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THE STATISTICAL THEORY OF THERMOELECTRIC, GALVANO- AND THERMOMAGNETIC PHENOMENA IN METALS

By A. Sommerfeld,* University of Munich and
N. H. Frank, Massachusetts Institute of Technology

THERMOELECTRICITY and the galvano- and thermomagnetic effects in metals have been the subjects of countless theoretical and experimental investigations during the past half century. In spite of the tremendous amount of work done in these fields, a satisfactory explanation of these phenomena has been lacking up to the past few years, when the electron theory of metals (especially as developed by Lorentz) was given new life by the application of the Fermi-Dirac statistics. The main theme of this report will be a more or less detailed development of the new electron theory in its application to the above mentioned subjects. We shall assume that the reader is familiar with the article "Statistical Theories of Matter, Radiation and Electricity" which Dr. K. K. Darrow has written for this journal. For the sake of completeness, it will be unavoidable to prevent a certain repetition of what is already presented in Dr. Darrow's report. We shall try to keep a repetition to a necessary minimum.

A. Thermoelectricity

We shall be concerned in the following with the thermoelectric effects in homogeneous metallic circuits, thus concentrating our attention on the Thomson effect in its various aspects and omitting such effects (e.g. Peltier effect) which appear only in circuits where two or more different metals are present.

A short review of the method developed by H. A. Lorentz for handling the problem of electrical and thermal conduction in metals is necessary for the understanding of what follows. We imagine a piece of metal in thermal equilibrium with its surroundings at a temperature T. The free electrons[1]

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* I wish to emphasize that the parts of this report as far as they carry further than the results of my paper, Zeits. f. Physik **47**, 1, 1928, are due mainly to Dr. Frank, on whom the credit and the responsibility thereof fall.—A. S.

[1] We fully realize that the assumption of totally free electrons is but a first approximation to the actual state of affairs, and that at low temperatures this assumption, and more especially that of elastic collisions which is used in deriving the right hand side of Eq. (6), is no longer

in the metal will then have a certain distribution of their velocities which we shall assume governed by the Fermi distribution law. Lorentz, of course, assumed the classical Maxwell distribution. The number of electrons per unit volume whose velocity components lie between the limits ξ and $\xi+d\xi$, η and $\eta+d\eta$, ζ and $\zeta+d\zeta$ is given by:

$$dn = G(m/h)^3 f_0(\xi, \eta, \zeta) d\xi d\eta d\zeta \tag{1}$$

G is a weight factor which takes the electron spin into consideration ($G=2$), m the mass of the electron and h the Planck constant. f_0 is given by:

$$f_0(\xi, \eta, \zeta) = \frac{1}{(1/A)e^{mv^2/2kT} + 1} \tag{2}$$

k is the Boltzmann gas constant per molecule, $v=(\xi^2+\eta^2+\zeta^2)^{1/2}$ the velocity of the electrons, and A is a factor which is fixed by the number of free electrons which are present in a unit volume of the metal, i.e. the integral of the right hand side of (1) is to be set equal to n, the number of free electrons per unit volume. The factor A is very large compared to unity for a degenerate gas, and very small compared to unity for the non-degenerate case (Maxwell distribution). We shall, of course, deal with the case that $A >> 1$.

If an electric field is now applied to the metal, let us say in the x-direction, the equilibrium distribution (2) will be disturbed, and we shall assume that the perturbed function can be written in the form:

$$f = f_0 + \phi \tag{3}$$

where ϕ is small compared to f_0. It is evident that the function ϕ cannot be symmetrical in ξ, η and ζ, but that it will depend in a special manner on ξ, the x-component of velocity, and will be symmetrical in η and ζ. Furthermore, we require of the function ϕ that the integrals $\int \phi d\xi d\eta d\zeta$ and $\int v^2 \phi d\xi d\eta d\zeta$ vanish, when the integration is carried out over all possible values of ξ, η and ζ. The vanishing of the first integral states that the number of free electrons in the metal is not changed by the presence of the external field, and the vanishing of the second one insures the fact that the temperature at each point of the metal maintains its specified value. The simplest conceivable form of the function ϕ which satisfies these conditions is $\xi\chi(v)$, where χ depends only on v. We hence write for (3):

$$f = f_0 + \xi\chi(v). \tag{3a}$$

The electric current in the x-direction is obviously given by:

$$I = e\int \xi f d\omega = e\int \xi^2 \chi(v) d\omega = \frac{e}{3}\int v^2 \chi(v) d\omega \tag{4}$$

and the heat current:

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sufficient. At ordinary temperatures, however, the results hereby obtained remained essentially unaltered by a more rigorous wave mechanical calculation, which of course, takes the crystal structure and the lattice field into account. We shall return to this point in §9.

$$W = \frac{m}{2}\int \xi v^2 f d\omega = \frac{m}{2}\int \xi^2 v^2 \chi(v) d\omega = \frac{m}{6}\int v^4 \chi(v) d\omega \tag{5}$$

e is the charge of the electron and $d\omega = G(m/h)^3 d\xi d\eta d\zeta$. There remains only the problem of determining χ. This is done by means of imposing the condition that the motion shall be steady, a condition first introduced by Boltzmann, which requires that the total number of electrons per unit volume entering a given velocity range $d\xi d\eta d\zeta$ in unit time at every point of the metal must be equal to the number leaving this range in the same time. $(\partial/\partial t = 0)$. This condition of the stationary state is expressed by the equation:

$$\frac{eF}{m}\frac{\partial f}{\partial \xi} + \xi\frac{\partial f}{\partial x} = -\frac{\xi}{l}v\chi(v). \tag{6}$$

Here l denotes the free path of the electrons, which in general is to be considered a function of the velocity and of the temperature, and F is the electric field strength in the x-direction. The terms on the left are the "drift" terms, and the expression on the right takes into account the effect of the collisions. We thus obtain for χ the equation:

$$\chi(v) = -\frac{l}{v}\left(\frac{eF}{m}\frac{1}{v}\frac{\partial f_0}{\partial v} + \frac{\partial f_0}{\partial x}\right). \tag{6a}$$

If we insert this value of χ in equations (4) and (5) and perform an integration by parts, we find easily for the general equations for the currents of heat and electricity:

$$I = \frac{4\pi e G}{3}\left(\frac{m}{h}\right)^3\left[\frac{e}{m}FH_2 - H_4'\frac{\partial T}{\partial x}\right] \tag{7}$$

$$W = \frac{4\pi m G}{6}\left(\frac{m}{h}\right)^3\left[\frac{e}{m}FH_6 - H_8'\frac{\partial T}{\partial x}\right]. \tag{8}$$

The H denotes the following integrals:

$$\left.\begin{aligned} H_2 &= \int_0^\infty f_0\frac{\partial}{\partial v}(lv^2)dv; \quad H_4 = \int_0^\infty f_0 l v^3 dv \\ H_6 &= \int_0^\infty f_0\frac{\partial}{\partial v}(lv^4)dv; \quad H_8 = \int_0^\infty f_0 l v^5 dv \end{aligned}\right\} \tag{9}$$

The dash denotes differentiation with respect to the temperature T, whereby only the function f_0 and not l is to be differentiated. (We have placed $\partial f_0/\partial x = (\partial f_0/\partial T)(\partial T/\partial x)$, which is valid only for homogeneous metals).[2]

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[2] It must be pointed out that although in the original paper in the Zeits. f. Physik **47**, (1928), the assumption was expressly made that the free path l depend only on the velocity of the electrons and not on the temperature, the general equations and results therein remain unaltered by this generalization. This fact was first recognized and pointed out by E. Kretschmann, Zeits. f. Physik **48**, 739, (1928).

