Analysis of Galvanomagnetic de Haas-van Alphen Type Oscillations in Graphite

D. E. Soule
National Carbon Research Laboratories, Cleveland, Ohio*
(Received June 30, 1958)

An analysis has been made of oscillations in the Hall effect and magnetoresistance for graphite single crystals at 4.2°K with the field parallel to the hexagonal axis. Two periods of 2.11×10^{-5} gauss^{-1} and 1.58×10^{-5} gauss^{-1} are shown to be due to the *majority* electrons and holes, respectively. These same two values were found in both galvanomagnetic effects and are in reasonable agreement with those observed in the susceptibility. There is a phase difference of π between the two galvanomagnetic properties. An analysis of the magnetic field dependence of the amplitude incorporating both effects in a "galvanomagnetic ratio," ρ/R, has been made giving effective-mass values of $0.030m_0$ for the electrons and $0.060m_0$ for the holes. These are in substantial agreement with those calculated from cyclotron resonance and from the temperature dependence of the susceptibility de Haas-van Alphen oscillations. Corresponding Fermi energies were found to be 0.018 ev for the electrons and 0.012 ev for the holes, giving a very slight band overlap in graphite of 0.030 ev.

I. INTRODUCTION

While the de Haas-van Alphen effect in the susceptibility has been investigated in many metals, attention has been given more recently to the analogous oscillations in the galvanomagnetic effects in metals such as Bi,[1–5] Zn,[6–8] Mg,[9] Sb,[10] Ga,[11] and Sn.[12,13] Following Shoenberg's investigation of the susceptibility oscillations in graphite,[14] Berlincourt and Steele[15] were the first to observe them in the magnetoresistance and Hall effects as well as in the susceptibility, all three measurements being on the same crystal. They showed that there was a direct correlation betweeen these three effects by obtaining one common period of 2.15×10^{-5} gauss^{-1}. An additional period was found in the susceptibility for temperatures below 1.4°K.

Measurements were made here on relatively high-purity (99.995%) purified natural graphite single crystals using extreme precautions in their handling and mounting as described in the preceding paper.[16] With such crystals it was believed that a further correlation could be made between the oscillations observed in the susceptibility and those in the magnetoresistance and Hall coefficient in that two analogous periods should similarly exist in the latter two phenomena. This was the first aim of the present study. In addition, a search was also made for a third and smaller period which was thought might exist as a result of the presence of heavier carriers.

A second objective of this investigation has been to relate the de Haas-van Alphen carrier densities to the normal conduction carrier densities. For most metals that exhibit the de Haas-van Alphen effect, the calculated number of carriers is considerably smaller ($\lesssim10^{-3}$ per atom) than that obtained from conduction phenomena. This suggests that what was observed was in reality only the effect due to a few carriers located in small pockets in the zone structure. The situation that exists here is rather unique in that a direct correlation can be made between the de Haas-van Alphen concentrations and the normal conduction concentrations[16] as determined from the same measurements on the same crystal.

Recently, theories for the magnetic quantization of the galvanomagnetic effects have been applied to a multicarrier system[17,18] with an arbitrary band structure.[17] The third main part of this investigation consists of analyzing the field dependence of the oscillation amplitudes to correlate the effective mass values thus derived with those obtained both from the temperature dependence of the susceptibility oscillations and from cyclotron resonance.

II. EXPERIMENTAL PROCEDURE

In general, the measurements were made as described in the preceding paper. A Moseley X-Y recorder with external bucking and filtering circuits for each axis was used in conjunction with a Leeds and Northrup K-2

* National Carbon Company, Division of Union Carbide Corporation.
[1] P. B. Alers and R. T. Webber, Phys. Rev. **91**, 1060 (1953).
[2] L. C. Brodie, Phys. Rev. **93**, 935 (1954).
[3] Reynolds, Hemstreet, Leinhardt, and Triantos, Phys. Rev. **96**, 1203 (1954).
[4] R. A. Connell and J. A. Marcus, Phys. Rev. **107**, 940 (1957).
[5] J. Babiskin, Phys. Rev. **107**, 981 (1957).
[6] N. M. Nachimovitch, J. Phys. U.S.S.R. **6**, 111 (1942).
[7] E. S. Borovik, Izvest. Akad. Nauk U.S.S.R. **19**, 429 (1955).
[8] Grenier, Reynolds, and Ali, *Proceedings of the Fifth International Conference on Low-Temperature Physics and Chemistry, Madison, Wisconsin, August 30, 1957* (to be published).
[9] E. S. Borovik, doctoral thesis, Kharkov University, 1954 (unpublished).
[10] M. C. Steele, Phys. Rev. **99**, 1751 (1955).
[11] J. Yahia and J. A. Marcus, *Proceedings of the Fifth International Conference on Low-Temperature Physics and Chemistry, Madison, Wisconsin, August 30, 1957* (to be published).
[12] E. S. Borovik, Doklady Akad. Nauk U.S.S.R. **69**, 767 (1949).
[13] P. B. Alers, Phys. Rev. **107**, 959 (1957).
[14] D. Shoenberg, Trans. Roy. Soc. (London) **245**, 1 (1952).
[15] T. G. Berlincourt and M. C. Steele, Phys. Rev. **98**, 956 (1955).
[16] See D. E. Soule, preceding paper [Phys. Rev. **112**, 698 (1958)].
[17] I. M. Lifshitz and A. M. Kosevich, J. Eksptl. Theoret. Phys. U.S.S.R. **29**, 730 (1955) [translation: Soviet Phys. JETP **2**, 636 (1956)]; and I. M. Lifshitz, J. Eksptl. Theoret. Phys. U.S.S.R. **30**, 814 (1956) [translation: Soviet Phys. JETP **3**, 774 (1956)].
[18] G. E. Zilberman, J. Eksptl. Theoret. Phys. U.S.S.R. **29**, 762 (1955) [translation: Soviet Phys. JETP **2**, 650 (1956)].

