a set of diagrams including all the fourth-order ones gave oscillations which went only slightly negative and it was a marked improvement on a summation including all the third-order diagrams but not all the fourth-order diagrams. This suggests that the violations of (43) may just be a consequence of a limited summation. A similar situation occurs in evaluating the density of states by summing the diagrams for Δ, where a limited sum can give negative answers. [For instance, this can happen in (39) if $|r|^2>\frac{1}{2}$.]

Computations were also carried out for the "zone" oscillations using the diagrams of Sec. 5. It was found that the oscillations were of the same order as the average conductivity for $H\approx 3H_B$, but negative conductivities were not obtained in this case. The magnitude was strongly modulated by the triangle oscillation. The magnitude fell for H going away from $3H_B$. Not too much weight should be attached to these results because of the neglect of other diagrams with the same area. [Thus in the high-field limit the diagrams chosen give a contribution of order ρ^4 (or H^{-2}), but the diagram in Fig. 8(d), which has not been included, is of order ρ^3.] However, it seems that the oscillations should be experimentally observable. They are unique in that they are not susceptible to "thermal washout" and are not severely reduced by the integration over k_z since the area is determined by the lattice parameters only, and is independent of k_z and the energy. Thus provided a very good sample can be made so that phase coherence can be maintained, the oscillations should be extraordinarily strong.

ACKNOWLEDGMENTS

The author would like to thank Dr. R. Young for showing him Professor R. W. Stark's results for the lens-orbit oscillations prior to publication and for drawing his attention to the problem. He would also like to thank Dr. J. Essam for the reference to the basic Kubo formula.

PHYSICAL REVIEW VOLUME 165, NUMBER 3 15 JANUARY 1968

Linear Magnetoresistance in the Quantum Limit in Graphite

J. W. McClure* and W. J. Spry†
Union Carbide Corporation, Carbon Products Division, Cleveland, Ohio
(Received 21 August 1967)

Measurements of the galvanomagnetic properties of single-crystal graphite were made at 4.2°K in pulsed magnetic fields up to 160 kG. With the magnetic field parallel to the c axis, the transverse magnetoresistance is approximately proportional to the magnetic field strength, and the Hall coefficient is constant above about 80 kG. The results imply that both the diagonal and off-diagonal elements of the magnetoconductivity tensor are inversely proportional to the magnetic field strength. The results are explained theoretically using the following facts: (1) both electrons and holes occupy their lowest Landau levels for fields stronger than about 60 kG, (2) degenerate statistics apply throughout the field range, and (3) the scattering is by ionized impurities whose range depends upon the magnetic field strength. The effect provides a simple way to determine the concentration of scattering centers in graphite. It is also definitely established that the concentration of excess carriers must be determined from the off-diagonal magnetoconductivity; use of the high-field Hall coefficient alone leads to large errors.

I. INTRODUCTION

PREVIOUS investigations[1–4] of the galvanomagnetic properties of graphite single crystals have been for magnetic fields not exceeding 25 kG, though investigations of the de Haas–van Alphen oscillations in the magnetic susceptibility[5,6] have extended up to 85 kG. These investigations have provided a great deal of information about the properties of the current carriers and the energy band structure. The present work extends the measurements of galvanomagnetic properties up to field strengths of 160 kG. The measurements of the transverse magnetoresistance and Hall coefficient of a graphite single crystal with the magnetic field parallel to the c axis were carried out at 4.2°K.

Above 60 kG, graphite is in the quantum limit regime, the term being coined by Adams and Holstein[7] to indicate that all carriers in each group occupy the lowest Landau level for the group. In this region, we have found that the magnetoresistance varies linearly with

* Present address, Department of Physics, University of Oregon, Eugene, Ore.
† Present address, Carborundum Company, P.O. Box 337, Niagara Falls, N.Y.

[1] G. H. Kinchin, Proc. Roy. Soc. (London) A217, 9 (1953).
[2] T. G. Berlincourt and M. C. Steele, Phys. Rev. 98, 956 (1955).
[3] D. E. Soule, Phys. Rev. 112, 698, 708 (1958).
[4] D. E. Soule, J. W. McClure, and L. B. Smith, Phys. Rev. 134, A453 (1964),
[5] W. J. Spry and P. M. Scherer, Phys. Rev. 120, 826 (1960).
[6] S. J. Williamson, S. Foner, and M. S. Dresselhaus, Phys. Rev. 140, A1429 (1965).
[7] E. N. Adams and T. D. Holstein, J. Phys. Chem. Solids 10, 254 (1959).