The Eqs. (7) and (8) provide two relations among the four quantities I, W, F and $\partial T/\partial x$, when the integrals have been evaluated. (We give the calculation of these integrals and others which appear elsewhere in this article in the Appendix). For our purposes, however, it is not necessary for the time being to evaluate the integrals, and hence the conclusions which we now draw are entirely independent of the statistics which the electrons obey. It is of importance to consider which of our four unknowns can be arbitrarily fixed or determined by an appropriate experimental arrangement, and which not. Obviously, the electric current and the temperature difference between the ends of the conductor (i.e. $\partial T/\partial x$) can be set at any desired value. The heat current W, however, can only be determined in the special case that no electric current flows; for should an electric current flow, a closed circuit is necessary and consequently any device inserted in this closed circuit for measuring the heat flow will have as much heat flowing into it per unit time as leaves it, thus preventing the determination of the heat current. The case $I=0$, on the other hand, offers no difficulty since then the total amount of heat which has traversed a given cross-section of the conductor in a given time can be collected and measured calorimetrically. We can therefore not look upon W as an arbitrarily given quantity. The electric field F can be fixed and determined only outside the metal (a given voltage can be applied to the ends of the conductor), but only under certain conditions will this applied field be equal to that field which is present inside the metal and which is, of course, all-important for the calculations. This quantity is therefore as little at our disposal as the heat current W. It is peculiar that in the case of the flow of electricity the current but not the potential gradient can be arbitrarily prescribed, and that in the case of the flow of heat exactly the opposite is true. This fact introduces a certain unavoidable asymmetry into our considerations. Particularly interesting from a theoretical standpoint are the special cases when one of the four available variables vanishes. Table I presents these four cases.

Case I: This case in which the temperature of the metal is held constant and the electric current is arbitrarily fixed represents the arrangement usually employed for the determination of the electrical conductivity σ. For this arrangement, but only for this one of the four under consideration, is the field inside the metal equal to the applied field. We see from Eq. (9b) that a heat current proportional to I must flow if the temperature is to be kept constant. (This is in addition to the Joule heat which, of course, must be removed). We denote this heat current as the *Thomson heat current* and define the coefficient μ_w thereof as:

$$\mu_w = \left(\frac{W}{F}\right)_{\frac{\partial T}{\partial x}=0} = \frac{m\sigma}{2e}\,\frac{H_6}{H_2}\,. \tag{13}$$

Case II: The conditions supposed in this case are hardly to be obtained practically as we must assume the possibility of the existence of an electric current without an accompanying heat flow. Nevertheless, the case is of theoretical interest. We see by consulting Eqs. (10a) and (10b) that the field existing in the interior of the metal is not equal to the applied field, (I/σ). Furthermore, a temperature gradient which is proportional to the inner field is set up as a consequence of the condition $W=0$. We call this temperature gradient the *Thomson temperature gradient* and define its coefficient μ_T by the relation:

$$\mu_T = \left(\frac{\partial T/\partial x}{F}\right)_{W=0} = \frac{e}{m}\,\frac{H_6}{H_8'}\,. \tag{14}$$

Case III: Here we imagine the conductor electrically insulated and with its ends maintained at different temperatures, an arrangement employed for the experimental determination of the heat conductivity. As a consequence of the electric insulation and the resulting accumulation of charge at one end of the conductor, we find according to Eq. (11a) an electric field established inside the conductor. This field shall be called the *Thomson potential gradient* and the coefficient μ_P thereof defined by:

TABLE I

	Fixed by experiment	Consequences of Eq. (7) and (8)	
I.	I	$F = \frac{I}{\sigma};\ \sigma = \frac{4\pi e^2 G}{3m}\left(\frac{m}{h}\right)^3 H_2$	(9a)
	$\frac{\partial T}{\partial x} = 0$	$W = \frac{m}{2e}\,\frac{H_6}{H_2} I = \frac{m\sigma}{2e}\,\frac{H_6}{H_2} F$	(9b)
II.	I	$F = \frac{m}{e}\,\frac{H_8'}{H_6}\,\frac{\partial T}{\partial x}$	(10a)
	$W = 0$	$\frac{\partial T}{\partial x} = \frac{m}{2e}.\frac{1}{\kappa}.\frac{H_6}{H_2} I$	(10b)
III.	$\frac{\partial T}{\partial x}$	$F = \frac{m}{e}\,\frac{H_4'}{H_2}\,\frac{\partial T}{\partial x}$	(11a)
	$I = 0$	$\left.\begin{array}{l} W = -\kappa\frac{\partial T}{\partial x} \\ \kappa = \frac{4\pi m G}{6}\left(\frac{m}{h}\right)^3\left[H_8' - \frac{H_6}{H_2}H_4'\right] \end{array}\right\}$	(11b)
IV.	$\frac{\partial T}{\partial x}$	$I = -\frac{m\sigma}{e}\,\frac{H_4'}{H_2}\,\frac{\partial T}{\partial x}$	(12a)
	$F = 0$	$W = -\frac{m^2\sigma}{2e^2}\,\frac{H_8'}{H_2}\,\frac{\partial T}{\partial x}$	(12b)

$$\mu_P = \left(\frac{F}{\partial T/\partial x}\right)_{T=0} = \frac{m}{e}\,\frac{H_4'}{H_2}\,. \tag{15}$$

Case IV: This case, which is similar to II inasmuch as it is hardly to be realized experimentally, is introduced for the sake of symmetry. We must imagine an electric current sent through the conductor, which is exactly large enough to compensate the electric field inside the conductor produced by the temperature gradient. This current is given by Eq. (12a) and the accompanying heat flow by Eq. (12b). We shall call this electric current the *Thomson electric current* and define its coefficient μ_S by the relation:

$$\mu_S = \left(\frac{I}{\partial T/\partial x}\right)_{F=0} = -\frac{m\sigma}{e}\frac{H_4'}{H_2} = -\mu_P\sigma. \tag{16}$$

In the preceding discussion we have carefully discriminated among four different "Thomson-coefficients." The need for such a discrimination becomes apparent when one considers the huge amount of work which has been done in attempting to prove or disprove the existence of the inversion of the "Thomson-effect," (see the article by A. Benedicks, "Ergebnisse der exakten Wissenschaften," Bd. VIII), in many cases without a precise definition of what is to be understood by this effect. If we mean, when we talk of Thomson effect, that electric field which is caused by a temperature gradient in a metal when no electric current is allowed to flow (μ_P in Case III), then the inversion of this effect is clearly the production of a temperature gradient by an electric field when no heat current is allowed to flow (μ_T in Case II). In an exactly corresponding manner we can consider Case I and Case IV as inversions of one another. Of these possibilities, none seems to have been realized in the experiments of Benedicks, which claim to have shown the existance of an inverted "Thomson effect."

The coefficient μ_P has been frequently called the "Thomson coefficient" without further specification. Unfortunately, the coefficient which is meaured in the usual manner is *none* of the four which we have considered.