potentiometer. Because of the importance of the low-field region, considerable effort was made to obtain the highest possible accuracy for these measurements. In the range from 6.1 to 2.8 kilogauss, small increments of the field range were examined by enlarging each portion on an X-Y trace with suitable overlapping between sections. Two extreme matching points were calibrated for each section by aligning the fluxmeter indicating needle on predetermined dial marks within 0.3% precision, utilizing a mirror for parallax correction, and measuring the ordinate variables with the potentiometer. As an indication of the stability of the entire arrangement, no movement of the fluxmeter needle—within the precision indicated above—could be detected for at least a half hour, the longest time over which it was tested.

III. THEORY

Recent important theoretical calculations of Lifshitz *et al.*[17] and Zilberman[18] on the effect of orbital quantization due to an applied magnetic field upon the galvanomagnetic properties and on the related susceptibility have led to a more general interpretation of these de Haas-van Alphen type oscillations than existed heretofore. In particular, a more physically realistic model is assumed having an arbitrary band structure,[17] containing two or more types of carrier, and assuming impurity scattering. Relaxation times, however, are still assumed to be independent of the magnetic field.

A quantity called the "galvanomagnetic ratio," defined[19] as

$$G \equiv \rho/R, \tag{1}$$

is introduced here in order to combine the measured magnetoresistance, ρ, and the Hall coefficient, R, which are complicated individually, in such a way as to reduce the relation to a simple sum of oscillatory and non-oscillatory terms. The oscillatory components of G are given for two carriers by

$$G_{\mathrm{osc}} = H^s \left\{ A \sum_{p=1}^{\infty} \frac{C(p)\cos[(2\pi p/P_1H)-\phi_1]}{\exp(X)\sinh(p\pi^2kTa/\beta_0H)} + B \sum_{q=1}^{\infty} \frac{D(q)\cos[(2\pi q/P_2H)-\phi_2]}{\exp(Y)\sinh(q\pi^2kTb/\beta_0H)} \right\}, \tag{2}$$

where $a=m_1^*/m_0$, $b=m_2^*/m_0$, $\beta_0=$ Bohr magneton and $\phi=$ phase. The summations are taken over all Fourier harmonics for each type of carrier with $C(p)$ and $D(q)$ being simple numerical factors. The quantities X and Y are identical to the arguments of their respective hyperbolic sine terms except that ΔT_i replaces T. The quantity ΔT_i represents the effect of collision damping upon the ith carriers in that the amplitude of the oscillations is decreased as though the temperature had been raised from T to $T+\Delta T_i$. It is given[20] by

$$\Delta T_i = \hbar/\pi k \bar{\tau}_i, \tag{3}$$

where $\bar{\tau}_i$ is the collision time averaged around an extreme orbit on the Fermi surface. In the relatively low-field region where an exponential approximation can be made to the hyperbolic sine, this contribution amounts effectively to a simple additive correction to the measured temperature. The approximation of this contribution will be discussed in Sec. D of the results.

The oscillatory periods, P_i, due to the ith type of carrier contained in Eq. (2) are related to the extreme (maximum or minimum) cross sections of the Fermi surface, A_m, perpendicular to the applied field, by

$$P_i = eh/cA_m, \tag{4}$$

where A_m is in momentum units. This is the Onsager-Lifshitz relation[21,22] which is quite general and exceedingly effective in directly ascertaining Fermi surface configurations. The period is also given by[23]

$$P_i = e\hbar/cm_i^*E_{0_i}, \tag{5}$$

where E_{0_i} is the Fermi energy as measured to the bottom of the conduction band for electrons and to the top of the valence band for holes. In addition, for the free-electron case

$$P_i = \left(\frac{4e}{\pi hc}\right)\left(\frac{\pi}{3}\right)^{\frac{2}{3}} \Big/ n_i^{\frac{2}{3}}, \tag{6}$$

where $n_i=$ carrier density.

