Analysis of Multicarrier Galvanomagnetic Data for Graphite

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The magnetic-field-dependent data of Soule for the Hall effect and magnetoresistance in graphite have been analyzed using a multicarrier model. An improved mode of analysis is used, in which the magnetoconductivity tensor elements are computed as functions of magnetic field strength from experimental data, and then fitted to simple formulas. The formulas represent solutions to the Boltzmann equation in the classical (nonoscillatory) range. The effects of electrons and holes are separated by applying a Kramers-Kronig type relation. The results, which agree with band-model predictions within 20 to 50%, are that there are 2.9×10^{18} holes and electrons per cm³ in pure graphite at 4.2°K, and 7.0×10^{18} cm^{-3} each at 300°K. The mobilities range from about 9×10^5 cm²/volt sec at 4.2°K to 1.0×10^4 cm²/volt sec at 300°K, with the hole-to-electron mobility ratio being 1.2 and 0.9 at the two temperatures. In addition, at room temperatures there are about 6×10^{14} minority holes per cm³ with a mobility of 15×10^5 cm²/volt sec and 5×10^{14} minority electrons per cm³ with a mobility 4×10^5 cm²/volt sec. The relaxation times for the majority carriers are distributed over a range of a factor of four. The average relaxation times are consistent with those deduced from cyclotron resonance experiments.

1. INTRODUCTION

THE two-band model for the understanding of the magnetic field dependence of electrical resistance was introduced by Blochintzev and Nordheim.[1] Numerous authors have contributed to the theory by including the Hall effect, and by considering various cases.[2–6] A discussion of the two-band model is given in Wilson's book.[7] Jones made early use of the theory to treat the magnetic-field-dependent effects in bismuth.[2] Several recent works have used the theory to analyze experiments, obtaining estimates of carrier densities and mobilities.[8–12] Most of these authors have fitted the experimental data for the Hall coefficient and magnetoresistance to specific formulas based on special assumptions. On the whole, the results have been successful and the estimates obtained reasonable.

However, there are many advantages to inverting the above procedure and obtaining the elements of the magnetoconductivity tensor[13] as functions of magnetic field directly from the experimental data, and then comparing with theory.[10,14] Firstly, the effects of different groups of carriers on the magnetoconductivity tensor elements are additive, whereas their effects on the Hall coefficient and magnetoresistance are given by complicated formulas. Further, as will be shown below, it is sometimes possible to separate the effects of carriers of different sign and to obtain carrier densities and mobilities without making assumptions as restrictive as heretofore. Finally, when it is desired to fit the data to a specific theory, the formulas for the magnetoconductivity tensor elements are simpler than those for the directly measured quantities, so that the process of curve-fitting is more easily carried out.

In Sec. 2 we develop the necessary theory, and in Sec. 3 we apply it to the data of Soule for graphite.[15] In Sec. 4 the results of Kinchin for graphite are discussed, and final conclusions are presented in Sec. 5.

2. THEORY

We restrict ourselves to the case of a conductor which has an axis of symmetry parallel to the magnetic field. Such is the case in the graphite experiments which we shall analyze. In fact, the majority of the carriers in graphite are associated with Fermi surfaces which have rotational symmetry about the c axis.[16] As the current is restricted to the layer planes, and this is perpendicular to the magnetic field, we need deal with only two independent elements of the magnetoconductivity tensor, σ_{xx} and σ_{xy} (the magnetic field is oriented parallel to the z axis, which is parallel to the c axis).

Assuming that the Boltzmann equation is valid to all fields with a relaxation time which is constant on precession orbits in k space (the relaxation time may have any dependence on energy and k_z), and making use of the fact that the orbits are practically circular,

* A portion of the work reported herein was performed while the author was on the staff of the University of Oregon, Eugene, Oregon.

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[1] D. Blochinzev and L. Nordheim, Z. Physik **84**, 168 (1933).

[2] H. Jones, Proc. Roy. Soc. (London) **A155**, 653 (1936).

[3] E. Sondheimer and A. Wilson, Proc. Roy. Soc. (London) **A190**, 435 (1947).

[4] E. Sondheimer, Proc. Roy. Soc. (London) **A193**, 484 (1948).

[5] M. Kohler, Ann. Physik **5**, 89, 99 (1950); **6**, 18 (1949).

[6] R. G. Chambers, Proc. Phys. Soc. (London) **A65**, 903 (1952).

[7] A. H. Wilson, *Theory of Metals* (Cambridge University Press, Cambridge, 1953), second edition, p. 198. See also J.-P. Jan, *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1957), Vol. 5, p. 1.

