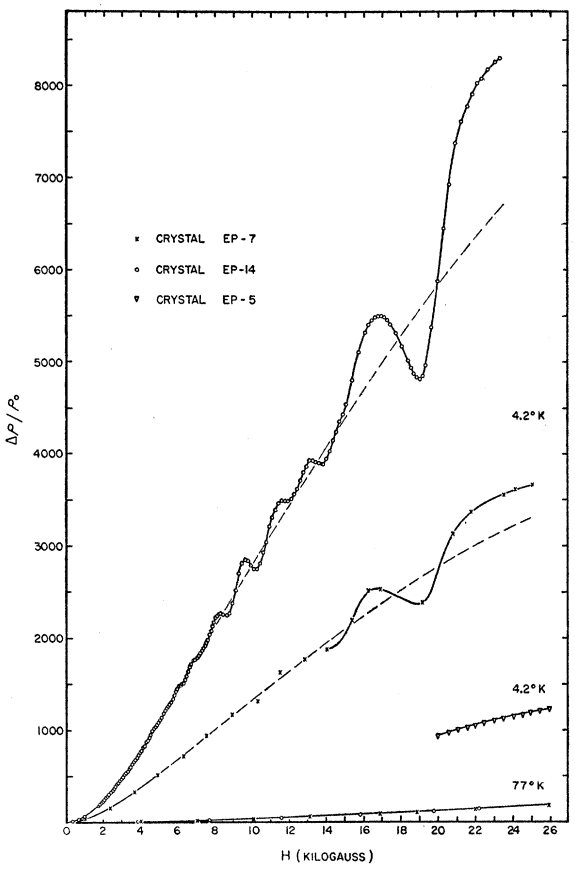

FIG. 4. Magnetoresistance magnetic-field dependence of EP-7 and EP-14 at 298°, 77°, and 4.2°K. The dashed curves are empirical midlines.

C. General Magnetoresistance Field Dependence

The transverse magnetoresistance has been measured as a function of magnetic field from 100 gauss to 26 000 gauss. The results at 77° and 4.2°K are shown in Fig. 4. The magnitude of $\Delta\rho/\rho_0$ is exceedingly large, increasing with decreasing temperature. For crystal EP-14 at 23 kilogauss, the value progresses from 5.77 at 298°K to 155 at 77°K, and to 8250 at 4.2°K. These results are consistent with the large anisotropy in graphite which has previously been observed in the zero-field electrical resistivity where $\rho_c/\rho_a \sim 10^2 - 10^3$. Such behavior is due to the peculiar layer-type crystal structure of graphite which has tight covalent bonding in the basal planes

[16] Galt, Yager, and Dail, Phys. Rev. **103**, 1586 (1956).
[17] B. Lax and H. J. Zeiger, Phys. Rev. **105**, 1466 (1957).
[18] P. Nozières, Phys. Rev. **109**, 1510 (1958).
[19] D. F. Johnston, Proc. Roy. Soc. (London) **A227**, 349 (1955).
[20] J. W. McClure, Phys. Rev. **108**, 612 (1957).

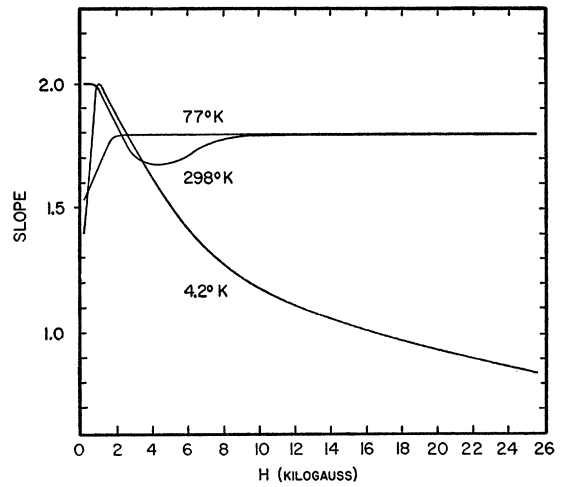

FIG. 5. Magnetic-field dependence of the log-log slope of the magnetoresistance at 298°, 77°, and 4.2°K for a typical sample, EP-7.