The quantities A and B are complex functions of band parameters, Fermi energies, temperature, and relaxation times. In the present analysis, however, they appear only as simple parameters independent of H. This analysis is based on the determination of the effective masses through the slope of a semilog plot thereby avoiding any dependence upon A or B, which have a doubtful theoretical interpretation. The foundation of this approach thus rests on the fact that the hyperbolic sine factor, or its exponential approximation,[24] and the cosine function[25] are the same in the theories for the susceptibility[23,26,17] and in the galvanomagnetic effects[17,18,27] even for the case of general band structure.[17] A complication arises as to the exact functional form of the term H^s. A value of $s=-\frac{1}{2}$

[19] G is similar to the ratio E_x/E_y, the inverse of that used by Borovik; see reference 9.

[20] R. B. Dingle, Proc. Roy. Soc. (London) **A211**, 517 (1952).

[21] L. Onsager, Phil. Mag. **43**, 1006 (1952).

[22] I. M. Lifshitz; see notes added in proof of D. Shoenberg, *Progress in Low-Temperature Physics* (North-Holland Publishing Company, Amsterdam, 1957), Vol. 2, 263.

[23] L. D. Landau; see appendix of D. Shoenberg, Proc. Roy. Soc. (London) **A170**, 341 (1939), and in modified form in A. H. Wilson, *Theory of Metals* (Cambridge University Press, London, 1953), p. 171.

[24] This approximation is used quantitatively only for $H \leq 5$ kilogauss where the error is $<0.1\%$.

[25] The phases, ϕ_i, are an exception since as yet they have not been clearly defined.

[26] M. Blackman, Proc. Roy. Soc. (London) **A166**, 1 (1938).

[27] E. G. Grimsal, doctoral thesis, Louisiana State University, 1955 (unpublished).

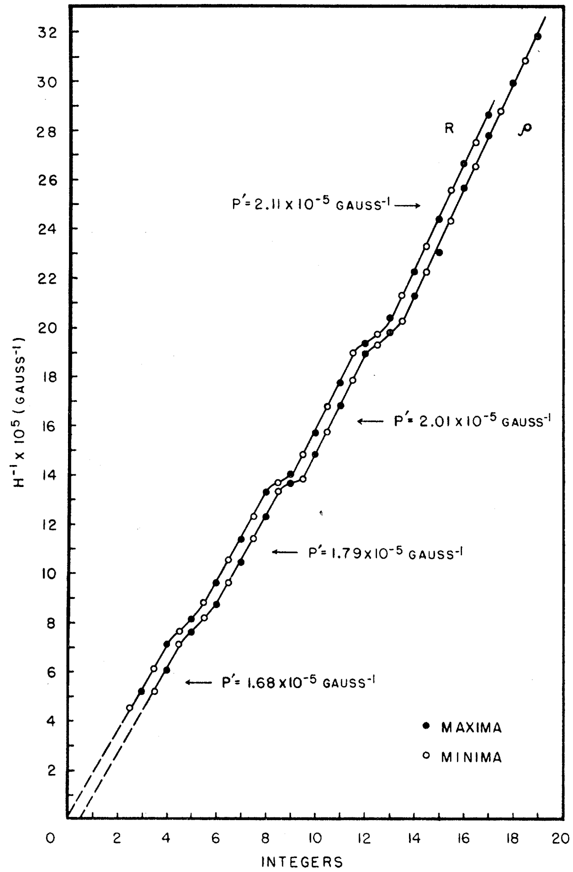

FIG. 1. Integer plot of magnetoresistivity and Hall coefficient extrema. The values of P' are the average observed periods.

is used here. This point will be discussed in Sec. D of the results.

One approximation inherent in the theory of the de Haas-van Alphen effect under which Eq. (2) holds is

$$kT/\beta^*H \lesssim 1. \tag{7}$$

This requires that the magnetic energy level separation be larger than the thermal broadening. Another is

$$kT/E_0 \ll 1. \tag{8}$$

In this approximation, Fermi statistics can be applied. And finally,

$$\beta^*H/E_0 \ll 1. \tag{9}$$

Here, the number of quantum levels below the Fermi level must be large in order that the Fresnel integrals in the derivation[23] may be evaluated at infinite limits. These are well satisfied in the present case, with the possible exception of (9) toward the highest field measured, 25 kilogauss, where there are only three remaining filled quantum levels (see Sec. A of the results).