One measures the heat which is reversibly absorbed or given up in unit volume of a metal per unit time, when heat and electric currents simultaneously flow through the conductor. This heat energy is called the Thomson heat "Q_T", and the *Thomson energy coefficient* μ_E (frequently called the specific heat of electricity) as defined by:

$$-\mu_E = \frac{Q_T}{I\partial T/\partial x}\cdot \tag{17}$$

We shall now proceed to derive an expression for μ_E in terms of the coefficients which have already been introduced. The energy produced in unit volume per unit time is IF and in general depends on the temperature gradient $\partial T/\partial x$. Of this energy an amount $\partial W/\partial x^*$ is carried away by thermal conduction, and there remains the energy:

$$E = IF - \partial W/\partial x. \tag{18}$$

We can write (7) in the form:

$$F = \frac{I}{\sigma} + \frac{m}{e}\frac{H_4'}{H_2}\frac{\partial T}{\partial x} \tag{19}$$

and (8) with the help of (19) and the definition of the heat conductivity κ as:

$$W = \frac{m}{2e}\frac{H_6}{H_2}I - \kappa\frac{\partial T}{\partial x}\cdot \tag{20}$$

The expression for E in (18) then becomes:

$$E = \frac{I^2}{\sigma} + \left\{ \frac{m}{e} \frac{H_4'}{H_2} - \frac{m}{2e} \frac{d}{dT} \left(\frac{H_6}{H_2} \right)^{*} \right\} I \frac{\partial T}{\partial x} + \frac{\partial}{\partial x} \left(\kappa \frac{\partial T}{\partial x} \right). \tag{21}$$

The first term of this equation is the Joule heat, the last term the heat coming by means of the thermal conductivity and the middle term is the reversible Thomson heat Q_T. We thus find for the coefficient μ_E:

$$\mu_E = \frac{m}{2e} \frac{d}{dT} \left(\frac{H_6}{H_2} \right)^{*} - \frac{m}{e} \frac{H_4'}{H_2} \cdot \tag{22a}$$

A comparison with equations (13) and (15) allows us to write:

$$\mu_E = \frac{d}{dT} \left(\frac{\mu_W}{\sigma} \right) - \mu_P. \tag{22b}$$

Proceeding now to the values of these coefficients as given by the values of the integrals H_2, H_6 and H_4' (taken from the Appendix) we get for μ_E:

$$\mu_E = \frac{2\pi^2 m k^2 T \lambda^2}{3eh^2} \tag{22c}$$

if we consider the number of free electrons as temperature independent and and the free path of the electrons independent of their velocity.** (Although this last assumption is only a rough approximation, it seems to suffice for the prediction of the order of magnitude of all the effects calculated by the electron theory). λ denotes the de Broglie wave-length of those electrons which have the critical velocity of the Fermi distribution function and depends essentially only on the density of free electrons. On the other hand, with the same neglect as above, we get for μ_P:

$$\mu_P = \frac{\pi^2 m k^2 T \lambda^2}{3eh^2} = \frac{\mu_E}{2} \cdot \tag{22d}$$

The difference between μ_p and μ_e has given rise to some misunderstanding in the literature. For example, in his book on "Statistical Mechanics," R. H. Fowler derives an expression for the Thomson effect from equilibrium theory considerations which is smaller by a factor two than the result here obtained for μ_e. Fowler identifies the Thomson coefficient with the increase of specific heat of the electrons in a metal caused by an increase of unity in the electron density. Obviously such a calculation corresponds to the case where energy (i. e. heat current) is transferred to the metal under consideration *without* an accompanying electric current, and leads to the value of μ_P, which is in fact just half as large as μ_E. This is exactly what Fowler found in his calcu-

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* In this differentiation it is necessary to take the dependence of l on T, hence on x, into account.

** It has been recently pointed out by R. H. Fowler that the sign of the Thomson heat as predicted by (22c) is the negative of that observed for the "normal" metals, (Au, Ag, Cu). This seems to be a difficulty of the classical theory which is carried over into this theory.

lation. T. E. Stern[3] has called attention to this discrepancy and considers it an example of the inability of equilibrium theory to handle problems belonging to a transport theory. It seems, however, that the danger of applying equilibrium theory to problems of metallic conduction is not so much one of principle, but lies more in the fact that one must be exceedingly careful in the identification of a calculated result with the experimentally determined quantity. We shall have occasion again to point out the necessity of discrimminating carefully among the various possibilities which we have discussed in connection with the equation proposed by Moreau.

B. Magnetic Effect in Metals

(1). **General principles.**

We consider a metallic conductor in a homogeneous magnetic field, and confine ourselves to a discussion of the action of this field on the free electrons in the metal as far as is necessary for the understanding of the galvano- and thermomagnetic phenomena. The magnetic field will, in general, act in two different ways on the electrons; first, the Lorentz force $e[v \times H]$ will act on each electron, a diamagnetic effect, and secondly, the energy of the electrons will change in the field due to their spin, a paramagnetic effect. The first question which presents itself is; how is the distribution function f_0 changed by the presence of the magnetic field? The Lorentz force can obviously have no effect on the distribution function as it acts at right angles to the motion of the electron, and hence leaves its energy unchanged. Since f_0 depends only on the energy (in its dependence on the velocity components), it can not be affected by the Lorentz force. The spin, however, gives rise to a change of energy equal to $\pm \mu_0 H$ where $\mu_0 = eh/4\pi m$ is the magnetic moment of the electron. If we place $\epsilon = mv^2/2$ (equal to the kinetic energy of the electrons), then the distribution function in a magnetic field is given by:

$$f_H = \frac{1}{2}\left[\frac{1}{(1/A')e^{(\epsilon+\mu_0 H)/kT} + 1} + \frac{1}{(1/A')e^{(\epsilon-\mu_0 H)/kT} + 1}\right]. \tag{23}$$

The factor $\frac{1}{2}$ must be introduced to compensate for the fact that the weight factor $G = 2$, which takes the spin degeneracy into account, remains in the formulas. We have purposely written A' in place of the former symbol A, as the value of A' now depends on the strength of the magnetic field. If we assume that the number of free electrons in the metal does not change when a magnetic field is applied, we must have (as in (1)):

$$n = \int f_H d\omega \tag{24}$$

as the equation which determines A', the integration to be carried out over the whole of momentum space. We obtain in this manner:

$$\left.\begin{aligned} \log A' &= \log A - \gamma^2/4 \log A \\ \gamma &= \mu_0 H/kT \end{aligned}\right\} \tag{25}$$

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[3] T. E. Stern, Proc. Roy. Soc. **A126**, 570 (1930).

where A is the value of A' for $H=0$, and we have neglected terms with higher powers of H than H^2. This is legitimate for all fields which can be obtained in practice. We now are in a position to see how the spin can be systematically introduced into all the following work. We must replace f_0 everywhere by f_H as given by (23) and use the modified value of $\log A$ as given by (25). It turns out that the effect of the spin is so small as to be of little interest in most cases, so that we shall neglect it in all but a few special cases. In the Appendix will be found the necessary values of the integrals to allow the introduction of the spin in all the work. We shall not stop here to discuss the interesting questions of the paramagnetism and diamagnetism of free electrons,[4] but turn directly to the questions of electrical and thermal conduction in magnetic fields.

(2). Conduction in a homogeneous magnetic field.

Leaving the spin for the present out of consideration, we can proceed in the determination of the various thermo- and galvanomagnetic effects by an extension of the method described in part A.