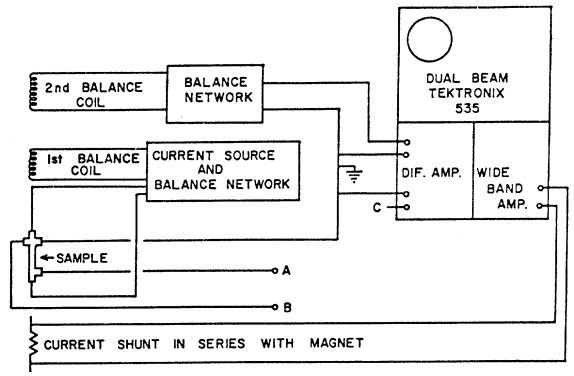

FIG. 1. Schematic diagram of experimental apparatus. The magnetic field is perpendicular to the plane of the sample. For measurement of the magnetoresistance point A was connected to point C, and for measurement of the Hall effect point B was connected to point C.

magnetic-field strength and that the Hall coefficient is constant. Instances of linear magnetoresistance are rare: Ziman's explanation[8] of Kapitza's observations[9] of linear magnetoresistance does not apply, as it requires the presence of open orbits, nor does Azbel's dc skin effect,[10] as it requires a very small Hall angle, nor does Herring's theory of macroscopic inhomogeneities[11] as it requires a larger impurity concentration. The explanation offered here makes use of the existing quantum theory of galvanomagnetic effects,[7,12] plus the fact that the screening of impurity scattering centers depends upon the magnetic field strength.[13] The results yield a method for measuring the number of scattering centers in a sample, as well as adding to our understanding of transport effects in the quantum limit.

In addition, the high-field Shubnikov–de Haas oscillations are correlated with the energy band structure. It is also demonstrated that accurate determinations of the difference between densities of electrons and holes must use the off-diagonal magnetoconductivity instead of the Hall coefficient, even when the high-field Hall coefficient is independent of field strength.

II. EXPERIMENTAL METHOD AND RESULTS

The magnetic fields required in this experiment were produced by the pulsed magnet described earlier.[5] The system consisted of an *LC* circuit with energy stored initially in the electric fields associated with a condenser bank, then transferred to an inductance, the electromagnet, to produce a damped, oscillating magnetic field of large amplitude. The sample was mounted within the electromagnet, and measurements were made with the assistance of an oscilloscope and other electronic instrumentation. The switch used to initiate current flow was built by mounting two tungsten rods in an insulated holder. These were brought together mechanically until an arc was formed to discharge the condenser bank. Recording equipment for this experiment was triggered by the initial induced voltage, and data were recorded during the second quarter cycle of the current pulse.

Crystals were obtained by individual selection from a chunk of Essex County Graphite. Selected single crystals were purified to an assay of 99.995% carbon. Defects appeared in some crystals during the purification process, and these crystals were eliminated from further consideration. The technique of sample preparation was conventional. A miniature sand blast was used to cut a single crystal to the shape outlined on the left in Fig. 1. The small "tabs" at conventional locations were used for the attachment of wire leads. The delicate surfaces of the crystal were protected by a steel collimating mask and a thin plastic cover. The final criteria of successful sample preparation had to be based on the values obtained for various electrical measurements at 4.2°K. These were the magnetoresistance of the crystal and the magnitude of pronounced de Haas–van Alphen oscillations.[5]

The sample was immersed in liquid helium, and measurements were made by using a modified dc method shown in the block diagram of Fig. 1. Leads were attached to the crystal tabs by a silver-bearing cement. The primary change from dc technique consisted of adjustable balance coils in series with each lead to compensate for induced voltages caused by pulsed magnetic fields. The voltages in these coils canceled induced voltages in the signal circuits. Magnetoresistance and the variation of the Hall coefficient with magnetic field were measured separately. Data were recorded by photographing the beam image on the calibrated oscilloscope face.

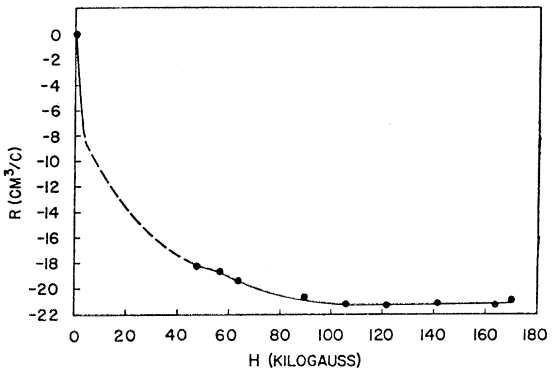

FIG. 2. The Hall coefficient as a function of the magnetic field strength parallel to the *c* axis.