and weak, predominantly van der Waals' type, attraction between the planes. From band calculations,[20] this structure has led to a major-to-minor ratio in the Fermi ellipsoid-like surfaces of about 12 to 1. Thus, for the present case where carriers travel in the basal plane, there would be small effective masses and large relaxation times similar, for example, to what has been found for the semimetal bismuth. These masses have been determined in an analysis of the field dependence of the de Haas–van Alphen type oscillations[11] which appear in both the Hall effect and magnetoresistance at 4.2°K for $H \gtrsim 3$ kilogauss as shown in Figs. 2 and 4. The calculated effective masses are $0.030m_0$ and $0.060m_0$ with corresponding relaxation times in EP-14 of 1.4×10^{-11} sec and 3.5×10^{-11} sec for the majority electrons and holes, respectively.

At intermediate fields, unusual changes in the slope on a log-log plot of the field dependence were observed as shown in Fig. 5 for a typical crystal, EP-7. A minimum occurs at the higher temperatures, which progresses toward smaller H with higher sample purity and lower temperature. Three other crystals gave essentially the same results, well within experimental error, differing mainly in the position of the minimum.

In the high-field region for the temperature range above 77°K, the magnetoresistance field dependence curiously obeyed the empirical relation

$$\Delta\rho/\rho_0 = BH^{(1.78\pm0.03)}, \qquad (10)$$

regardless of sample purity as determined by measurements on four samples. B is a parameter dependent upon the temperature and purity. This behavior is in substantial agreement with the results of Kinchin who obtained a dependence of $H^{1.74}$ for a single crystal and with $H^{1.77}$ obtained by McClelland[21] using polycrystalline graphite.

[21] J. D. McClelland, Phys. Rev. **100**, 1807(A) (1955).

At liquid helium temperature, however, the field dependence is modified by the onset of saturation. A dependence of about $H^{0.82}$ was found at 25 kilogauss in substantial agreement with Berlincourt and Steele who found a dependence of $H^{0.80}$. The behavior of EP-5, in the limited region where it was measured, and of EP-14 were identical to that shown in Fig. 5. Also, at this temperature, a sharp maximum equal to 2.0 occurred in the slope at 1 kilogauss, the exact field where R changed sign (see Fig. 3). No maximum was observed at 77°K where R changed sign (4 kilogauss), however. Therefore, such a correlation might be fortuitous.

D. Low-Field Magnetoresistance

The low-field room-temperature behavior is shown in Fig. 6 where $\Delta\rho/\rho_0 H^2$ is plotted *versus* H to emphasize the conversion to a quadratic dependence occurring below a critical field, H_c. A range of residual impurity concentrations is represented by the results of several samples. The quantity $\Delta\rho/\rho_0 H^2$ increases and H_c decreases with purity due to an increase in relaxation time which is equivalent to a corresponding decrease in the saturation field. A quadratic dependence was not observed at the lower temperatures down to the lowest field measured of 100 gauss. Such a dependence would be anticipated at 77°K only at $H \lesssim 1$ gauss as determined from an extrapolation of H_c observed in the higher temperature region.

The relationship of the magnetoresistance to the mobility and hence to temperature and impurity concentration can be seen by considering it in terms of the