We consider a metallic plate lying in the xy plane, through which a primary current may flow in the x direction and which lies in a homogeneous magnetic field perpendicular to the plane of the plate. With this arrangement only two of the components of the Lorentz force are different from zero, *viz.*, the x component equal to $e\eta H$ and the y component equal to $-e\xi H$. We now write in place of (3):

$$f = f_0 + \xi\chi_1(v) + \eta\chi_2(v) \tag{26}$$

as we must now consider the y-axis as well as the x-axis as preferred. We consider χ_1 and χ_2 as dependent only on $v=(\xi^2+\eta^2+\zeta^2)^{\frac{1}{2}}$ and the reasons for writing f in the above form are similar to those which we have already discussed in the case of (3a). Instead of (6) we now have for the condition of steady flow:

$$\left(\frac{e}{m}F_x + \frac{e}{m}H\eta\right)\frac{\partial f}{\partial \xi} + \xi\frac{\partial f}{\partial x} + \left(\frac{e}{m}F_y - \frac{e}{m}H\xi\right) + \eta\frac{\partial f}{\partial y} = -\frac{v}{l}(\xi\chi_1 + \eta\chi_2). \tag{27}$$

With the left hand side of this equation the exact expression (26) for f in the terms which contain H (so as to keep the calculation valid for strong fields), and the approximate expression f_0 in the remaining terms as we have done before, we obtain after a simple reduction:

$$\chi_1 = -\frac{l}{v}\,\frac{f_1 + \mu l f_2/v}{1 + \mu^2 l^2/v^2} \tag{28}$$

$$\chi_2 = -\frac{l}{v}\,\frac{f_2 - \mu l f_1/v}{1 + \mu^2 l^2/v^2} \tag{29}$$

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[4] W. Pauli, Jr. Zeits. f. Physik **41**, 81 (1927); L. Landau, Zeits. f. Physik **64**, 626 (1930).

With the abbreviations:

$$\left.\begin{aligned} \mu &= eH/m \\ f_1 &= \frac{e}{m}F_x\frac{1}{v}\,\frac{\partial f_0}{\partial v}+\frac{\partial f_0}{\partial x} \\ f_2 &= \frac{e}{m}F_y\frac{1}{v}\,\frac{\partial f_0}{\partial v}+\frac{\partial f_0}{\partial y} \end{aligned}\right\} \tag{30}$$

Proceeding exactly as in the case of Eq. (4) and (5), we can now write for the electric and heat currents in the x and y directions:

$$\left.\begin{aligned} I_x &= e\int \xi f d\omega = (e/3)\int v^2\chi_1 d\omega \\ I_y &= e\int \eta f d\omega = (e/3)\int v^2\chi_2 d\omega \\ W_x &= (m/2)\int \xi v^2 f d\omega = (m/6)\int v^4\chi_1 d\omega \\ W_y &= (m/2)\int \eta v^2 f d\omega = (m/6)\int v^4\chi_2 d\omega \end{aligned}\right\} \tag{31}$$

Before writing these equations explicitly, we shall discuss them as they stand, and show that certain general results can be predicted without further knowledge of the integrals involved. It is well known that for a completely degenerate electron gas, ($T=0$), the only electrons which take part in the conduction process are those which have the critical velocity $\bar{v}$ defined by:

$$\frac{1}{A}e^{m\bar{v}^2/2kT} = 1.$$

Only for this value of v is $\partial f_0/\partial v$ different from zero. One can, in first approximation, consider the electron gas completely degenerate even at ordinary temperatures. The error thus made is of the order of $1/(\log A)^2$. If we suppose that all the conduction electrons have exactly the same velocity $\bar{v}$, then we see that the requirement that the current in the y direction vanish (a usual experimental arrangement) is equivalent to the condition $\chi_2=0$. Equation (29) then gives as this condition:

$$f_2 = \mu l f_1/\bar{v}. \tag{32}$$

Inserting this value of f_2 in (28), we obtain for χ_1, which determines the current in the x direction:

$$\chi_1 = -\,l f_1/\bar{v}$$

an expression which no longer contains the magnetic field. We thus see that the resistance of a metal stays unchanged in a magnetic field if the conducting electrons all have the same velocity. Assuming now a conductor at constant temperature ($\partial f/\partial x = \partial f/\partial y = 0$) we find from (32):

$$\frac{f_2}{f_1} = \frac{F_y}{F_x} = \frac{eH}{m} \frac{l}{\bar{v}} \cdot \tag{33}$$

Introducing the isothermal Hall constant, defined by:

$$R = \frac{F_y}{I_x H} = \frac{F_y}{\sigma H F_x} \tag{34}$$

and the de Broglie wave-length of the electrons:

$$\lambda = h/m\bar{v} \tag{35}$$

we obtain for the Hall constant:

$$R = \frac{1}{\sigma} \cdot \frac{el\lambda}{h} = \frac{1}{ne} \cdot \tag{36}$$

The last step is obtained by inserting the values of $\sigma = (8\pi/3)(e^2 l/h\lambda^2)$ and $\lambda^3 = 8\pi/3n$, which are valid in this approximation.

We notice that because of Eqs. (31), the vanishing of the electric current insures the vanishing of the heat current in this first approximation.[5] This is of importance, not only as it means that the heat conductivity vanishes in this first approximation, but that an adiabatic condition (one which requires W_x or W_y or both vanish) gives no more information than the condition that the corresponding electric current vanish. We may therefore be sure that in order to obtain results for adiabatic conditions, the calculations must be carried out to a second approximation, thus taking into account deviations from complete degeneracy.

After these general remarks, we proceed to write the equations (31) after the values of χ_1 and χ_2 have been introduced by means of (28) and (29) and an integration by parts have been carried out. We obtain (for homogeneous metals):

$$\left.\begin{aligned}
I_x &= \frac{4\pi e G}{3}\left(\frac{m}{h}\right)^3 \left[\frac{e}{m}K_2 F_x + \mu\frac{e}{m}K_1 F_y - K_4'\frac{\partial T}{\partial x} - \mu K_3'\frac{\partial T}{\partial y}\right] \\
I_y &= \frac{4\pi e G}{3}\left(\frac{m}{h}\right)^3 \left[-\frac{e}{m}\mu K_1 F_x + \frac{e}{m}K_2 F_y + \mu K_3'\frac{\partial T}{\partial x} - K_4'\frac{\partial T}{\partial y}\right] \\
W_x &= \frac{4\pi m G}{6}\left(\frac{m}{h}\right)^3 \left[\frac{e}{m}K_6 F_x + \mu\frac{e}{m}K_5 F_y - K_8'\frac{\partial T}{\partial x} - \mu K_7'\frac{\partial T}{\partial y}\right] \\
W_y &= \frac{4\pi m G}{6}\left(\frac{m}{h}\right)^5 \left[-\mu\frac{e}{m}K_5 F_x + \frac{e}{m}K_6 F_y + \mu K_7'\frac{\partial T}{\partial x} - K_8'\frac{\partial T}{\partial y}\right]
\end{aligned}\right\} \tag{37}$$

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[5] Since the first approximation is equivalent to considering all the electrons as possessing a single velocity, the integration in (31) is to be disregarded, (with the result that the heat current must vanish for $I=0$). Since the heat conductivity κ is defined by $\kappa = -W/(\partial T/\partial x)$, κ must also vanish.

The dashes denote differentiation with respect to T as before (l constant in this differentiation!) and the K's are the following integrals:

$$\left.\begin{aligned}
K_1 &= \int_0^\infty f_0\frac{\partial}{\partial v}\left(\frac{l^2v}{1+\mu^2l^2/v^2}\right)dv; & K_5 &= \int_0^\infty f_0\frac{\partial}{\partial v}\left(\frac{l^2v^3}{1+\mu^2l^2/v^2}\right)dv\\
K_2 &= \int_0^\infty f_0\frac{\partial}{\partial v}\left(\frac{lv^2}{1+\mu^2l^2/v^2}\right)dv; & K_6 &= \int_0^\infty f_0\frac{\partial}{\partial v}\left(\frac{lv^4}{1+\mu^2l^2/v^2}\right)dv\\
K_3 &= \int_0^\infty f_0\frac{l^2v^2dv}{1+\mu^2l^2/v^2}; & K_7 &= \int_0^\infty f_0\frac{l^2v^4dv}{1+\mu^2l^2/v^2}\\
K_4 &= \int_0^\infty f_0\frac{lv^3dv}{1+\mu^2l^2/v^2}; & K_8 &= \int_0^\infty f_0\frac{lv^5dv}{1+\mu^2l^2/v^2}
\end{aligned}\right\} \tag{38}$$

The integrals H which were introduced at the beginning of this article are the values of the corresponding K for $\mu=0$. The Eqs. (37) are the fundamental equations from which all the galvanomagnetic and thermomagnetic effects can be derived. The equations are entirely independent of the statistics used, only the values of the integrals K depend thereon. If one wishes to introduce the spin into these equations, it is only necessary to modify the values of the integrals K.