IV. RESULTS AND DISCUSSION

A. Periods

The dependence of the Hall coefficient upon the magnetic field at 4.2°K is shown in Fig. 2 of the preceding paper[16] while the magnetoresistance results are given in Fig. 4. of that paper. Empirical[28] midlines are shown by the dashed lines. The results for crystal EP-7 are included showing the striking similarity to EP-14, the crystal for which this analysis is made. The oscillations are very pronounced in the high-field range, being 20% of the nonoscillatory component at 20 kilogauss in the case of the magnetoresistance and 38% for the Hall coefficient. They were observed down to about 2.9 kilogauss where they amounted to 0.22% and 0.37%, respectively.

Integer plots for R and ρ are shown in Fig. 1 with the corresponding $H^{\frac{1}{2}}G$ function with damping removed shown in Fig. 2. As will be noted in these two diagrams, the two oscillatory components mesh and unmesh every four of the observed cycles. This four-cycle interval, $4P_{\mathrm{Av}}'$, must be an integer multiple of each of the component periods or

$$lP_1 = rP_2 = 4P_{\mathrm{Av}}'. \tag{10}$$

It was found that only values of $l=3$ and $r=4$ reproduced the observed curve. This 3 to 4 ratio, also found by Shoenberg in the susceptibility, is apparently quite insensitive to impurity content. Analysis of both R and

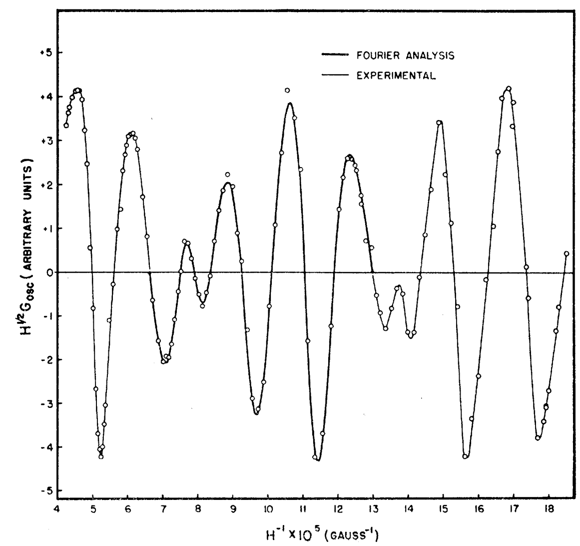

FIG. 2. Oscillatory component of the galvanomagnetic ratio with damping removed. The Fourier analysis, extended to the eighth harmonic and indicated by the heavy curve, was made over the interval from 6.65×10^{-5} gauss^{-1} to 13.01×10^{-5} gauss^{-1}. The lighter curve is empirically fitted.

[28] This midline fitting was complicated by the presence of two oscillatory components with similar periods. An iteration process was developed where use was made of the insensitivity of an integer plot to the exact trial midline and of the insensitivity to the cosine function of the extrema amplitudes located in the constructive interference regions.

TABLE I. Periods from galvanomagnetic de Haas-van Alphen type oscillations.

Measurement	$P_1\times10^5$ (gauss^{-1})	$P_2\times10^5$ (gauss^{-1})
Magnetoresistance	2.12 ± 0.08	1.59 ± 0.06
Hall coefficient	2.08 ± 0.05	1.56 ± 0.04

ρ over the interval from 3 to 11.5 (see Fig. 1) gives the period values shown in Table I.

There is thus essential agreement between the two effects within experimental error. The average P_1 value is further substantiated by the average value of 2.11×10^{-5} gauss^{-1} measured directly for the period observed in the low-field region where P_2 has sufficiently damped out. The period P_2 is then three fourths of this value. It is interesting to correlate these latter results with those observed previously from susceptibility, magnetoresistance, and Hall effect measurements as is done in Table II where the temperatures indicated are the lowest at which measurements were taken. It will be seen that there is reasonable agreement between these values.

These measurements show, in addition to the results discussed in the preceding paper, that the major reason for finding a second period here is undoubtedly the initial crystalline perfection of these crystals plus their increased purity due to purification.

The assignment of the particular type of carrier that is related to each of the oscillatory periods cannot in this case be made from the de Haas-van Alphen effect alone. Actually, this is done by referring to the cyclotron resonance results[29] noting that the electron is the lighter carrier (see Table IV). The longer dominant period is related to the lighter carrier and hence to the electrons. Similar identification is made for the holes.

Further information can be derived from the integer plot in Fig. 1 by extrapolating to $1/H=0$ as shown by the dashed lines. It is then observed that only about three more oscillations would be expected if the measurements were carried to infinite H. Even at the highest extremum, 22.2 kilogauss, the carriers have already been magnetically condensed down to the third quantum level in graphite. This approach to the limit of a small number of filled quantum levels, where approximation (9) breaks down, is also indicated by the cusplike shape of the last oscillation occurring at 5.25×10^{-5} gauss^{-1} as shown in Fig. 2. Such a behavior resembles more closely the exact relation obtained by Peierls[30,31] for a free-electron gas at 0°K where approximation (9) used in applying the Poisson summation formula was not made. This effect has also been observed and discussed for the case of bismuth by Babiskin.[5]

TABLE II. De Haas-van Alphen periods in graphite determined from several measurements.