[8] Willardson, Harman, and Beer, Phys. Rev. **96**, 1512 (1954).

[9] E. S. Borovik, J. Exptl. Theoret. Phys. (U.S.S.R.) **27**, 355 (1954); Izvest. Akad. Nauk, S.S.S.R., Ser. fiz. **19**, 429 (1955).

[10] Adams, Davis, and Goldberg, Phys. Rev. **105**, 865 (1956).

[11] B. R. Coles and J. C. Taylor, J. Phys. Chem. Solids **1**, 270 (1957).

[12] Howarth, Jones, and Putley, Proc. Phys. Soc. (London) **B70**, 124 (1957).

[13] For a discussion of the determination of the magnetoconductivity, see R. M. Broudy and J. D. Venables, Phys. Rev. **105**, 1757 (1957).

[14] R. G. Chambers, Proc. Roy. Soc. (London) **A238**, 344 (1956).

[15] D. E. Soule, this issue [Phys. Rev. **112**, 698 (1958)].

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

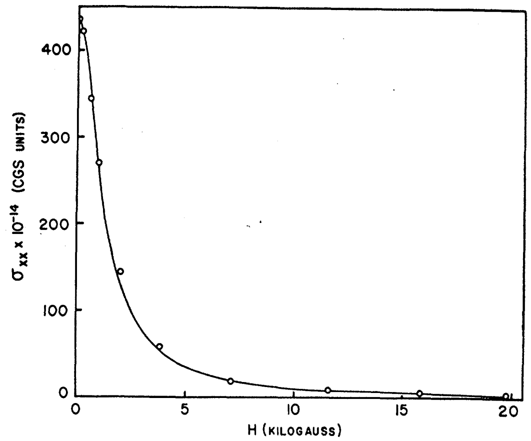

FIG. 1. The diagonal magnetoconductivity of graphite in the layer plane, with the magnetic field parallel to the c axis. The curve is for sample $EP14$ at 77°K. The circles are experimental points, and the line is a theoretical curve consisting of two "Lorentz" terms.

the conductivity components may be written[17]

$$\sigma_{xx}=\sigma_{xx}{}^p+\sigma_{xx}{}^n=\int\frac{ds\, g_p(s)}{1+(sH)^2}+\int\frac{ds\, g_n(s)}{1+(sH)^2}, \tag{2.1a}$$

$$\sigma_{xy}=\sigma_{xy}{}^p+\sigma_{xy}{}^n=\int\frac{ds\, g_p(s)sH}{1+(sH)^2}-\int\frac{ds\, g_n(s)sH}{1+(sH)^2}. \tag{2.1b}$$

In the preceding, σ^p and σ^n stand for partial conductivities due to positive and negative carriers, H is the magnetic field, g_p and g_n are distribution functions for the positive and negative carriers, and limits of integration are from 0 to ∞. The formulas allow the cyclotron frequency to depend upon energy and k_z, which it does in graphite.[18] An important fact in the present analysis is that the number of carriers is given by the high-field behavior of σ_{xy}.[5,19,20] Specifically, we have

$$pec=\int ds\, g_p(s)/s, \tag{2.2}$$

where p is the number of holes per cm^3, e the electron charge, and c is the velocity of light. A similar relation holds for the electrons.

It is seen that if one has experimental data covering a great enough magnetic field range, and if the electron and hole terms could be separated, the number of each kind of carrier can be found. The separation can be effected by using the Kramers-Kronig relations,[21] yielding

$$\frac{P}{\pi}\int\frac{dH'}{H-H'}\sigma_{xx}(H')=\sigma_{xy}{}^p-\sigma_{xy}{}^n, \tag{2.3a}$$

$$\frac{P}{\pi}\int\frac{dH'}{H-H'}\sigma_{xy}(H')=-\sigma_{xx}{}^p+\sigma_{xx}{}^n. \tag{2.3b}$$

In the above, the limits of the integrals are from $-\infty$ to $+\infty$; the symbol P means that the principal part of the integral is to be taken. It is seen that by applying the relation, and then adding and subtracting, the individual σ's for positive and negative carriers can be obtained. If there are only carriers of one sign, separation is not effected, but a consistency check is provided, which has been used by Adams.[22] Once the partial conductivities have been obtained, the total number of electrons and total number of holes can be found by using (2.2). As the zero-field partial σ_{xx}'s are also known, the average mobility of electrons and average mobility of holes can be found. Furthermore, information is contained in the manner in which the partial conductivities depend on magnetic field. If, for example, there are two kinds of holes, it should appear in the field dependence. The scattering law (dependence of relaxation time on energy and k_z) affects the field dependence, and it may be possible to deduce information concerning the law from the form of the partial conductivities.