(3). Isothermal effects. (General formulas).

By an isothermal effect is meant a galvano- or thermomagetic effect so produced that the temperature in the y direction (perpendicular to the primary current) is kept constant, i.e. $\partial T/\partial y=0$.

The *Hall effect* is, as we have seen, the production of a transverse potential gradient F_y by a primary electric current I_x in a magnetic field. We have already defined the Hall constant as:

$$R = F_y/I_xH. \tag{34}$$

We obtain its isothermal value by placing $I_y=\partial T/\partial x=\partial T/\partial y=0$ in the second equation of (37) as:

$$R = \frac{e}{m}\cdot\frac{1}{\sigma}\cdot\frac{K_1}{K_2}\cdot \tag{39}$$

The condition $\partial T/\partial x=0$ denotes that the temperature in the direction of the primary current flow is constant. The condition $I_y=0$ denotes that we have to do with the open circuit Hall potential.

The *conductivity* in a magnetic field is obtained as follows: with the value of the Hall constant in (39) and the corresponding value of F_y, we can write the first equation of (37) as:

$$\sigma = \frac{I_x}{F_x} = \frac{4\pi e^2G}{3m}\left(\frac{m}{h}\right)^3K_2\left[1+\mu^2\left(\frac{K_1}{K_2}\right)^2\right]$$

and since the conductivity when no magnetic field is present is given by:

$$\sigma_0 = \frac{4\pi e^2 G}{3m}\left(\frac{m}{h}\right)^3 H_2 \tag{39a}$$

we find for the ratio of these conductivities

$$\frac{\sigma}{\sigma_0} = \frac{K_2}{H_2}\left[1 + \mu^2\left(\frac{K_1}{K_2}\right)^2\right] \tag{40}$$

The *Nernst effect* is the production of a transverse electric field F_y by a primary heat current W_x. To calculate this field, we place $I_x = I_y = \partial T/\partial y = 0$ in the first two equations of (37) and obtain two linear equations for F_x and F_y, out of which follows:

$$\frac{e}{m}F_y = \mu\frac{K_1K_4' - K_2K_3'}{K_2^2 + \mu^2K_1^2}\cdot\frac{\partial T}{\partial x}$$

and as the constant Q of the Nernst effect is defined by the equation:

$$F_y = QH\partial T/\partial x$$

we obtain

$$Q_i = \frac{K_1K_4' - K_2K_3'}{K_2^2 + \mu^2K_1^2} \tag{41}$$

The subscript i denotes the fact that this is the isothermal Nernst constant, as it is obtained with the condition $\partial T/\partial y = 0$.

We also obtain from the two equations for F_x and F_y the following expression for F_x:

$$\frac{e}{m}F_x = \frac{K_2K_4' + \mu^2K_1K_3'}{K_2^2 + \mu^2K_1^2}\cdot\frac{\partial T}{\partial x}\,.$$

Using the definition of the *Thomson potential gradient coefficient* (Eq. (15)):

$$\mu_P = \left(\frac{\partial T/\partial x}{F_x}\right)_{I_x=0}$$

there follows for the isothermal value of this coefficient in a magnetic field:

$$\mu_P = \frac{m}{e}\,\frac{K_2K_4' + \mu^2K_1K_3'}{K_2^2 + \mu^2K_1^2} \tag{41a}$$

and for the ratio of these coefficients with and without a magnetic field present:

$$\frac{\mu_P}{(\mu_P)_0} = \frac{H_2}{H_4'}\cdot\frac{K_2K_4' + \mu^2K_1K_3'}{K_2^2 + \mu^2K_1^2}\,. \tag{41b}$$

With the help of the expressions for F_x and F_y so obtained, the third equation of (37) for the *thermal conductivity* in the x direction can be written:

$$\kappa = -\frac{W_x}{\partial T/\partial x} = \frac{4\pi m G}{6}\left(\frac{m}{h}\right)^3 \left[K_8' - \frac{K_2K_6K_4' + \mu^2 K_5(K_1K_4' - K_2K_3') + \mu^2 K_1K_6K_3'}{K_2^2 + \mu^2 K_1^2}\right]$$

There follows immediately for the ratio of the thermal conductivities of a metal in and out of a magnetic field (measured isothermally):

$$\frac{\kappa}{\kappa_0} = \frac{H_2}{K_2}\cdot\frac{K_2K_8' - K_6K_4'}{H_2H_8' - H_6H_4'}\cdot\frac{1}{K_2^2 + \mu^2 K_1^2}$$

$$\left[1 + \mu^2\left\{\frac{K_1(K_1K_8' - K_6K_3') - K_5(K_1K_4' - K_2K_3')}{K_2(K_2K_8' - K_6K_4')}\right\}\right] \qquad (41c)$$

We return to the question of the evaluation of these expressions and the discussion of the results so obtained in a later paragraph.

(4). Adiabatic effects. (General formulas).

By an adiabatic effect, we mean an effect produced when no heat is allowed to flow in the y direction, i.e., with the condition $W_y = 0$. The question as to what to assume in regard to the x direction is a little annoying. To place $W_x = 0$ when there is an electric current in the x direction is obviously incorrect, since in a closed metallic circuit, heat will inevitably flow along with the current (compare p. 4). In view of the extremely large heat conductivities of metals, it seems reasonable to suppose that heat is carried away fast enough along the metal so that the temperature in the x direction (at least in that part of the circuit which is in the magnetic field) remains constant. Certainly this condition is more nearly reached than the alternative $W_x = 0$. We shall accordingly place $\partial T/\partial x = 0$ when $I_x \neq 0$.

The two *transversal galvanomagnetic* effects produced by a primary electric current are obtained by placing:

$$I_x \neq 0 \quad W_y = I_y = \partial T/\partial x = 0.$$

The second and fourth equations of (37) then become:

$$\left.\begin{aligned} K_4'\frac{\partial T}{\partial y} - \frac{e}{m}K_2F_y &= -\mu\frac{e}{m}K_1F_x \\ K_8'\frac{\partial T}{\partial y} - \frac{e}{m}K_6F_y &= -\mu\frac{e}{m}K_5F_x \end{aligned}\right\} \qquad (42)$$

The *Ettinghausen constant P* is defined by the equation:

$$\partial T/\partial y = PHI_x.$$

(Obviously the Ettinghausen effect is zero for an isothermal arrangement.) The *adiabatic Hall constant* is denoted by R_a. We thus obtain as the values of the Hall and Ettinghausen constants:

$$R_a = \frac{e}{m\sigma}\cdot\frac{D_1}{D_0} \qquad (43)$$

$$P = \frac{c^2}{m^2\sigma}\,\frac{D_2}{D_0}\,\cdot \tag{44}$$

With the following abbreviations:

$$D_0 = \begin{vmatrix} K_4' & K_2 \\ K_8' & K_6 \end{vmatrix};\; D_1 = \begin{vmatrix} K_4' & K_1 \\ K_8' & K_5 \end{vmatrix};\; D_2 = \begin{vmatrix} K_2 & K_1 \\ K_6 & K_5 \end{vmatrix}. \tag{45}$$