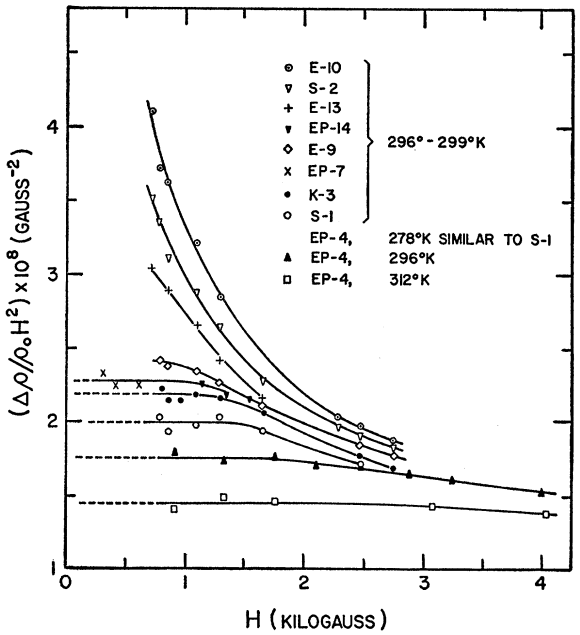

FIG. 6. Low-magnetic-field magnetoresistance room-temperature behavior for several samples representing a range of impurity concentrations.

components of the magnetoconductivity tensor as given by

$$\rho=\sigma_{xx}/(\sigma_{xx}^2+\sigma_{xy}^2). \tag{11}$$

For three types of carrier at small H, $\Delta\rho/\rho_0$ reduces to

$$\frac{\Delta\rho}{\rho_0}=\frac{H^2}{(\sigma_{01}+\sigma_{02}+\sigma_{03})}\left\{\frac{\sigma_{01}}{H_{s1}^2}+\frac{\sigma_{02}}{H_{s2}^2}+\frac{\sigma_{03}}{H_{s3}^2}-\frac{c^2}{(\sigma_{01}+\sigma_{02}+\sigma_{03})}\left[\frac{n_1e_1}{H_{s1}^2}+\frac{n_2e_2}{H_{s2}^2}+\frac{n_3e_3}{H_{s2}^2}\right]^2\right\}$$

$$=\tfrac{1}{2}A-B. \tag{12}$$

For a simple one-carrier isotropic system, the expected zero magnetoresistance results. Numerical evaluation of these terms shows that B is negligible at room temperature as before. In A the minority carriers contribute 83% and the majority electrons and holes about 8% each. A comparison of Fig. 3 and Fig. 6 shows that the magnetoresistance data could not be reliably measured to low enough fields to encompass the region where the fast carriers are most effective in the Hall coefficient. With such a low-field magnetoresistance measurement, however, one might expect that a still higher quadratic $\Delta\rho/\rho_0H^2$ value would be found. It is presumed, then, that the H^2 regions shown in Fig. 6 actually represent those due to the majority carriers predominantly, since the fast carriers by comparison would have a much smaller H_c. In the region where $H<H_c$ for the majority carriers, $\Delta\rho/\rho_0H^2$ should be proportional to an average mobility squared. The absolute value depends on the ratios a and b as is shown by reducing Eq. (12) to the two-carrier form, again with the assumption that $\mu_c/\mu'=1$, giving

$$\frac{\Delta\rho}{\rho_0H^2}=\frac{ab}{c^2}\left[\frac{1+b}{a+b}\right]^2\mu_h^2. \tag{13}$$

Since $a\simeq 1$ then this goes approximately to

$$\frac{\Delta\rho}{\rho_0H^2}\simeq\frac{b}{c^2}\mu_h^2=\frac{1}{c^2}\mu_e\mu_h. \tag{14}$$

This is a good approximation especially in the higher temperature region where a is within a few percent of unity. The individual mobilities as determined from Eqs. (8) and (13) are given as functions of temperature in Table III.

TABLE III. Mobilities of the majority carriers derived from the low-field magnetoresistance results for EP-14.

Temperature (°K)	$\mu_e\times10^{-4}$ (cm²/v sec)	$\mu_h\times10^{-4}$ (cm²/v sec)
298	1.6	1.5
77	9.0	10.
4.2	100.	130.