It is important to note that the carrier densities and mobilities can be found without having to deal with integrands containing singular points. The total number of carriers (electrons plus holes) is proportional to the area under the total σ_{xx} curve,

$$(n+p)ec=(2/\pi)\int_0^\infty dH\sigma_{xx}(H), \tag{2.4a}$$

and the difference in zero-field conductivities is likewise an integral,

$$\sigma_{xx}{}^p-\sigma_{xx}{}^n=(2/\pi)\int_0^\infty dH\sigma_{xy}/H. \tag{2.4b}$$

Equation (2.4b) does not have a singular point, as Eq. (2.1b) shows that σ_{xy} is proportional to H for low values of H.

3. APPLICATION TO GRAPHITE

The magnetoconductivity tensor elements were calculated from the experimental data of Soule[15] by the following simple formulas which hold in this case:

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

$$\sigma_{xy}=\sigma_{xx}(R\sigma H), \tag{3.1b}$$

where σ is the experimental conductivity and R is the

[17] Results of this form have been obtained by many authors. See, for example, J. W. McClure, Phys. Rev. **101**, 1642 (1956).
[18] P. P. Nozières, Phys. Rev. **109**, 1510 (1958).
[19] J. A. Swanson, Phys. Rev. **99**, 1799 (1955).
[20] Lifshitz, Azbel, and Kaganov, J. Exptl. Theoret. Phys. (U.S.S.R.) **31**, 63 (1956) [translation: Soviet Phys. JETP **4**, 41 (1957)].
[21] See, for example, R. Kronig, J. Opt. Soc. Am. **12**, 547 (1926). The relations (2.3) can be proved by substituting from Eqs. (2.1) and carrying out the integral over H'.
[22] E. N. Adams (private communication).

Hall coefficient, all in cgs units. Then, the σ_{xx} and σ_{xy}/H were fitted to a linear combination of "Lorentz curves,"

$$S=\sum_n\{A_n/[1+(H/H_n)^2]\}, \tag{3.2}$$

using the method of least squares to choose the best values of A_n's and H_n's in two- or three-term expressions.[23] The justification for the form of (3.2) is that we are replacing integrals over peaked distribution functions by the integrand at the peak. Expression (3.2) has the correct behavior in small and large magnetic fields and, in fact, we find with two or three terms it is capable of representing the σ's to accuracies ranging from 1% to 5% for different curves. Of course, it is not necessary to make analytical fits to the curves in order to integrate and find the total carrier densities and average mobilities for electrons and holes. However, in some of the cases there are two types of electrons (or holes), so that curve fitting is the only way to effect separation. Even if the curves were not fitted, it would be necessary to extrapolate to high fields in order to get the complete integral. Finally, with the type of analytic formula used it is especially easy to apply the Kramers-Kronig relations. Two of most satisfactory σ's are exhibited in Figs. 1 and 2. Note that Fig. 2 is a plot of $H\sigma_{xy}$ *versus* $1/H$, which is described by a formula of the type (3.2) with H replaced by $1/H$. The final fitting parameters are listed in Table I.

If we insisted that each term in (3.2) represented a single type of carrier, and required the Kramers-Kronig relation to apply term by term, then our procedure would be equivalent to the simplest two-band model, though carried out in terms of the σ's. However, we regard the analytical representation of the σ's to be a convenient step in applying the Kramers-Kronig relation to the entire σ. Thus, we allow each fitting parameter to be adjusted completely independently, and then interpret combinations of the fitting parameters instead of individual parameters.[24] That the latter procedure is better is borne out by experiments in changing the weighting of the data points in the least-squares fitting; for though individual parameters are affected considerably ($\simeq$20%), the over-all fit and integrals are not much changed.

TABLE I. Parameters from least-squares fit of magnetoconductivity tensor elements. Substitution of parameters in Eq. (3.2) gives a representation of the indicated quantity. All quantities are in cgs (Gaussian) units.