[8] J. M. Ziman, Phil. Mag. **3**, 1117 (1958).
[9] P. Kapitza, Proc. Roy. Soc. (London) **123A**, 292 (1929).
[10] M. Y. Azbel', Zh. Eksperim. i Teor. Fiz. **44**, 983 (1963) [English transl.: Soviet Phys.—JETP **17**, 667 (1963)].
[11] C. Herring, J. Appl. Phys. **31**, 1939 (1960).
[12] A general review of the quantum theory of galvanomagnetic effects plus important new results can be found in R. Kubo, S. J. Miyake, and M. Hashitsume, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1965), Vol. 17, p. 269.
[13] P. N. Argyres and E. N. Adams, Phys. Rev. **104**, 900 (1956).

TABLE I. Estimation of the zero-field resistivity ρ_0 by comparison of the magnetoresistance ratio $\Delta\rho/\rho_0$ with other measurements.

Sample	$10^{-2}\,\Delta\rho/\rho_0$ at 20 kG	$\rho_0(10^{-6}\,\Omega\,\text{cm})$	$\rho_0(\Delta\rho/\rho_0)^{1/2}$ $(10^{-6}\,\Omega\,\text{cm})$
EP-5[a]	9.3	3.7	113
EP-7[a]	28.0	2.4	127
EP-14[a]	58.0	1.0_8	82
Present	16.0	(3.0)[b]	(120)[c]

[a] Reference 3.
[b] Obtained by dividing entry in column three by entry in column one.
[c] Obtained by taking average of same quantity for EP-5 and EP-7.

Figures 2 and 3 are plots of Hall coefficient and the magnetoresistance, respectively, versus the magnetic field. Oscillations were observed in both measurements. In the case of sample resistance versus magnetic field, these oscillations appear directly as shown in Fig. 3. At fields below thirty kG, rapid oscillations were observed with high gain on the oscilloscope. However, these oscillations have been studied in detail by Soule[3] so they will not not be considered further here. The electronic gain of the oscilloscope was reduced to obtain the complete behavior on single photographs. The circles on the graphs represent magnetic fields which were measured in several photographs to check the repeatability of the operation. The linear dependence of resistance on magnetic field is clearly evident. In obtaining the Hall coefficient as a function of magnetic field, the behavior only at fields greater than 50 kG was plotted, since the low-field work has been done previously by Soule.[3] Saturation of the Hall coefficient occurred at about 90 kG. The circles represent magnetic fields at which repetitive measurements were made from different magnetic pulses.

The reliability of these measurements must be considered with regard to the interpretation being placed on the experiment. The reliability of the behavior of the measured quantities versus magnetic field can be estimated by the repeatability of the experiment. In the present case, major portions of each of the curves were repeated in at least three independent attempts. Both the trend of the data versus magnetic field and the magnitude of the signal voltages at given magnetic fields were repeatable to within 5%. The absolute accuracy of the Hall coefficient or magnetoresistance values are not known. The absolute value of the magnetic field shown in the data is based on the calibration of the pulsed magnet against a dc magnet of known characteristics. A flip coil was used for this comparison,[5] and the best estimate of absolute accuracy is plus or minus 3%.

By an oversight, the zero-field resistivity was not measured. However, this is not a serious problem, as the interpretation of the results does not depend critically upon the exact value. A reasonable estimate can be made by comparing the measured magnetoresistance ratio with those of two similar samples whose resistivities were measured by Soule.[3] All these samples are quite pure, so that the total carrier densities (electrons plus holes) are essentially the same in all samples. Thus, the resistivity is inversely proportional to the average mobility. Simple two-carrier theory[3] yields the result that the magnetoresistance ratio is proportional to the square of the average mobility. Thus, the product of the resistivity and the square root of the magnetoresistance ratio should be constant. As Table I shows, this relation is reasonably valid for the two samples most nearly resembling the present one, so that the estimate of $\rho_0 = 3.0\times10^{-6}\ \Omega$ cm is fairly reliable.

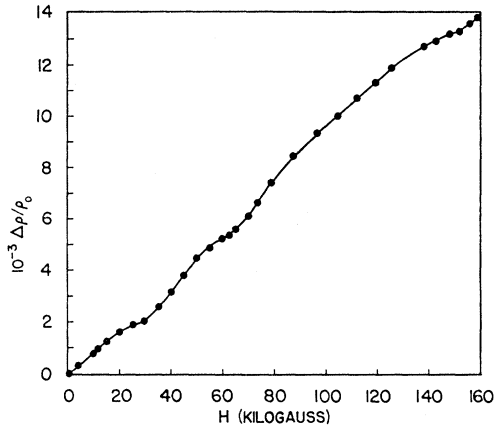

FIG. 3. The transverse magnetoresistivity ratio as a function of the magnetic-field strength parallel to the c axis.