The two *transversal thermomagnetic effects* are produced by a primary heat current and are obtained by placing:

$$W_x \neq 0;\; I_x = I_y = W_y = 0.$$

The first, second, and fourth equations of (37) can then be written:

$$\left.\begin{aligned} \mu\frac{e}{m}K_1F_y + \frac{e}{m}K_2F_x - \mu K_3'\frac{\partial T}{\partial y} &= K_4'\frac{\partial T}{\partial x} \\ -\frac{e}{m}K_2F_y + \mu\frac{e}{m}K_1F_x + K_4'\frac{\partial T}{\partial y} &= \mu K_3'\frac{\partial T}{\partial x} \\ -\frac{e}{m}K_6F_y + \mu\frac{e}{m}K_5F_x + K'_8\frac{\partial T}{\partial y} &= \mu K'_7\frac{\partial T}{\partial x} \end{aligned}\right\}. \tag{46}$$

It follows from these equations, that

$$\left.\begin{aligned} \frac{e}{m}F_y &= \frac{D_4}{D_3}\cdot\frac{\partial T}{\partial x} \\ \frac{\partial T}{\partial y} &= \frac{D_5}{D_3}\cdot\frac{\partial T}{\partial x} \\ \frac{e}{m}F_x &= \frac{D_6}{D_3}\cdot\frac{\partial T}{\partial x} \end{aligned}\right\} \tag{47}$$

with the following abbreviations:

$$\begin{aligned} D_3 &= \begin{vmatrix} \mu K_1 & K_2 & -\mu K_3' \\ -K_2 & \mu K_1 & K_4' \\ -K_6 & \mu K_5 & K_8' \end{vmatrix};\; D_4 = \begin{vmatrix} K_4' & K_2 & -\mu K_3' \\ \mu K_3' & \mu K_1 & K_4' \\ \mu K_7' & \mu K_5 & K_8' \end{vmatrix} \\ D_5 &= \begin{vmatrix} \mu K_1 & K_2 & K_4' \\ -K_2 & \mu K_1 & \mu K_3' \\ -K_6 & \mu K_5 & \mu K_7' \end{vmatrix};\; D_6 = \begin{vmatrix} \mu K_1 & K_4' & -\mu K_3' \\ -K_2 & \mu K_3' & K_4' \\ -K_6 & \mu K_7' & K_8' \end{vmatrix} \end{aligned} \tag{48}$$

The constant of the *Leduc-Righi effect* S is defined by:

$$\frac{\partial T}{\partial y} = SH\frac{\partial T}{\partial x}\,\cdot$$

With this and calling the adiabatic *Nernst constant* Q_a, we obtain with the help of (47):

$$Q_a = \frac{1}{\mu}\frac{D_4}{D_3} \tag{49}$$

$$S = \frac{e}{m\mu}\frac{D_5}{D_3} \tag{50}$$

If we insert the values of F_y and $\partial T/\partial y$ as found in (43) and (44) into the first equation of (37), we find easily for the *ratio of the electrical conductivities* in and out of a magnetic field:

$$\frac{\sigma}{\sigma_0} = \frac{K_2}{H_2}\left[1 + \mu^2\left(\frac{K_1 D_1}{K_2 D_0} - \frac{K_3' D_2}{K_2 D_0}\right)\right]. \tag{51}$$

On the other hand, using the values of F_y, $\partial T/\partial y$ and F_x as given by (47) in the third equation of (37), we find for the corresponding *ratio of thermal conductivities*:

$$\frac{\kappa}{\kappa_0} = \frac{H_2}{H_2 H_8' - H_6 H_4'}\left[K_8' - K_6\frac{D_6}{D_3} + \mu\left(\frac{D_5 K_7' - D_4 K_5}{D_3}\right)\right]. \tag{52}$$

The third equation of (47) gives the value of the *Thomson potential gradient coefficient* μ_P in a transverse magnetic field. With the help of Eq. (15), we find:

$$\frac{\mu_P}{(\mu_P)_0} = \frac{H_2 D_6}{H_4' D_3}\,. \tag{53}$$

We thus have obtained general formulas for the four transversal effects and three of the longitudinal effects in a transverse magnetic field. The results hitherto are independent of the statistics obeyed by the electrons, and accordingly have been grouped together. We now shall consider the consequences of introducing the Fermi statistics in the evaluation of the expressions which have been obtained.

(5). The change of resistance of a metal in a magnetic field.

We now turn to a more or less detailed discussion of the different effects, and consider first the change of resistance of a metal in a magnetic field. This question has caused a great deal of interest recently because of the measurements of Kapitza[6] in strong fields, and because of the resulting speculations about the nature of the effect.

We have already seen that, in the first approximation, the change of resistance vanishes. We must therefore calculate the integrals to a second approximation, and consider first the isothermal case, for which:

$$\frac{\sigma}{\sigma_0} = \frac{K_2}{H_2}\left[1 + \mu^2\left(\frac{K_1}{K_2}\right)^2\right]. \tag{40}$$

If we introduce the variable $u = mv^2/2kT$, the integrals K_1 and K_2 can be written: (compare 38)

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[6] P. Kapitza, Proc. Roy. Soc. **A123**, 292 (1929).

$$\left.\begin{aligned} K_i &= \int_0^\infty f_0 \frac{d\phi_i}{du} du \text{ with } \phi_1 = \left(\frac{2kTu}{m}\right)^{1/2} \frac{l^2}{1 + wl^2/u} \\ \phi_2 &= \frac{2kTu}{m} \frac{l}{1 + wl^2/u} \end{aligned}\right\} \tag{54}$$

Here w is used in place of $m\mu^2/2kT$. Carrying out the evaluation of the integrals to a second approximation without any neglect with respect to w, we obtain:

$$K_1 = \left(\frac{2kTu_0}{m}\right)^{1/2} \frac{l^2}{1 + wl^2/u_0}\left[1 - \frac{\pi^2}{24u_0^2} - \frac{\pi^2}{6u_0^2}\left(\frac{wl^2/u_0}{1 + wl^2/u_0}\right) + \frac{\pi^2}{3u_0^2}\left(\frac{wl^2/u_0}{1 + wl^2/u_0}\right)^2\right]$$

$$K_2 = \frac{2kTu_0}{m} \frac{l}{1 + wl^2/u_0}\left[1 + \frac{\pi^2}{3u_0^2}\left(\frac{wl^2/u_0}{1 + wl^2/u_0}\right)^2\right]$$

and

$$H_2 = \frac{2kTu_0 l}{m}\cdot$$

H_2 is of course obtained from K_2 by placing $w = 0$. u_0 is an abbreviation for $\log A$. We now introduce the following notation:

$$\left.\begin{aligned} a &= \frac{\pi^2}{3u_0^2};\ a < < 1 \\ b &= \frac{wl^2/u_0}{1+wl^2/u_0};\ 0 \leqq b \leqq 1 \end{aligned}\right\} \tag{56}$$

At room temperature a has a value of the order of magnitude 10^{-4} and becomes smaller with decreasing temperature. We can now write:

$$\frac{K_2}{H_2} = \frac{1 + ab^2}{1 + wl^2/u_0}$$

and

$$\mu^2\left(\frac{K_1}{K_2}\right)^2 = \frac{wl^2}{u_0}\left[1 - a\left(b + \frac{1}{4}\right)\right].$$