Sample	Temp. (°K)	A_1	H_1	A_2	H_2	A_3	H_3
			For $\sigma_{xx}\times10^{-14}$				
*EP*14	4.2	1430	267	5720	74.4	1.63	17 750
*EP*14	77	416	1230	19.2	6630		
*EP*14	298	181	7290	36.0	19 800		
*EP*7	4.2	442	428	341	116	1.7	14 000
*EP*7	77	358	1190	60.9	3710		
*EP*7	300	181	7200	38.3	22 000		
			For $(\sigma_{xy}/H)\times10^{-11}$				
*EP*14	4.2	−1240	267	15 010	74.4		
*EP*14	77	−87.4	1410	128	1140	15	180
*EP*14	300	−2.22	6870	0.123	28 300	−1.09	260
*EP*7	4.2	−236	487	2220	145		
*EP*7	77	−210	1240	315	1000	500	50
*EP*7	300	−2.28	6850	0.0863	32 010	18.3	67

[23] The least-squares fit was accomplished by an IBM–650 computer, using an iterative procedure.

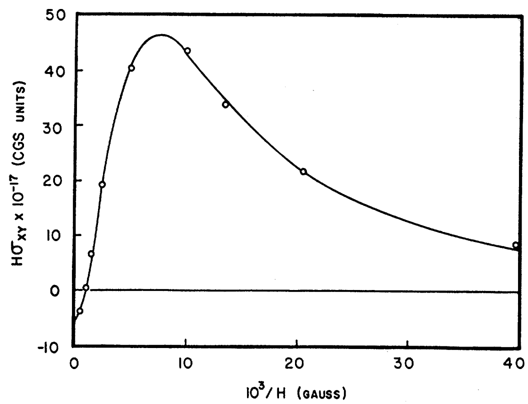

FIG. 2. The off-diagonal magnetoconductivity of graphite in the layer plane, with the magnetic field parallel to the c axis. The curve is for sample *EP*14 at 4.2°K. The circles are experimental points, and the line is a theoretical curve made up of two "Lorentz" terms, the positive one having less height and greater width.

There are several facts about the results displayed in Table I which must be noted. At 4.2°K, careful consideration was given only to the field region below 2 kilogauss (only these points are shown in Fig. 2), because of the oscillatory behavior at higher fields. The oscillations are treated by Soule,[25] but an analysis of the entire behavior is postponed. The first two terms in the table for 4.2°K fit the low-field results, and the third term is added to make the curve follow a rough average at higher fields. At the other temperatures the entire field range was utilized and the third terms were added when necessary, usually to fit a very striking feature of the curve. Theoretical Hall coefficients and magnetoresistances were calculated from the fitted formulas, some of the results being exhibited in Figs. 3 to 6. In general, the calculated magnetoresistance reproduced the experimental quantity extremely well, and the greatest deviations are in the Hall coefficient.

The resulting carrier densities and mobilities are listed in Table II. The results are in harmony with the qualitative prediction which can be made from the Hall effect: since the high-field Hall effect is negative, electrons outnumber holes; since the low-field Hall effect is positive at the lowest two temperatures, the holes must have the higher mobility at those temperatures. The total number of electrons and of holes have been determined by applying the Kramers-Kronig relation to the entire σ's, as outlined above. The first two terms

[24] In an earlier report [J. W. McClure, Bull. Am. Phys. Soc. Ser. II, **1**, 255 (1956)], the individual parameters were interpreted, with much less satisfactory results than in the present paper.

[25] D. E. Soule, preceding paper [Phys. Rev. **112**, 708 (1958)].

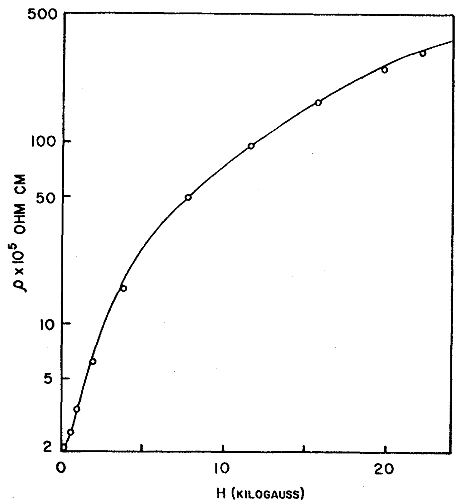

FIG. 3. The magnetoresistance of graphite in the same orientation as Fig. 1. The curve is for sample *EP*14 at 77°K. The circles are experimental points and the line is calculated from theory. Note that the total resistance is plotted.