III. PRELIMINARY INTERPRETATION

The results are much easier to interpret in terms of the elements of the magnetoconductivity tensor, which are given for the orientation of the experiment by the simple formulas[14]

$$\sigma_{xx}=\sigma/[1+(R\sigma H)^2], \tag{3.1}$$

$$\sigma_{xy}=\sigma(R\sigma H)/[1+(R\sigma H)^2]. \tag{3.2}$$

In the above, σ is the measured (magnetic-field-dependent) value of the conductivity, the current is in the x direction, and the magnetic field is in the z direction. The experimental value of $R\sigma H$, which is the tangent of the Hall angle, is practically constant and equal to -0.75 for fields greater than about 40 kG. Thus, the Hall angle itself is only about 37°, and there are no troublesome geometrical effects even at the highest magnetic fields. Both elements of the magnetoconductivity tensor are of the same order of magnitude and are inversely proportional to the magnetic field strength above about 80 kG. In Gaussian units, σ_{xx} can be approximated by the formula $2.03\times10^{18}/H$ and σ_{xy} by $-1.53\times10^{18}/H$. The deviations from these expressions are less than 6% from 80 to 140 kG. Any

[14] J. M. Ziman, *Electrons and Phonons* (Oxford University Press, New York, 1960), pp. 487–494.

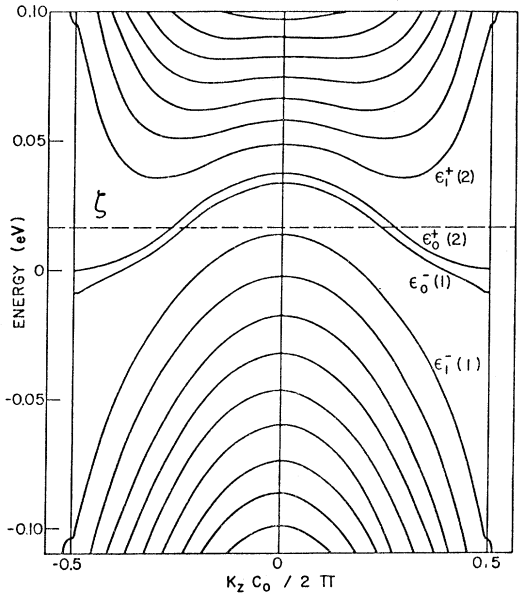

FIG. 4. The Landau levels in graphite for a magnetic field of 70 kG parallel to the c axis. The abscissa is the wave number parallel to the c axis and the ordinate is the energy. The labeling of the levels follows Inoue (Ref. 17). Levels with superscript + are in the conduction band; those with superscript − are in the valence band. The level $\epsilon_0^+(2)$ is independent of magnetic field and marks the lower edge of the conduction band and the upper edge of the valence band in the absence of the magnetic field. The Fermi level for pure graphite is denoted by a dashed line. The values of the graphite band parameters (Ref. 18) used are: $\gamma_0=3.21$ eV, $\gamma_1=0.40$ eV, $\gamma_2=0.0185$ eV, $\gamma_3=0.0$ eV, $\gamma_4=-0.25$ eV, $\gamma_5=0.0185$ eV, and $\Delta=-0.009$ eV.

error in the value of ρ_0 will merely cause multiplicative errors in σ_{xx} and σ_{xy} without changing the field dependence above 80 kG.

The behavior of σ_{xy} is in agreement with both classical and quantum theory[7,12] which predict that σ_{xy} is equal to $(p-n)ec/H$, where p and n are the density of holes and electrons respectively, e is the magnitude of the electronic charge, and c is the velocity of light. Thus, the experiment yields the result that the excess of electrons over holes $(n-p)$ is equal to 1.06×10^{17} cm^{-3}. This is about 2.7 times that found by the same method[15] for crystal EP-14 and about 1.8 times that found for EP-7. If the differences in resistivity were caused by different amounts of the same ionized impurity, the results of Table I would predict that the excess carrier density in the present sample is 2.8 times that in EP-14 and 1.25 times that in EP-7. These results are reasonably consistent. The fact that σ_{xy} is proportional to H^{-1} over such a large field range indicates that $p-n$ is independent of the magnetic field. This is evidence against there being any bound states whose degree of ionization depends upon the magnetic field strength; i.e., there are no "freeze-out" effects.

It is important to note that the carrier excess deduced from setting the saturation value of the Hall coefficient equal to $1/(p-n)ec$ is in error. For this simple rule to be correct, the quantity $R\sigma H$ must be large enough so that Eq. (3.2) becomes $\sigma_{xy}=1/RH$. The carrier excess estimated from the Hall coefficient alone would be a factor 3 too high for the present sample, and that estimated by Soule[3] for crystal EP-14 is a factor 10 too high.