Measurement	$P_1\times10^5$ (gauss^{-1})	$P_2\times10^5$ (gauss^{-1})	T (°K)	Reference
Susceptibility	2.20	1.65	1.27	Shoenberg[a]
Susceptibility		1.61[b]	1.36	Berlincourt
Magnetoresistance	2.15	...	1.37	and
Hall coefficient		...	1.37	Steele[c]
Magnetoresistance	2.12 ± 0.01	1.59 ± 0.01	4.2	Present
Hall coefficient	2.10 ± 0.01	1.57 ± 0.01	4.2	results

[a] See reference 14.
[b] This value is taken as ¾ of 2.15×10^{-5} gauss^{-1}, though not quoted by the authors.
[c] See reference 15.

[29] Galt, Yager, and Dail, Phys. Rev. **103**, 1586 (1956).

B. Phases and Harmonics

Figure 1 shows that there is a phase difference of π between the oscillations in the magnetoresistance and the Hall coefficient taking the sign of R into account. This is contrary to the results of Berlincourt and Steele who found a phase difference of $\pi/4$. Apparently, this

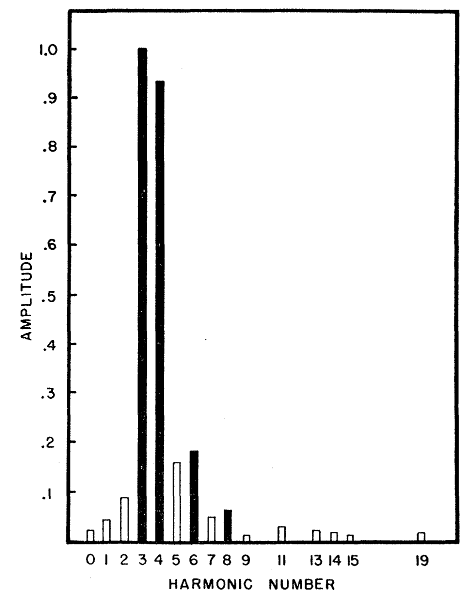

FIG. 3. Harmonic amplitudes from Fourier analysis normalized to the third harmonic. The dominant terms are shown in solid bars along with their respective first harmonics.

difference is a matter of sample purity where the relative electron and hole contributions are affected. In general, the orientation of H with respect to the crystallographic axes also affects this phase difference.[4] It is interesting to find that similar results to those obtained here have been found for the case of H parallel to the principal axis with Bi,[4] Zn,[8] and Ga,[11] where it was found that $|R|$ was in phase with ρ in the high-field range. On the other hand, phase differences[9,32] of π and intermediate values[10] have also been observed. It will require considerably more careful work to understand this phase of the problem.

[30] R. Peierls, Z. Physik **81**, 186 (1933).
[31] This was kindly pointed out to the author by J. Babiskin.
[32] N. E. Alekseevskii and N. G. Brandt, Proceedings of the Conference on Low-Temperature Magnetism, Kharkov, 1954 (unpublished).

To determine the absolute phases, a Fourier analysis was made. In addition, information was simultaneously obtained about the total harmonic content. The average damping was first removed by an exponential fit to the total $H^{\frac{1}{2}}G$ function over the repeat interval[33] from 6.65×10^{-5} gauss^{-1} to 13.01×10^{-5} gauss^{-1}. The analysis, carried out on an IBM-650 computer, was extended to the twentieth harmonic. A histogram of the normalized harmonic amplitudes is shown in Fig. 3 demonstrating that the third and fourth harmonics are indeed dominant. The first harmonics of each of these (solid black bars) are also seen to be present, amounting to about 18% or less of their respective fundamentals. Since only those harmonics from 2 to 8, containing 92% of the total, are significant, the sum of these is plotted (heavy black line) in Fig. 2 showing the fit to the experimental data.

The phases of the dominant terms are $\phi_1=0.347\pi$ for the third harmonic and $\phi_2=0.859\pi$ for the fourth harmonic. Zilberman obtained a theoretical value of $\pi/4$ for both ϕ_1 and ϕ_2. Evidently, the theory concerning this point has been oversimplified and requires further careful evaluation.