in each σ are regarded as the combined effects of majority electrons and majority holes. The third term is regarded as representing a minority carrier, as when it is present its H_3 is much more different from H_1 or H_2 than H_1 and H_2 are from each other. With this assumption, the Kramers-Kronig relation applied to the first two terms gives the properties of the majority carriers. Note that the resulting partial σ for a majority carrier usually contains four terms, which represent a distribution of relaxation time (strictly speaking, the product of the relaxation time and cyclotron frequency) over a range of about a factor of four. Using the expressions for the individual σ's, we have calculated the values of the ratio of Hall mobility to conductivity mobility that each carrier would have if present alone. We find values of μ_H/μ_c ranging from 1.2 to 1.6 for both majority carriers at all temperatures. Except at helium temperatures, the third term represents higher-mobility carriers and appears only in σ_{xy}. We applied the Kramers-Kronig relation to it individually to obtain the minority-carrier properties. The predicted σ_{xx} for

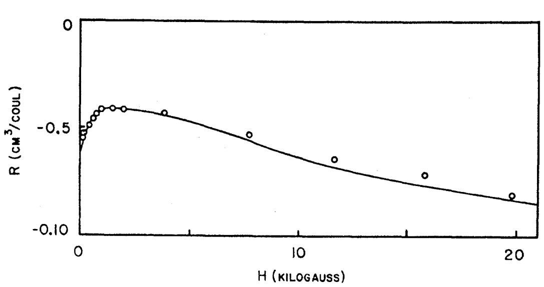

FIG. 4. The Hall coefficient of sample *EP*14 at 298°K, in the orientation of Fig. 1. The circles are experimental points and the line is the theoretical curve. The drop at low field is due to a minority electron.

the minority carrier is a very much smaller fraction of the total σ_{xx} than the minority σ_{xy} is of the total σ_{xy}, explaining why the minority effect is not seen in σ_{xx}. At helium temperatures the situation is reversed, with a low-mobility carrier appearing in σ_{xx} only. The origin of this "slow carrier" will be discussed later. The reason that the high-mobility minority carriers are not seen at helium temperature is presumably because they saturate at magnetic fields which are so low that their effects were not included in the experimental data. The sharp changes in the Hall coefficient in Figs. 4 and 5 are associated with the high-mobility carriers, while that in Fig. 6 is due to the distribution of relaxation times of the majority carriers.

On the whole, the results presented in Table II are satisfactory. It should be pointed out that the sums of the carrier densities for electrons and holes are more reliable than the differences given here. This is because the sums are given by integrals over the entire magnetic field range, whereas the differences rely upon extrapolations to infinite field. An alternate method of obtaining the difference in carrier concentrations by extrapolating the Hall coefficient is discussed by Soule.[15] One possible error in the results is the fact that the majority carrier densities for *EP*14 at 77°K are less than those for the same sample at 4.2°K. There are two explanations for such behavior: (1) electron traps cause the Fermi level to shift in such a way as to reduce the total number of carriers; or (2) the high-magnetic-field extrapolation (discussed below) may be in error. For comparison we have made numerical calculations of carrier densities for pure graphite, using the density-of-states curve given by the Slonczewski-Weiss[26] model, with parameters chosen to fit the de Haas-van Alphen effect.[16] The values are listed in Table II, and compare favorably with those derived here at 4.2°K, the values for higher temperatures falling above those derived

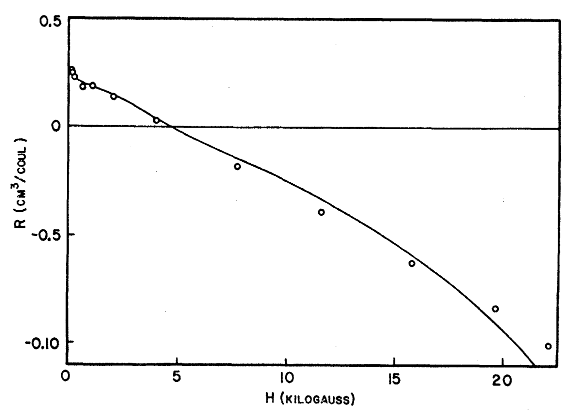

FIG. 5. The Hall coefficient of sample *EP*14 at 77°K, in the orientation of Fig. 1. The circles are experimental points and the line is the theoretical curve. The sharp rise at very low fields is due to a minority hole.

[26] J. C. Slonczewski and P. R. Weiss, Phys. Rev. **99**, 636(A) (1955); **109**, 272 (1958).

TABLE II. The properties of the current carriers in graphite as derived from galvanomagnetic data. The mobilities refer to motion in the layer plane. The row labeled theoretical density is the result of a numerical calculation using the theoretical density of states, as described in the text.