The behavior of the diagonal magnetoconductivity σ_{xx} is unusual. The classical theory predicts that σ_{xx} should fall off as the inverse second power of the magnetic field strength if there are no "open orbits," and all the results on the energy band structure of graphite indicate that the orbits should be closed for the orientation considered. The highest fields are in the "quantum limit" region, i.e., all the carriers are in the lowest Landau levels, so we shall apply the theory of Adams and Holstein.[7] For this application it is necessary to discuss the energy levels in the magnetic field.

IV. ENERGY BAND STRUCTURE AND LANDAU LEVELS

The Brillouin zone of graphite is a hexagonal pill box, and the electron and hole Fermi surfaces are placed along the six vertical zone edges.[16] The holes are in a highly elongated surface centered on the edge, and the electrons are in two elongated surfaces near the corners of the zone. Because of strong interband interactions, the Landau levels deviate from the semiclassical Onsager-Lifshitz result and must be found by solving a fourth-order secular equation.[17,6] A plot of the levels for a particular set of band parameters[18] and for a magnetic field of 70 kG is given in Fig. 4. Note that the lowest conduction band level has no zero-point energy, and the highest valence band level has an anomalously small zero-point energy.

The number of states per unit volume per increment of k_z for each quantum level is proportional to the magnetic field strength, and the proportionality constant is the same as that for free electrons. For pure graphite, the hole density is equal to the electron density. In the quantum limit, this condition is met when the length of k_z for the lowest occupied conduction band level is equal to that for the highest unoccupied valence band level. Thus, the Fermi energy is a very slowly varying function of the magnetic field strength in the quantum limit. This is quite different from the case of one type of carrier only, in which the Fermi energy strongly depends upon the magnetic field strength in the quantum limit. Furthermore, due to the small zero-point energy, there is a finite band overlap for magnetic fields less than about 750 kG. Above this

[15] J. W. McClure, Phys. Rev. **112**, 715 (1958).

[16] For a recent review, see J. W. McClure, IBM J. Res. Develop. 8, 255 (1964).

[17] Y. Uemura and M. Inoue, J. Phys. Soc. Japan **13**, 382 (1958); J. W. McClure, Phys. Rev. **119**, 606 (1960); M. Inoue, J. Phys. Soc. Japan **17**, 808 (1962); M. S. Dresselhaus and J. G. Mavroides, IBM J. Res. Develop. 8, 262 (1964).

[18] M. S. Dresselhaus and J. G. Mavroides, Carbon 3, 465 (1966).

field, graphite would become a semiconductor. For the fields and temperatures of the present experiment, the overlap is large enough that degenerate Fermi-Dirac statistics apply. The sample under consideration is not perfectly pure, but has about 10^{17} cm^{-3} more electrons than holes. However, the electron density in pure graphite at 4.2°K and with no magnetic field is about 3×10^{18} cm^{-3}, so that this concentration of impurities has only a very slight effect on the Fermi level. Detailed calculations of the variation of the Fermi level for fields up to 60 kG have been published by Sugihara and Ono.[19] The electron density (and hole density) increases linearly with magnetic field strength in the quantum limit and is equal to about 7×10^{18} cm^{-3} at 100 kG.

The last dip in the resistivity as a function of magnetic field strength theoretically corresponds to the top of the $n=1$ level for the holes being equal to the Fermi energy. If the simple periodicity of the Shubnikov–de Haas effect held at high fields, the dip would come at $H^{-1}=(\frac{3}{2})P_h$, where P_h is the period of oscillation associated with the holes. As P_h is about[2–4] $1.5\times10^{-5}\,G^{-1}$, the dip would come at $H=45$ kG. However, the simple periodicity breaks down for two reasons. (1) The Onsager-Lifshitz rule does not apply for small quantum numbers. Solution of the secular equation[19,20] shows that the dip associated with the $n=1$ level would occur at a field about 8% higher due to this effect. (2) The Fermi level changes with magnetic field.[19] For low fields, the Fermi level is about 0.022 eV, but in the quantum limit it is about 0.017 eV. The field at which a particular dip occurs is proportional to the difference between the Fermi level and the top of the valence band (which is at 0.037 eV). These two factors together predict[19] that the dip associated with the $n=1$ hole level will come around 55 to 65 kG, which is about where a dip occurs in the experiment. Magnetic fields stronger than this are in the quantum limit region. Both the $n=1$ level for electrons and the $n=2$ level for holes should give dips at a magnetic field of about 30 kG, where one is actually observed. The apparent dip at about 155 kG is assumed to be due to experimental error.