While the third and fourth harmonics are comparable in magnitude in this region, the fourth with its larger effective mass (see Table IV) damps out at a faster rate upon going to lower magnetic field as shown in Eq. (2). In addition, the damping of any harmonic increases with its order as is also shown in Eq. (2). Consequently, it would be expected that at a low enough field, only the third harmonic (electron) would remain as the dominant term. This is seen to be the case as is shown in Figs. 1 and 5. Additional proof is evidenced by the fact that when the calculated third Fourier harmonic was extrapolated to the field region beyond $H^{-1}\simeq21\times10^{-5}$ gauss^{-1}, it was found to be exactly in phase with the oscillations measured in that region.

In the low-field region below 6 kilogauss, a subordinate oscillatory component was found. The oscillations occur as sharp indentations in the primary oscillation extrema causing a double-peaked appearance. They appear in both V_ρ, the measured magnetroresistance voltage drop, and V_H, the Hall voltage, with a phase difference of π. One of the two or more periods that make up this component is approximately 1.64×10^{-5} gauss^{-1}. Consequently, they are probably not beat periods of the primary oscillations or harmonics since not only are the period values wrong, but also harmonics would be expected to become more evident at higher fields as shown in Eq. (2). Recent evidence indicates that they may be due to a size effect.

A general search for any auxiliary small-period oscillations was also made in the high-field region where V_ρ and V_H were measured very accurately on the K-2 potentiometer over the limited region from 21.8 to 23.3 kilogauss as is shown in Fig. 4. Additional oscillatory components could not be detected in this range.

C. Amplitude Dependence upon Magnetic Field

The dependence of the total oscillation extrema envelope of $H^{\frac{1}{2}}G$ upon $1/H$ is shown in Fig. 5. The alternate regions of constructive and destructive interference can be seen, gradually diminishing in size with decreasing field as the electron component becomes increasingly more dominant. The slope of the superimposed envelope gives a certain average effective mass ratio, a'. This ratio progresses from a value of 0.056 down to 0.031 where all but the electron component have essentially damped out.

The contribution of just the electron component throughout the region measured was determined by evaluating $H^{\frac{1}{2}}G$ at points where the hole component was zero, and making the suitable cosine corrections where the remaining harmonics were neglected. The resultant electron effective mass ratio, a, was found to be 0.030 in good agreement with the above-mentioned asymptotic value. The best value of a within the intrinsic accuracy of the theory is 0.030 ± 0.002. This electron contribution is also shown in Fig. 5 normalized at the point of tangency where the value for A was found to be 0.0090 ohm coul cm^{-2} gauss$^{\frac{1}{2}}$.

With the electron term evaluated, it was then subtracted from the total $H^{\frac{1}{2}}G$ to obtain the residual hole component with accompanying small additions due to the remaining harmonics. A plot of the extrema positions of this residual is shown in Fig. 6, where the slope gives the hole effective-mass ratio, $b=0.060$, which is

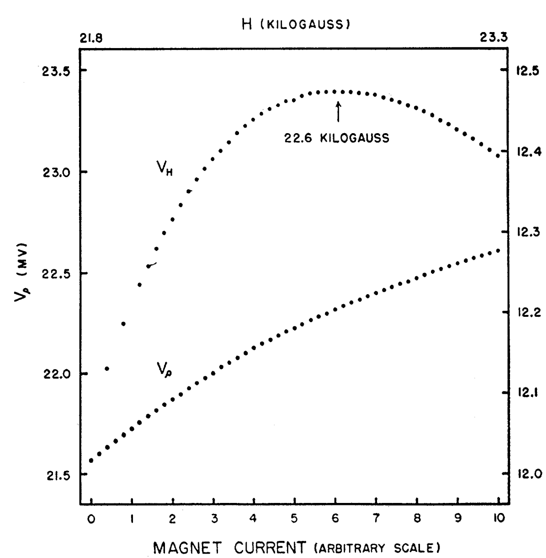

FIG. 4. Amplified plot of the first extremum in V_H and V_ρ employed in a search for an additional smaller period.

[33] This region was limited because a single exponential fit could not be made over a more extended region. Also, the highest-field region was avoided because of the cusp-like distortion resulting from an inapplicability of the theory and inaccuracy in the mid-line determination.

somewhat less accurate than the electron value. The corresponding hole amplitude parameter, B, was found to be 0.051 ohm coul cm^{-2} gauss$^{\frac{1}{2}}$ as determined from the ratio of the hole component to the total function averaged over the region where Fourier analysis was made as indicated in Fig. 3. This fraction is 38% as compared to the corresponding electron contribution of 40%.