Sample temperature	*EP*14 4.2°K	*EP*14 77°K	*EP*14 298°K	*EP*7 4.2°K	*EP*7 77°K	*EP*7 300°K
Majority hole						
Density$\times 10^{-18}$ (cm^{-3})	2.8_8	2.1_9	7.0_4	2.0_8	2.3_9	7.2_2
Mobility$\times 10^{-4}$ (cm^2/volt sec)	104	7.3_3	1.0_1	$64._5$	6.5_3	0.9_9
Majority electron						
Density$\times 10^{-18}$ (cm^{-3})	2.9_2	2.2_4	7.0_4	2.1_4	2.4_6	7.3_6
Mobility$\times 10^{-4}$ (cm^2/volt sec)	83.9	6.3_8	1.1_3	$59._1$	4.8_6	1.0_9
Hole mobility/electron mobility	1.2_4	1.1_5	0.8_9	1.0_9	1.3_4	0.9_0
Theoretical density$\times 10^{-18}$ (cm^{-3})	2.4	3.6	13.4	2.4	3.6	13.4
Minority hole						
Density$\times 10^{-15}$ (cm^{-3})		$3._3$			$8._7$	0.5_7
Mobility$\times 10^{-4}$ (cm^2/volt sec)		5_7			20_0	15_0
Minority electron						
Density$\times 10^{-15}$ (cm^{-3})	200		0.5_0	200		
Mobility$\times 10^{-4}$ (cm^2/volt sec)	0.7		39	0.7		

here. Shortcomings in the high-field extrapolations could also cause this discrepancy. Our extrapolated curves for σ_{xx} fall off like H^{-2} for magnetic fields stronger than the observed fields. The existence of an additional "Lorentz term" with a high saturation field (such as that found at 4.2°K) would increase the area under a σ_{xx} curve over that found here. As the saturation fields (H_n's) increase with temperature (due to the decrease in the relaxation time), the extrapolation errors should be larger at the higher temperatures. The total carrier concentrations found by Soule are also below the band model values at the higher temperatures. Note that our mobility ratios for the majority carriers are given in Table II, and at the low temperatures the holes are more mobile. The ratios are in good agreement with those calculated by Soule, using another method.

From the three values of the mobility as a function of temperature for each carrier, we infer that the mobility *versus* temperature is a smooth function, dropping rather faster with temperature than $1/T$. The carrier density, however, does not change much up to 77°K, and then increases by a factor of 2.5 up to room temperature. Thus, the qualitative explanation for the break[15,27] in the resistance *versus* temperature curve at about 120°K must be as follows: below that temperature the increase in resistivity is due to the decrease in mobilities, while above 120°K the carrier densities begin to increase, slowing down the rate of increase of resistance. The temperature of the break must be roughly equal to the average degeneracy temperature of electrons and holes, which corresponds to one-half of the band overlap. The band overlap thus deduced is about 0.02 ev, compared to about 0.03 ev from the de Haas-van Alphen effect and band model.[16]

Finally, knowing the average mobilities and the de Haas-van Alphen masses derived by Soule,[25] we can make estimates of the average relaxation times and mean free paths (see Table III). The relaxation time is computed from the simple formula $\mu = e\tau/m^*$. Thus, the calculated time is only approximate as it does not take into account the distribution of effective masses in graphite. The velocities at the Fermi surface are calculated for the maximum horizontal cross section of the surface, using the band model, and the room-temperature value is corrected for thermal excitation. From the table of relaxation times we may calculate the value of

TABLE III. The average relaxation times, velocities at the Fermi surface, and mean free paths for the majority carriers in graphite, as derived from the galvanomagnetic properties and the band model. All quantities refer to motion of the carriers in the layer plane.

Sample temperature	*EP*14 4.2°K	*EP*14 77°K	*EP*14 298°K	*EP*7 4.2°K	*EP*7 77°K	*EP*7 300°K
			Majority hole			
$\tau \times 10^{12}$ (sec)	$35._5$	2.5_0	0.34	22.0	2.2_3	0.33
$v \times 10^{-8}$ (cm/sec)	0.54	0.54	0.8_0	0.54	0.54	0.8_0
l (microns)	18	1.2	0.3	11	1.1	0.3
			Majority electron			
$\tau \times 10^{12}$ (sec)	$15._0$	1.1_4	0.20	10_6	0.8_7	0.19
$v \times 10^{-8}$ (cm/sec)	0.93	0.93	1.5	0.93	0.93	1.5
l (microns)	15	1.0	0.3	11	0.8	0.3