Here quantities which contain a^2 have been consistently neglected. Inserting these expressions in (40), we get:

$$\frac{\sigma}{\sigma_0} = (1 + ab^2)(1 - ab[b + \tfrac{1}{4}]) = 1 - ab/4$$

and finally for the relative change of resistance:

$$\frac{\Delta\rho}{\rho} = -\frac{\Delta\sigma}{\sigma_0} = \frac{a}{4}b.$$

Using the value of $u_0 = h^2/2mkT\lambda^2$ we obtain:

$$\frac{\Delta\rho}{\rho} = \frac{BH^2}{1 + CH^2} \tag{57}$$

with

$$B = \frac{\pi^2}{3}(emlkT)^2\left(\frac{\lambda}{h}\right)^6 \tag{57a}$$

and

$$C = (el\lambda/h)^2. \tag{57b}$$

I. The constant C; Measurements of Kapitza. If we now consult (36) we find that C can be written as:

$$C = \sigma^2 R^2. \tag{57c}$$

The relative change of resistance, as given by (57), increases proportional to H^2 for weak fields, then increases more slowly and finally tends to the "saturation" value B/C for extremely large values of H. $(CH^2 >> 1)$ Up to the time of Kapitza's measurements, a quadratic law had always been observed except in the case of Bi, which is decidedly abnormal in its magnetic behaviour. Kapitza, with his skillful methods of producing magnetic fields up to a magnitude of 300 kilogauss, showed that all metals show a departure from the quadratic law at sufficiently strong fields and low temperatures. For the case of normal metals, such as Cu, Ag and Au, this effect can be first measured with a reasonable degree of precision when the temperature has been reduced to about 100° K. From a series of extensive measurements, Kapitza was led to believe that the true law of change of resistance is a linear one and that the observed quadratic law for small fields is due to an internal disturbance in the the metal lattice, which he represents by a randomly distributed magnetic field. The *only* reason for assuming a linear law is that the measurements for strong fields can be thus well represented, except in the cases of Te, Ge, and C. For further details of Kapitza's theoretical standpoint and its implications with regard to supraconductivity, the reader is referred to the original papers.[7]

The need of an empirical law to explain the measurements is completely removed by our formula (57). In the transition region between the quadratic law and the approach to saturation, this function represents all of Kapitza's results fully as well as this linear law. Figs. 1 and 2 show this clearly. In Fig. 1 are shown the measurements on annealed copper at a temperature of 88°K (Curve II). Curve I is a plot of $\Delta\rho/\rho = BH^2$. In Fig. 2, curve I is for

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[7] P. Kapitza, Proc. Roy. Soc. **A123,** 292 (1929).

gold and curve II for tellurium, the latter showing the saturation effect predicted by (57) most clearly. The measurements were made at the temperature of liquid nitrogen (88°K). The constant B has been so chosen as to give the correct curve for small values of II, and C has been then determined with the help of (57) to fit one point on the curve. (Usually $\Delta\rho/\rho$ for $H=300$ kg).

Not only is the correct form of the function given by (57) but the constant C, which alone determines the departure from the quadratic law, is correctly given (in its order of magnitude) by the theory. According to (57c),

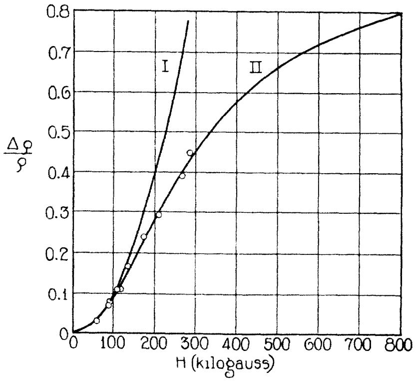

Fig. 1. Measurements on annealed copper at a temperature of 88°K (Curve II). Curve I is a plot of $\Delta\rho/\rho=BH^2$

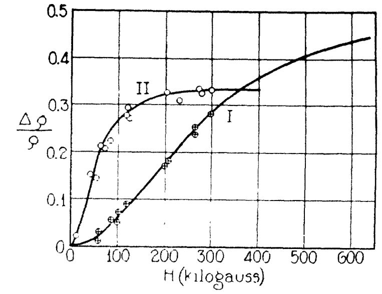

Fig. 2. Measurements on gold and tellurium at a temperature of 88°K. Curve I is for gold and curve II is for tellurium.

from the values of C from Kapitza's measurements, we can calculate σR at the temperature of the measurements. We then can calculate the Hall constant, using the known conductivity of the metal at room temperature and the ratio of conductivities at room temperature and at the temperature for which $\Delta\rho/\rho$ is measured. Kapitza gives only the last data, and we must use an average value of the conductivity at room temperature. In Table II are given the values of R so determined in the first column. In the second column are the values of R observed by direct measurement at room temperature, and in the third column, the theoretical values of R calculated by means of Eq. (36). The temperature refers to that at which the $\Delta\rho/\rho$ measurements are made.

TABLE II.

Metal	$R\times10^4$ from $\Delta\rho/\rho$	$R\times10^4$ directly measured	$R\times10^4$ theor. from (36)	T
Cu$_{\text{I}}$ (annealed)	7.5	5.5	7.4	88° K
Cu$_{\text{II}}$ (half annealed)	6.8	5.5	7.4	88
Cu$_{\text{I}}$ (hard drawn)	5.0	5.5	7.4	88
Ag (annealed)	12.5	8.4	10.4	88
Ag (hard drawn)	7.8	8.4	10.4	∽90
Au$_{\text{I}}$ (annealed)	17.5	6.5	10.5	88
Au$_{\text{II}}$ (hard drawn)	12.8	6.5	10.5	∽90
Au$_{\text{II}}$ (Meissner and Scheffers)	19.7	6.5	10.5	20.4

We see that for these normal metals the agreement is satisfactory as far as the order of magnitude is concerned. There are several reasons why a better agreement cannot be expected. In the first place, it is experimentally known that R increases for normal metals with decreasing temperature, so that somewhat larger values of R are to be expected from the determinations at low temperatures. Furthermore, the metals used in the $\Delta\rho/\rho$ measurements are characterized by their extreme purity, especially the gold Au$_{\text{II}}$ of Meissner and Scheffers. As we have used an average value of σ in calculating R, we have probably used too small a value and hence are led to somewhat too large values of R. The difference found between annealed and hard drawn metals is also worthy of notice. The electrical conductivity σ is certainly smaller for hard-drawn than for annealed metals. The values of R would agree more closely among themselves for the same metal if this fact is taken into consideration. Finally, the values of R vary a good deal from sample to sample of the same metal, even two different samples of the same purity can give different Hall effects, so that all in all the most that can be expected is the agreement in order of magnitude which has been found. In Table III are given the same results for a number of other metals. We see that the correct order of magnitude of R is obtained in all cases except those of Cd and Bi. The abnormality of Bi is not surprising. In the case of Cd, it has been observed that the value of the Hall constant has an abnormally large negative temperature coefficient.

TABLE III.

	Zn	Zn	Zn	Cd	Cd	Al	Al	Al	Sb	Sb	Sb	Bi
$R\times10^3$ (from $\Delta\rho/\rho$)	3.7	4.2	2.8	8.1	12.5	1.6	1.2	1.3	178	105	36	800
$R\times10^3$ (meas.)	0.76	0.76	0.76	0.88	0.88	0.4	0.4	0.4	219	219	219	6330

If, in treating the question of change of resistance of a metal in a magnetic field, the field is considered as a small perturbation, one is led to a quadratic law. The magnetic field can only be considered as a small perturbation as long as the mean free paths of the electrons are small compared to the radii of curvature of their paths. When these two quantities become comparable, it is to be expected that departures from the quadratic law shall appear. This is exactly what is shown by our formula (57).