V. THEORY OF MAGNETOCONDUCTIVITY

There are now a number of theoretical treatments[12] of electron transport in a strong magnetic field which agree with the early work of Titeica.[21] We shall use the formulation of Adams and Holstein,[7] hereafter referred to as AH. The AH theory was used in a simplified manner[4] to explain the Shubnikov–de Haas results in graphite for fields less than 25 kG, and recently has been used in a more realistic calculation[19] for the same purpose. In the quantum limit and for scattering by fixed, randomly placed point imperfections, the AH result for σ_{xx} may be written

$$\sigma_{xx}=\frac{be^2n_s}{4m_1\omega}\int dE\left(-\frac{df}{dE}\right)[N(E)]^2\langle V^2\rangle, \quad (5.1)$$

where

$$\langle V^2\rangle=\int dq_x\int dq_y q_y^2\{|V(k_x,k_y,0)|^2 + |V(k_x,k_y,-2k_z)|^2\}e^{-q^2/2}. \quad (5.2)$$

In the above, n_s is the number of scattering centers per volume, m_1 is the effective mass perpendicular to the c axis, ω is the cyclotron frequency ($\omega=eH/m_1c$), E is the energy, f the Fermi-Dirac distribution function, $N(E)$ is the total density of states (per volume and energy), and $bN(E)$ is the density of states into which a particle may be scattered without a change in its spin state. The q's are dimensionless variables ($q^2=q_x^2+q_y^2$) and are related to the wave-vector components by

$$q_x=k_x(\hbar/m_1\omega)^{1/2}=k_x(\hbar c/eH)^{1/2}.$$

The quantity k_z in Eq. (5.2) is dependent upon the energy through $E=\frac{1}{2}\hbar\omega+\hbar^2k_z^2/2m_3$, where m_3 is the effective mass parallel to the c axis. Finally, the potential of a *single* scattering center at position $\mathbf{R}$ is given by

$$v(\mathbf{r})=(2\pi)^{-3}\int d^3k V(k_x,k_y,k_z)\exp[i\mathbf{k}\cdot(\mathbf{r}-\mathbf{R})]. \quad (5.3)$$

It is seen that the integral in Eq. (5.1) is dimensionless, and that the quantity in front of the integral has the dimensions of a conductivity.

The derivation of AH was for a simple free-electron gas, but as written the result also applies if the effective mass in the direction of the magnetic field (m_3) is different from that perpendicular to the field (m_1). We shall assume that it also applies to the graphite band structure. In the quantum limit, the length of the "hole Fermi surface" is about one half of the zone height, and the two pieces of "electron Fermi surface" can be put together to make one "electron Fermi surface" about as long as the "hole Fermi surface." For simplicity, we will assume that the energy versus k_z is parabolic for each carrier and that the magnitude of m_3 is the same for each carrier. One can see from Fig. 4 that these are not serious approximations. Ono and Sugihara[19] have shown that the scattering between the electron surface and hole surface is negligible, arguing from the selection rules of matrix elements and the range of the scattering potential. Thus, our model consists of two similar sets of carriers acting independently, but whose Fermi levels are sufficiently independent of magnetic field to the extent that degenerate statistics can be applied. We also must remember that there are two nonequivalent edges of the Brillouin zone, so that

[19] K. Sugihara and S. Ono, J. Phys. Soc. Japan **21**, 631 (1966).
[20] S. J. Williamson, Ph.D. dissertation, MIT, 1965 (unpublished).
[21] S. Titeica, Ann. Phys. **22**, 129 (1935).

there are two complete electron and two complete hole Fermi surfaces, not counting spin degeneracy. We will neglect scattering between the nonequivalent edges, as it is shown below that the matrix element of the scattering potential is very small for such large changes in k vector. Thus, we have that the factor b is equal to $\frac{1}{8}$, the product of $\frac{1}{2}$ because of spin, $\frac{1}{2}$ because of the two nonequivalent zone edges, and $\frac{1}{2}$ because of two types of carriers (electrons and holes).

Remembering that ω is proportional to H, we see from Eq. (5.1) that to obtain σ_{xx} inversely proportional to H, the integral must be independent of magnetic field. This is not the behavior of the one-carrier cases investigated by AH. In such cases, the effective Fermi level must vary like H^{-2} in order to keep the number of carriers constant, and consequently the density of states at the Fermi level varies at H^2. In addition, the factor $\langle V^2\rangle$ has different magnetic field dependences for different scattering mechanisms so that AH find σ_{xx} variations ranging from H^1 to $H^{7/2}$. However, when the scattering centers are screened impurities and it is taken into account that the range of the screening depends upon magnetic field, the variation of $[N(E)]^2$ can compensate that of $\langle V^2\rangle$.