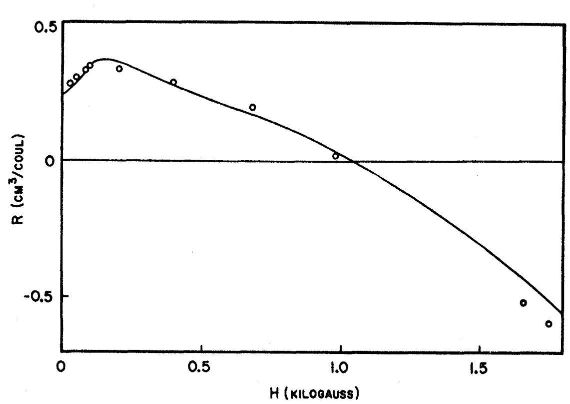

FIG. 6. The Hall coefficient of sample *EP*14 at 4.2°K, in the orientation of Fig. 1. The circles are experimental points and the line is the theoretical curve. Note that the field range shown is less than in Figs. 4 and 5.

[27] W. Primak and L. H. Fuchs, Phys. Rev. 95, 22 (1954).

$\omega\tau$ for a cyclotron resonance experiment such as that of Galt *et al.*[28] For a frequency of 24 kMc/sec and helium temperature we find for $\omega\tau$ for electrons and holes, respectively, 2.2 and 5.2 for $EP14$, and 1.6 and 3.2 for $EP7$. In analyzing Galt's data, Lax and Zeiger[29] assumed an average $\omega\tau$ of 3 and Nozières[18] assumed one of 2.5. The approximate agreement of these figures supports Galt's contention that his samples are of good quality. (Of course, allowance should be made for the fact that the cyclotron resonance experiment was carried out at 1.2°K.)

4. COMPARISON WITH KINCHIN

The most striking feature of Kinchin's experimental results[30] for graphite is the fact that at low temperatures the Hall coefficient reaches a negative minimum in the neighborhood of 2 to 3 kilogauss, and then tends to zero with increasing field. We have computed the magnetoconductivity tensor elements for the 4.2°K data and made approximate fits. We find that σ_{xx} is represented by the sum of two "Lorentz" terms with saturation fields of 110 and 2900 gauss, plus a constant term equal to about 10^{-3} of the zero-field conductivity. It is the constant term which causes the minimum in the Hall coefficient; for when the constant term is subtracted out and the Hall effect computed from the σ's, the Hall coefficient decreases monotonically with increasing field (at about $\frac{1}{3}$ the rate of Soule's). The way in which the minimum arises deserves further comment. For the case under discussion, the Hall coefficient is given by

$$R=\sigma_{xy}/H(\sigma_{xx}^2+\sigma_{xy}^2). \tag{4.1}$$

In the high-field limit, σ_{xy} normally falls off like $1/H$ and σ_{xx} like $1/H^2$ [see Eqs. (2.1)]. Thus R normally becomes equal to $1/H\sigma_{xy}$, which is independent of magnetic field. However, if σ_{xx} tends to a constant (not zero) value at high fields, the Hall coefficient tends toward $\sigma_{xy}/H\sigma_{xx}^2$, which falls off like $1/H^2$. Since at low fields R is negative and decreasing with increasing field, a minimum is produced. The Hall extremum discussed here has a different origin than those discussed by Borovik,[9] though both cases have in common the fact that the product $R\sigma H=\sigma_{xy}/\sigma_{xx}$ is anomalously small. The data of Berlincourt and Steele[31] also require a constant term in σ_{xx}. In their experiment the Hall coefficient tends monotonically to zero, but the lowest field of measurement was 3 kilogauss.

There are several possible explanations for the appearance of a constant term in σ_{xx}. Perhaps the most plausible is that it is simply another "Lorentz" term with a very large saturation field, such as the extra term we added for Soule's data at 4.2°K. It is interesting to note that the magnitude of this extra term at 10 kilogauss is about one half of the value of the constant found in Kinchin's 4.2°K data. Such an extra term could represent another slow carrier, or could be just a short relaxation-time part of the majority carrier distribution. Another possibility[32] is that there may be a small contribution from surface conductance, which is not affected by the magnetic field. A third possibility is that the quantization of electron energy by the magnetic field is responsible for the constant term. However, the quantization effects (oscillations) are exhibited most strongly in Soule's data, whereas the Hall minimum is most pronounced in Kinchin's. Lastly, it was thought that small errors in aligning the magnetic field parallel to the hexagonal axis might produce the effect, but a careful theoretical investigation disproved this hypothesis.