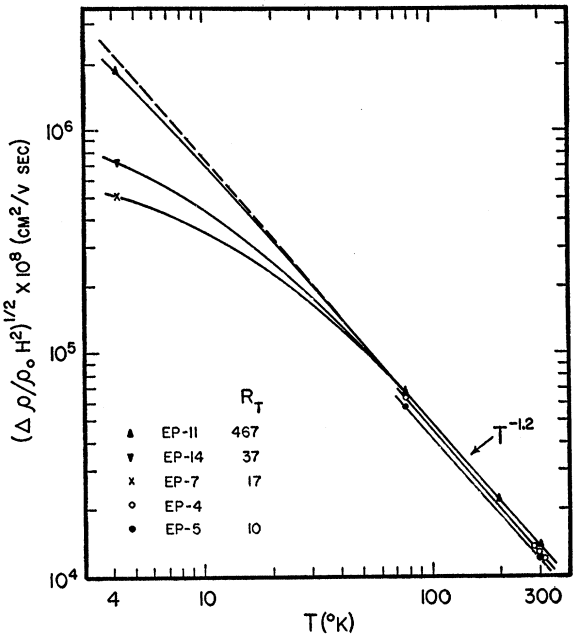

FIG. 7. Temperature dependence of the average mobility as determined from the magnetoresistance at 3 kilogauss. The dashed line is a straight-line extrapolation from the high-temperature region where the points for EP-11, EP-14, and EP-7 essentially coincide. $R_T\equiv\rho_{273°K}/\rho_{4.2°K}$ values show relative purities.

These values are approximate because of the original assumption that $\mu_c/\mu'=1$ and because they could not be evaluated at fields where $H<H_c$, where Eq. (12) holds strictly.

E. Temperature Dependence of Resistivity and Magnetoresistivity

The general trends[22] of the mobility temperature behavior as derived from the magnetoresistance and low-temperature resistivity measurements have been considered to obtain some indication of the dominant scattering laws operative in this temperature range. A plot of the quantity $(\Delta\rho/\rho_0H^2)^{\frac{1}{2}}$ given in Eq. (13) *versus* temperature should give an average mobility behavior since a and b are slowly varying functions of temperature. Measurements were made on EP-4 for $H<H_c$ in the temperature range from 278°K to 312°K. A $T^{-1.24}$ dependence was obeyed. It was further found that this temperature dependence was independent of the particular field used even for $H>H_c$ as determined from temperature plots at several fields out to 8 kilogauss throughout the temperature region down to 77°K. Utilizing this fact, the temperature behaviors of EP-5, EP-7, EP-14, and EP-11 were also plotted for several fields greater than H_c. Again a $T^{-1.2}$ behavior was found from room temperature down to at least 77°K.† The

[22] The results of a detailed investigation will be presented in a later publication.

† *Note added in proof.*—Recent more extensive measurements on EP-11 show that this behavior is obeyed even down as far as 25°K.

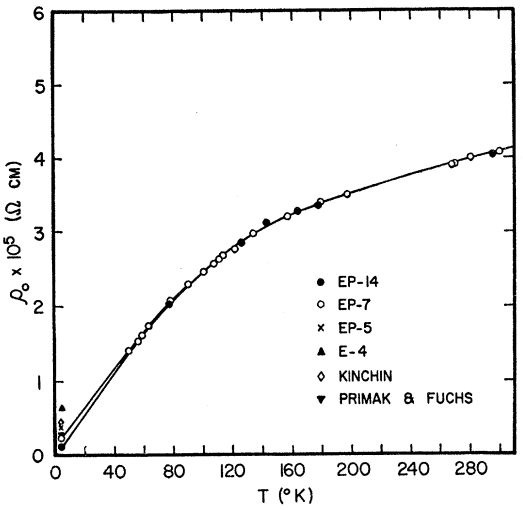

FIG. 8. Resistivity temperature dependence. The higher-temperature points for EP-4 and EP-5 have been omitted for clarity.

results taken at 3 kilogauss are shown in Fig. 7. A type of lattice scattering is evidently dominant in this temperature range as would be expected, though the exponent is somewhat larger than the value of -1.0 that would be predicted for lattice scattering in a typical metal.[23]

At low temperatures, on the other hand, the mobility slopes tend to lower values indicating the increasing effect due to impurity scattering. EP-11, an excellent crystal, is believed to have almost no impurity scattering even down to liquid helium temperature where its log-log slope is equal to -1.0. These slopes range in magnitude down to a value of about -0.5 for EP-7.