The resistance of the present sample is certainly limited by impurities. It has a zero-field resistivity three times greater than EP-14, which has a temperature-independent resistivity[4] below 4.2°K. It is reasonable to assume that the scattering centers are charged, and probably are the centers which contributed the excess carriers (though, of course, compensation may be present). Because of the relatively high carrier concentration in graphite, the potential of a scattering center will be screened out in a short distance. We shall use the simple linearized Thomas-Fermi model[22,13] to discuss the scattering potential. The potential is then given by

$$v(r)=-[\Delta Ze^2/\epsilon r]\exp(-r/a)\,, \tag{5.4}$$

so that

$$V(k)=-[\Delta Ze^2 4\pi/\epsilon]/(k^2+a^{-2})\,. \tag{5.5}$$

For degenerate statistics, the range is given by

$$a=[\epsilon/4\pi e^2 N(\zeta)]^{1/2}\,, \tag{5.6}$$

where $\Delta Z=Z-4$ is the valence of the impurity minus the valence of carbon, ϵ is the dielectric constant (equal to about 4.1 at optical frequencies[23] and about 9.0 in the infrared[24]), and ζ is the energy of the Fermi level. In the absence of the magnetic field, the density of states for graphite is about[16] 5×10^{-3} eV^{-1} atom^{-1} or 3.6×10^{32} erg^{-1} cm^{-3} so that a is in the range 6 Å to 9 Å. (In the quantum limit, the density of states is proportional to the magnetic field strength, being about 4.4×10^{-3} eV^{-1} atom^{-1} at 100 kG.) The values of the projection of k in the $x-y$ plane which contribute most to the integral in Eq. (5.2) are those corresponding to the maximum value of $q^2\exp(-\frac{1}{2}q^2)$, or q^2 equal to two. At a magnetic field of 100 kG, this gives a value of about 1.7×10^6 cm^{-1} for the projection $\kappa=(k_x^2+k_y^2)^{1/2}$. The product of κa is then about 0.1 to 0.15, so that we may take

$$V(k_x,k_y,0)=-\Delta Z 4\pi e^2 a^2/\epsilon=-\Delta Z/N(\zeta)\,. \tag{5.7}$$

This simple result is actually Friedel's sum rule[25] $\langle V\rangle N(\zeta)=-\Delta Z$, and states that the addition of $|\Delta Z|$ carriers of opposite charge from the scattering center screens out the potential so that the Fermi level far away is unchanged.

The value of $2k_z$ which goes in Eq. (5.2) is the length of the Fermi surface, which is about $\pi/c_0=4.7\times10^7$ cm^{-1}, where c_0 is the lattice constant in the c_0 direction. The ratio of $V(k_x,k_y,-2k_z)$ to $V(k_x,k_y,0)$ is then no more than 0.1. As the squares of the two quantities enter in Eq. (5.2), we are justified in keeping only the $V(k_x,k_y,0)$ term.

With these approximations, the two integrals become trivial. The evaluation of (5.2) yields

$$\langle V^2\rangle=2\pi(\Delta Z)^2/[N(\zeta)]^2\,. \tag{5.8}$$

Substituting this result into (5.1) and using the result for degenerate statistics $\int dE(-\partial f/\partial E)g(E)=g(\zeta)$ for any function $g(E)$, the density of states factors cancel to yield

$$\sigma_{xx}=2\pi(\Delta Z)^2e^2n_s/32m_1\omega=\pi(\Delta Z)^2n_s ec/16H\,. \tag{5.9}$$

The result is remarkable in that it is independent of any properties of the carriers and is independent of any property of the scattering centers save their valence and concentration. The result should not be used to predict conductivity in the absence of carriers, as the derivation assumed the existence of carriers obeying degenerate statistics. The result would also become invalid for fields so large that the screening length became less than the interatomic spacing. However, in the present case the field limit from this consideration is greater than 1 MG.