D. Analytical Approximations

1. Collision Damping

Collision damping has been considered small here compared to thermal damping, that is $\Delta T_i \ll T$. This relation is satisfied in the present case as determined in two ways. The oscillatory structure of the de Haas-van Alphen effect becomes more distinct with decreasing temperature and increasing sample purity. Shoenberg observed two periods in the susceptibility below 1.4°K which, in addition, shows more structure than the galvanomagnetic effects. Comparison of his results with those of Berlincourt and Steele shows that their crystals were roughly comparable in the degree of oscillatory structure in the susceptibility. Shoenberg calculated a value of $\Delta T \simeq 1.5 \pm 0.5$°K. Since the structure observed here at 4.2°K is at least as sharply defined as that seen by Berlincourt and Steele at $\sim$1.4°K, then the present value is very approximately

$$\Delta T \lesssim 1.5° - (4.2° - 1.4°).$$

Secondly, ΔT has been calculated independently using the effective mass values derived here and the mobility values found from the nonoscillatory components.[34] The resultant ΔT values calculated from Eq. (3) are

$$\Delta T_e = 0.17\text{°K}, \quad \Delta T_h = 0.068\text{°K},$$

for the electrons and holes, respectively. Thus, the ΔT's are $\leq 4\%$ of T. Consequently, the effect of collision damping is small in EP-14.

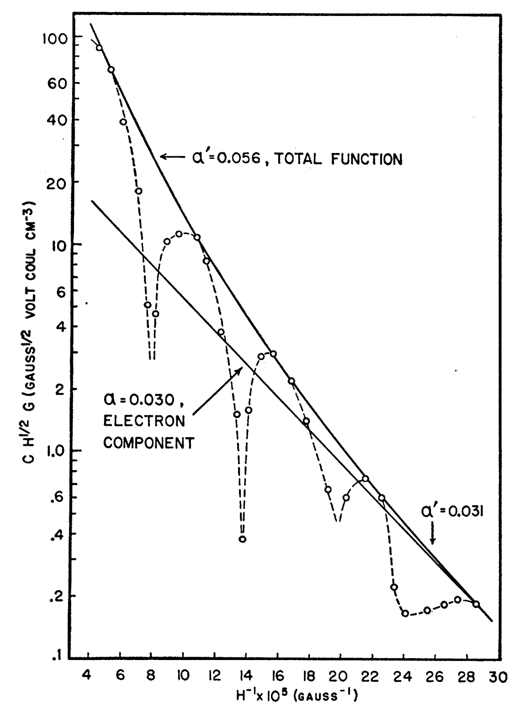

FIG. 5. Galvanomagnetic ratio extrema envelope. Both maxima and minima are plotted. The dashed curve is the extrema envelope itself while the solid curve is a superimposed envelope, the slope of which represents an average effective mass ratio, a'. $C = 3.98 \times 10^3$ amp/cm.

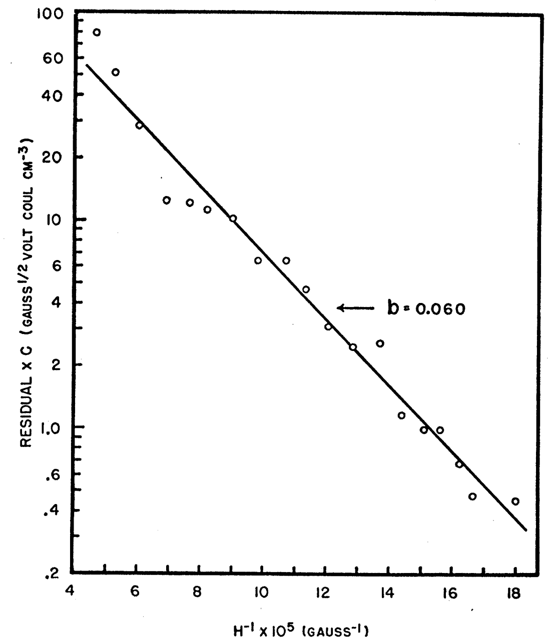

FIG. 6. Residual hole component extrema of the galvanomagnetic ratio. The hole effective mass ratio, b, is proportional to the slope. $C = 3.98 \times 10^3$ amp/cm.

2. Field Dependence

Throughout this analysis, a value of $s = -\frac{1}{2}$ obtained by Zilberman was used for the H^s term in Eq. (2). There is still the unsettled question of whether a value of $+\frac{1}{2}$, calculated by Lifshitz *et al.*, might represent a more appropriate form. Consequently, the latter value was also used to test the resultant difference made in the final effective mass value. This latter value reduced the electron effective mass ratio by only 6.5%.

V. CONCLUSIONS

Two dominant periods have been observed in the magnetoresistance and Hall effect which correspond to those observed in the susceptibility by Shoenberg and by Berlincourt and Steele. Estimates of the carrier

[34] For this analysis, see J. W. McClure, following paper [Phys. Rev. **112**, 715 (1958).

TABLE III. Carrier densities determined from the galvanomagnetic de Haas-van Alphen periods and from the nonoscillatory component of the galvanomagnetic effects in *EP*-14 at 4.2° K.