Supporting evidence is seen in the zero-field resistivity results shown in Fig. 8. These are in good agreement with those of Primak and Fuchs[5] whose 4.2°K value is also shown ($\rho_{273°K}/\rho_{4.2°K}=15$) along with that of Kinchin. As pointed out by McClure,[14] the knee corresponds approximately to the average degeneracy temperature. This was found to be about 140°K for the electrons and 210°K for the holes as determined from the Fermi energies calculated from the galvanomagnetic de Haas–van Alphen results discussed in the following paper. Thus, in the neighborhood of liquid helium temperature, the carrier concentrations would be expected to be essentially constant, or at most slowly varying functions of temperature. The trends of the average low-temperature mobilities, determined from the resistivity, showed very similar slopes to the magnetoresistance, progressing down to a value of about -0.2 for E-4, an unpurified crystal—the poorest of the group, which had a $\rho_{273°K}/\rho_{4.2°K}$ ratio of 5.8.

It is interesting that a rough determination of the total carrier density can be made from zero-field and low-field results using the resistivity and magnetoresistance data alone, *independent* of the Hall effect. This is possible for the case of graphite because $b/a\simeq 1$. The total carrier density is then given by

$$n_e+n_h\simeq 1/[e\rho_0(\Delta\rho/\rho_0 H^2)^{\frac{1}{2}}\times 10^8]. \quad (15)$$

Approximate values evaluated at fields of 1000 gauss at 298°K, 400 gauss at 77°K and 100 gauss at 4.2°K are given in Table IV. The largest error in these values is contained in the mobility approximations as mentioned previously. They agree surprisingly well, however, with those calculated by other methods.[14] This is especially true at liquid helium temperature as demonstrated by a comparison with the individual results in Table I.

F. Correlation of Residual Impurity-Dependent Effects

The magnetoresistance ratio and the resistivity temperature ratio, $R_T\equiv\rho_{273°K}/\rho_{4.2°K}$, make sensitive measures of relative impurity content. For the present case in dealing with these tiny graphite crystals, they have the added asset of being relatively independent of the exact sample geometry. While these effects are predominantly mobility-dependent, the high-field Hall coefficient, measuring n_e-n_h, should also reflect a strong impurity dependence. Since $b/a\simeq 1$, R is small; thus, it is sensitive to slight shifts in the Fermi level by impurities. For comparison, a measure of the individual electron carrier concentration, n_e, is given by its corresponding de Haas–van Alphen period and the total relative carrier concentration, n_e+n_h, is given by the quantity $\rho_{273°K}/(\rho_0\Delta\rho)^{\frac{1}{2}}{}_{4.2°K}$, a modification of Eq. (15). It is expected that this quantity would be quite insensitive because of the band overlap.[11]

Observed amplitudes of the de Haas–van Alphen type oscillations are related, in part, to the impurity content by way of the collision damping term, ΔT, as discussed n the following paper and defined there in Eq. (3). In addition, the Fermi energies, carrier concentrations, and scattering effects also enter in the components of the amplitudes represented there[11] by the quantities A and B given in Eq. (2). As a result, an increase in the amplitude can be interpreted as a reduction in impurity content. The present measurements, along with those of Kinchin and of Berlincourt and Steele, are presented in Table V where the results are arranged in two sections: those which can be related to approximate equivalent parameters as shown in the last line and those that have, as yet, not been clearly defined by

TABLE IV. Total carrier densities of EP-14 and EP-7.

Temperature (°K)	$(n_e+n_h)\times 10^{-18}$ (cm^{-3}) for EP-14	$(n_e+n_h)\times 10^{-18}$ (cm^{-3}) for EP-7
298	9.9	10.1
77	3.3	3.5
4.2	5.2	3.2

[23] See reference 13, p. 264.

TABLE V. Correlation of relative residual impurity dependencies. The last line indicates the approximate equivalent parameters proportional to the respective measured quantities.