The most serious approximation in the derivation is the use of the linearized Thomas-Fermi method. An improved treatment[26] of the potential yields a similar result with a different numerical factor. Another source of error is that the AH theory is based on the first Born approximation. In the improved treatment,[26] this approximation is corrected using the method of Kubo *et al.*[12] A simple way to estimate the error introduced by use of the first Born approximation is provided by the work of Kahn,[27] who solved the scattering problem exactly for δ function potentials. His result was that the Born approximation expression is divided by the

[22] N. H. March, Advan. Phys **6**, 1 (1957).
[23] J. T. McCartney and S. Ergun, in *Proceedings of the Third Conference on Carbon* (Pergamon Press, Inc., New York, 1959), p. 223.
[24] E. A. Taft and H. R. Philipp, Phys. Rev. **197**, A138 (1965).
[25] J. Friedel, Advan. Phys. **3**, 446 (1954).
[26] G. A. Barnes and J. W. McClure (to be published).
[27] A. H. Kahn, Phys. Rev. **119**, 1189 (1960).

factor $1+\pi^2[bN(\zeta)]^2V_0^2$, where V_0 is the strength of the δ function. If we use our $V(0,0,0)$ for V_0 (which is also the Fourier transform of the delta function potential) the factor becomes $1+(\pi/8)^2=1.15$. Thus, an accurate treatment must go beyond the first Born approximation.

The result for σ_{xx} has the same form as σ_{xy} with $p-n$ replaced by $(\Delta Z)^2\pi n_s/16$. If there are several types of impurities, the conductivity would be proportional to $\sum_s n_s(\Delta Z_s)^2$. Let us assume that the valence differences in the present case are $\Delta Z_s=\pm 1$. The experimental result for σ_{xx} yields an estimate of 7.2×10^{17} cm^{-3} for $\sum_s n_s$. Together with the result from σ_{xy}, this would imply a concentration of about 4.1×10^{17} cm^{-3} of ionized donors and 3.1×10^{17} cm^{-3} of ionized acceptors.

Next, we shall show that the model also gives the correct order of magnitude for relaxation time in the absence of a magnetic field. The scattering is isotropic in the plane of the crystal so that the relaxation time is given by

$$\tau^{-1}=\tfrac{1}{4}(2\pi/\hbar)N(\zeta)\langle M^2\rangle, \tag{5.10}$$

$$\langle M^2\rangle=n_sV^2(0)\langle(1+a^2k_z^2)^{-2}\rangle. \tag{5.11}$$

In the above, we have taken b equal to one fourth and allowed scattering between electron and hole surfaces on the same Brillouin zone corner, so that the average in Eq. (5.11) extends over the entire height of the Brillouin zone. If we did not allow scattering between electron and hole surfaces, the results would differ very little. The indicated average in Eq. (5.11) gives about 0.12, so that we find $\tau^{-1}\cong 6.2\times10^{-7}n_s$, where n_s is in cm^{-3}. For sample EP-14, if n_s is equal to the number of excess electrons (4×10^{16} cm^{-3}), then τ would be about 4×10^{-11} sec. The average value found experimentally[15] is about 3×10^{-11} sec, which gives agreement for σ_{xx} in both the zero-field and high-field classical limits.

It is interesting to examine the conditions for the same kind of linear magnetoresistance to exist in other materials. The most important requirement is that all carriers be in the quantum limit, which rules out materials such as zinc, in which a small number of light carriers coexist with a large number of heavy carriers. We have made explicit use of the extreme anisotropy of the graphite Fermi surface to neglect the second term in Eq. (5.2). However, a different approximation is valid in the isotropic case: $2k_z$ is smaller than the value of $\kappa=(2eH/\hbar c)^{1/2}$ which corresponds to $q^2=2$. In this case, the approximation $\kappa a\ll 1$ may not be valid, but it does not change the field dependence of σ_{xx}. Our derivation does not require the nearly constant Fermi level characteristic of a two carrier system; it requires only that the statistics be degenerate. However, in the case of a single kind of carrier, the factor b would be equal to $\frac{1}{2}$, and the corrections to the first Born approximation would be of the order of 70%. Thus, it appears that this particular type of linear magnetoresistance may appear only for systems of several carriers which are rather similar.

Finally, we should point out that Kubo *et al.*[12] predicted that σ_{xx} is proportional to H^{-1} for scattering by long-ranged impurities when the effective Fermi energy is constant. However, the screened impurities do not meet the condition for long range, $a^2\gg(eH/\hbar c)^{-1}$. Kubo *et al.*[12] list a linear magnetoresistance for a case in which σ_{xx} is proportional to H, but this result does not apply in the present case due to their assumption that $|\sigma_{xy}|\gg\sigma_{xx}$.

VI. CONCLUSIONS

We have found experimentally and explained theoretically a linear magnetoresistance in the quantum limit. With the correction of a numerical factor,[26] the effect can provide an easy way to analyze for the number of scattering centers in graphite. The conditions for such a linear magnetoresistance to appear in other material have been found to be rather special.

It has been definitely established that the use of the high-field Hall coefficient alone to determine the excess carrier concentration in graphite leads to large errors.

ACKNOWLEDGMENT

The authors are indebted to M. H. Cohen for emphasizing to us the importance of the change in screening with magnetic field.