	$n_{\mathrm{osc}}\times10^{-18}$ (cm^{-3})	$n_{\mathrm{nonosc}}\times10^{-18}$ (cm^{-3})
Electrons	2.8	3.1
Holes	2.2	2.7

densities determined from these periods using Eq. (6) are 5.86×10^{16} cm^{-3} and 9.00×10^{16} cm^{-3} for P_1 (electrons) and P_2 (holes), respectively. The Fermi surfaces calculated for graphite by McClure[35] consist of four electron ellipsoids and two hole ellipsoids. These ellipsoids, having major-to-minor axis ratios of approximately 12:1, are slightly distorted from a true ellipsoidal shape and are oriented with their major axes parallel to the hexagonal crystallographic axis. The above density values suitably corrected for ellipsoid number and eccentricity are compared in Table III with those obtained from the nonoscillatory high-field components calculated in the previous paper.[16]

It might be mentioned that additional substantiation is given by the results obtained with crystal *EP*-7. While not analyzed in detail, it showed similar periods and, hence, similar n_{osc} values. The n_{nonosc} values are about 2.1×10^{18} cm^{-3} for both the electrons and holes. These results show that in the case of graphite, the carriers responsible for the major nonoscillatory galvanomagnetic effects are probably also responsible for the de Haas-van Alphen effects. They are the *normal* majority carriers. The identification as to whether they are electrons or holes, as was pointed out previously, is made by reference to the cyclotron resonance results. Eventually, an independent method will be used where the increase or decrease of the respective periods with acceptor or donor doping will be studied. This has the advantage of being internally consistent within the galvanomagnetic measurements themselves.

It is interesting to compare the effective mass ratios calculated here as evaluated at the maximum cross sections of the Fermi surfaces with values obtained from other types of measurement as is done in Table IV. As shown in the table, there is substantial agreement between the respective values. This is especially true with the cyclotron resonance values, believed to be the most accurate of the first two methods. This agreement further supports the contention that these electrons and holes are the normal conduction carriers.

The respective Fermi energies have been calculated from Eq. (5) to be 0.018 ev for the electrons and 0.012 ev for the holes. The band overlap for graphite is consequently equal to about 0.30 ev. With such a small overlap, large changes would be expected to be found for only a small shift of the Fermi level accomplished by such means as impurity doping. In addition, from Eq. (3) with the mobility values, the most probable relaxation times in *EP*-14 at 4.2° K are

$$\tau_e=1.4\times10^{-11}\text{ sec},$$
$$\tau_h=3.5\times10^{-11}\text{ sec}.$$

At low magnetic fields, effects due to light minority carriers, that are strongly sensitive to the position of the Fermi level, have been observed in the Hall effect and are described in the preceding paper.[16] There is only a small probability that oscillations due to these light carriers would be detected because of their small number ($\lesssim0.1\%$ of the majority carrier densities).[16,34] Also, their periods would be longer (light-to-normal mass ratio roughly 0.5)[36] thus making them difficult to differentiate in practice from the beat frequency of the two dominant periods. The presence of m^* in the hyperbolic-sine term of Eq. (2), however, would tend to increase the amplitude, but only by $\simeq60\%$.

TABLE IV. Effective mass values of the majority electrons and holes in graphite evaluated at the maximum cross sections of the Fermi surfaces by different methods.

Measurement	m_e^*/m_0	m_h^*/m_0	Reference
Susceptibility, de Haas-van Alphen temperature dependence	0.036	$\sim$0.07	Shoenberg[b]
Cyclotron resonance[a]	0.031	0.066	Galt, Yager, and Dail[c]; Nozières[d]
Galvanomagnetic effects, de Haas-van Alphen field dependence	0.030	0.060	Present results

[a] These values are taken at the maximum dn_e/dm for electrons and at the maximum cutoff of dn_h/dm for the holes in order to make a proper comparison with the de Haas-van Alphen values.
[b] See reference 14.
[c] Experimental measurements; see reference 29.
[d] Theoretical interpretation; P. Nozières, Phys. Rev. **109**, 1510 (1958).

The general functional form of the H^s term is still theoretically uncertain, and requires further study. For an exact and unequivocal experimental determination of H^s, it would probably be necessary to analyze a curve that contained only one oscillatory component. Such a study for graphite might be successfully carried out at higher temperatures and/or lower fields.

ACKNOWLEDGMENTS

The author wishes to express his appreciation to Dr. J. W. McClure for many interesting and valuable discussions and to Miss B. J. Vizi and Mr. A. L. Cline for assistance during the course of this work. Additional thanks are due to Mr. M. Janes for help in performing the Fourier analysis on the IBM-650 computer.

[35] J. W. McClure, Phys. Rev. **108**, 612 (1957).

[36] B. Lax and H. J. Zeiger, Phys. Rev. **105**, 1466 (1957).