Reference	$\rho_{273°K}/\rho_{4.2°K}$	$\Delta\rho/\rho_0$ (4.2°K, 9420 gauss)	$\rho_{273°K}/[(\rho_0\Delta\rho)^{\frac{1}{2}}]_{4.2°K}$ (9420 gauss)	$(P_e\times10^{5})^{-\frac{1}{3}}$ in gauss$^{\frac{1}{3}}$	$1/\lvert R\rvert$ in cm^3/coul (4.2°K, 23 kilogauss)	$\Delta\rho_{osc}/\Delta\rho_{Av}$ (4.2°K, 20 kilogauss)	R_{osc}/R_{Av} (4.2°K, 20 kilogauss)
Kinchin[a]	12.0	526	0.53		$\gtrsim2.5$		
Berlincourt and Steele[b]		~480		0.32	1.60	0.07	0.06
EP-7	16.7	1220	0.48		0.061	0.12	0.33
EP-14	37.0	2600	0.73	0.33	0.074	0.20	0.38
	τ_{imp}	τ_{imp}^2	n_e+n_h	n_e	n_e-n_h		

[a] See reference 1.
[b] See reference 2.

theory. One of the most striking facts that is immediately evident from these data is the large difference that is affected in the mobility and concentration difference accompanied by only a relatively small change in n_e+n_h or n_e alone. This implies that probably the major impurities are not ionized. Also, the direction of the change in R shows that they are effectively donor impurities. This could be caused by impurities such as Ca, Fe, and Na which are usually present in sizable amounts in such unpurified natural crystals.

Similar differences are seen in the oscillatory results. It is interesting to note that the relationship between the oscillatory and nonoscillatory components as a function of the particular type, or types, of residual impurity concentration here is given roughly by

$$\Delta\rho_{osc}\propto\Delta\rho_{Av}^{1.5}, \tag{16}$$

$$R_{osc}\propto R_{Av}^{1.5}. \tag{17}$$

The Hall-effect dependence is not as well behaved as the magnetoresistance, however, since it is further complicated by the tailing-off of R at high fields as observed by Kinchin and by Berlincourt and Steele. Controlled doping is necessary to conclusively determine this correlation in detail. Relations (16) and (17) imply that the parameters A and B in Eq. (2) of the following paper,[11] as they pertain to the magnetoresistance or Hall effect individually, are related to the mobility and carrier density in a fashion similar to that of the nonoscillatory components.

ACKNOWLEDGMENTS

It is a pleasure for the author to express his appreciation to Dr. J. W. McClure for many interesting and very profitable discussions, to Mr. W. P. Eatherly for his helpful suggestions, to Mr. A. L. Cline and Miss B. J. Vizi for assistance during the course of the measurements, and to Mr. G. A. Mazaris for supplying the liquid helium.

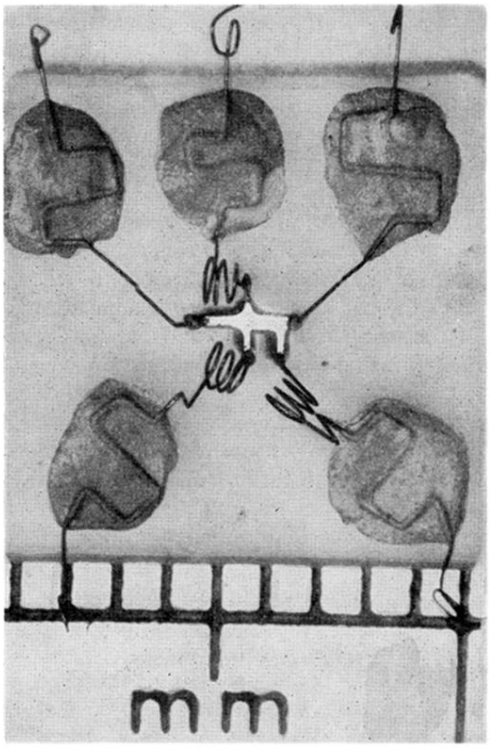

FIG. 1. Mounting of graphite single crystal, EP-14, for galvanomagnetic measurements. Auxiliary lighting shows the high metallic reflectivity of the basal plane.