Assuming that the constant term in Kinchin's σ_{xx} represents a "Lorentz" term, we can deduce a lower limit for the total carrier concentration (electrons plus holes) at 4.2°K of 2.1×10^{18} cm^{-3}, with a corresponding upper limit on the average mobility of about 7×10^5 cm^2/volt sec. By a different mode of analysis, Kinchin found the electron concentration (equal to the hole concentration) to be 1.2×10^{18} cm^{-3} at 4.2°K and 6.2×10^{18} cm^{-3} at 273°K.

Kinchin also found that the Hall curves for different temperatures could be reduced to a universal curve by subtracting the zero-field value, and by scaling both the residual Hall coefficient and the magnetic field. Such a result implies that all relaxation times change by the same factor with change in temperature. If exact scaling applied to Soule's samples, the change with temperature in all H_n's for a given sample should be by the same factor (proportional to the change in inverse relaxation time), the change in all A_n's for σ_{xx} should be by another factor (proportional to the change in the product of relaxation time and carrier density), and the change in all A_n's for σ_{xy} should be by still another factor (proportional to the change in the product of the carrier density and the square of the relaxation time). It can be seen from Table I that such scaling rules are but poorly obeyed for Soule's samples. Assuming exact scaling, Kinchin's magnetic field scaling parameter (β) should be proportional to the mobility, and in fact obeys the same $T^{-1.2}$ temperature dependence law found by Soule.[15] The inverse of the Hall coefficient scaling parameter (α), and the inverse of the product of the resistivity and β, should both be proportional to the carrier concentration; and they do show the same general temperature dependence, being relatively constant from 4.2°K to 77°K and then increasing by about a factor of three up to 273°K. The zero-field value of the Hall coefficient depends upon the mobility ratios, but is not well determined at low temperatures in Kinchin's data.

Finally we note that the mean free paths deduced in

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[29] B. Lax and H. J. Zeiger, Phys. Rev. **105**, 1466 (1957).
[30] G. H. Kinchin, Proc. Roy. Soc. (London) **A217**, 9 (1953).
[31] T. G. Berlincourt and M. C. Steele, Phys. Rev. **98**, 956 (1955).
[32] D. Mattis (private communication).

the last section agree fairly well (except at helium temperature) with those calculated by Kinchin using a different method.

5. DISCUSSION

The results for graphite are fairly consistent with the band model and other treatments. The estimates of total carrier density using the Kramers-Kronig relation are about a factor of five larger than those gotten by interpreting individual terms.[24] We interpret this to mean that the majority electrons and holes are so similar that they cancel 80% of each other in the Hall effect. The existence of minority carriers is provided for in the band model.[16,18] We believe that the theory presented is sound in the range applied. Furthermore, the integrals are accurate to 1 to 2% in the range of field strengths where data exist. Thus, the chief source of error is in extrapolating to higher fields (in some cases also to lower fields). This points up the need for experiments at very high magnetic fields. The theory used here is not valid in the quantum region, but recent advances in theory[33,34] should make it possible to give a fundamental treatment in such a case.

Of course, the spirit of the method of analysis used here is the same as the usual two-band theory. In fact, our results are similar to those of Borovik[9] on magnesium, in which two kinds of electrons and two kinds of holes were assumed. It may be that in order to represent a broad distribution of relaxation times for a single kind of hole (and electron), two terms were needed. However, we do believe that the method used here is more convenient and reliable than the usual treatment. Unfortunately, the simple Kramers-Kronig relation does not hold if the energy surfaces do not have rotational symmetry about the magnetic field. The information which can be gained in more complicated cases has been studied by Adams.[22]

In a very recent paper Uemura and Inoue[35] have worked out the Hall effect in graphite assuming a simple band model and acceptor levels in the conduction band. They find that the orbital quantization due to the magnetic field changes the carrier concentrations so that Kinchin's high-field Hall effect curves are reproduced. Their theory does not give the correct low-field behavior as they use a much simplified model. Thus it may be that their theory will explain the high-field behavior discussed in Sec. 4.

[33] I. M. Lifshitz and A. M. Kosevich, J. Phys. Chem. Solids **4**, 1 (1958); I. M. Lifshitz, J. Phys. Chem. Solids **4**, 11 (1958).

[34] P. N. Argyres, Phys. Rev. **109**, 1115 (1958).

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[35] Y. Uemura and M. Inoue, J. Phys. Soc. Japan **13**, 382 (1958).