Let us consider for simplicity an electron which is moving in the x direction with the critical velocity $\bar{v}$. Under the influence of the magnetic field it will move in a circle whose radius of curvature r is given by:

$$\frac{1}{r} = \frac{eH}{m\bar{v}} = \frac{e\lambda H}{h}.$$

If we consult (57b) we see that

$$CH^2 = (l/r)^2.$$

The denominator of (57) thus becomes appreciably different from unity when l becomes comparable to r. The type of orbit for the case $l \gg r$ is of a different nature from that for $l \ll r$. In the first case, the electron moves through several complete circular orbits before it collides with an ion, in the second, on the other hand, a collision is to be expected when the electron covers but a small fraction of the periphery of the circle.

II. The magnitude of the constant B. We now turn to a difficulty in the theory, namely that the value of B as predicted by (57a) is far too small (a factor of about 10^{-4} at room temperature) to explain the observed results for small fields. In the discussion of this problem, we can restrict ourselves to the case of weak fields, where the relative change of resistance follows a quadratic law. In order to explain this discrepancy, we shall find that the simple assumption of totally *free* electrons is no longer sufficient. We have already seen, that as long as we consider the conduction electrons as possessing one and the same velocity, the resistance of a metal remains unaltered in a magnetic field. The constant B, therefore, which is different from zero only when the conducting electrons possess different velocities, depends essentially on the fluctuations of v (or more exactly of l/v) among the electrons. We see this most easily by means of the following considerations. The condition that the current in the y direction vanish is, according to (31) and (29):

$$-\frac{e}{3}\left[\int \frac{l}{v}\cdot\frac{e}{m}F_y\frac{1}{v}\,\frac{\partial f_0}{\partial v}\cdot\frac{d\omega}{1+\mu^2l^2/v^2} - \mu\int\frac{l^2}{v^2}\,\frac{e}{m}F_x\frac{1}{v}\,\frac{\partial f_0}{\partial v}\,\frac{d\omega}{1+\mu^2l^2/v^2}\right]=0$$

or for small fields: (we develop in powers of μ):

$$F_y\int\frac{l}{v}\cdot\frac{1}{v}\,\frac{\partial f_0}{\partial v}d\omega - \mu F_x\int\frac{l^2}{v^2}\cdot\frac{1}{v}\,\frac{\partial f_0}{\partial v}d\omega = 0. \tag{58}$$

We now denote l/v by β; and define:

$$\bar{\beta} = \int\frac{l}{v}\cdot\frac{1}{v}\,\frac{\partial f_0}{\partial v}d\omega$$
$$\bar{\beta}^2 = \int\frac{l^2}{v^2}\cdot\frac{1}{v}\,\frac{\partial f_0}{\partial v}d\omega. \tag{59}$$

We then obtain

$$F_y = \mu F_x \bar{\beta}^2/\bar{\beta}. \tag{60}$$

The expression for the current in the x direction, I_x, is according to (31) and (29):

$$I_x = -\frac{e}{3}\left[\int \frac{l}{v}\cdot\frac{e}{m}F_x\frac{1}{v}\frac{\partial f_0}{\partial v}\frac{d\omega}{1+\mu^2l^2/v^2} + \mu\int\frac{l^2}{v^2}\frac{e}{m}F_y\frac{1}{v}\frac{\partial f_0}{\partial v}\frac{d\omega}{1+\mu^2l^2/v^2}\right] \tag{61}$$

or developing in powers of μ and keeping terms in μ^2:

$$I_x = -\frac{e^2}{3m}\left[F_x(\bar{\beta} - \mu^2\bar{\beta}^3) + \mu F_y\bar{\beta}^2\right]. \tag{62}$$

Here $\bar{\beta}^3$ is defined similarly as

$$\bar{\beta}^3 = \int\left(\frac{l}{v}\right)^3\cdot\frac{1}{v}\frac{\partial f_0}{\partial v}d\omega.$$

Inserting the value of F_y as given in (60) in the expression for I_x, we find:

$$\sigma = \frac{I_x}{F_x} = -\frac{e^2}{3m}\left(\bar{\beta} - \mu^2\frac{\bar{\beta}\bar{\beta}^3 - (\bar{\beta}^2)^2}{\bar{\beta}}\right).$$

The value of σ_0 is obtained by placing $\mu = 0$, and we get for:

$$-\frac{\Delta\sigma}{\sigma_0} = \frac{\Delta\rho}{\rho} = \mu^2\frac{\bar{\beta}\cdot\bar{\beta}^3 - (\bar{\beta}^2)^2}{(\bar{\beta})^2}\cdot \tag{63}$$

We see, therefore, that the relative change of resistance depends, as we have already remarked, on the fluctuations of β, i.e. of l/v. We have hitherto considered the only reason for fluctuations in l/v as the distribution in velocity of the electrons as given by the Fermi function, and this has proved to be too small to explain the observations.

There is, of course, another reason the values of l/v vary among the conduction electrons. The assumption that the electrons in a metal are totally free is only an approximation. As a matter of fact the electrons move in the potential field of the metal lattice and when this fact is taken into consideration the energy of the electrons no longer depends simply on the absolute magnitude of their velocity, but explicitly on the direction of the velocity. This means that the fluctuations of l/v become very much larger. One can show[8] that a fluctuation of some ten percent in the velocity of the electrons which have the same energy is sufficient to raise the value of $\underline{B}$ to the correct order of magnitude. We must content ourselves here with these more or less qualitative remarks; however, it should be pointed out that Eq. (63) loses its validity in a more exact calculation, as it presupposes the possibility of

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[8] This result is due to R. Peierls and was communicated in a letter to H. Bethe.

separating the equation of the steady state (27) into the two functions χ_1 and χ_2. This is no longer possible when the energy of the electrons does not depend on v^2 alone, and hence the exact calculation becomes very much more complicated.[9]

III. The influence of the spin. We now shall consider the effect of electron spin in this connection. We here show how this is to be obtained in the simplest manner from our preceding equations. We start from (39a):

$$\sigma = \frac{4\pi e^2 G}{m}\left(\frac{m}{h}\right)^3 H_2{}^s. \tag{64}$$

Here the upper index s denotes that the integral H_2 is to be calculated with the distribution function f_H as given by (23), thus taking the spin into account. We have therefore

$$\frac{\sigma}{\sigma_0} = \frac{H_2{}^s}{H_2}\cdot \tag{65}$$

Taking the value of $H_2{}^s$ from the appendix

$$H_2{}^s = H_2\left(1 - \left[\frac{\mu_0 H}{2kT \log A}\right]^2\right) \tag{66}$$

we find for the relative change of resistance:

$$\frac{\Delta\rho}{\rho} = \left(\frac{\mu_0}{2kT \log A}\right)^2 \cdot H^2 \tag{67}$$

for such values of H, that $\Delta\rho/\rho \ll 1$. Inserting the numerical values for Ag, ($T = 300$, $\mu_0 = 9.1 \times 10^{-21}$, $\log A = 210$), we find:

$$\Delta\rho/\rho = 3 \times 10^{-19} \cdot H^2 \tag{68}$$

which is about 50times smaller than the value found in (57a). ($B = 1.2 \times 10^{-17}$). It is clear that there will be no departure from the quadratic law for this effect in the magnetic fields which can be experimentally produced. The effect of the spin is independent of the direction of the magnetic field relative to the current, whereas our previous results were obtained for the case that they were mutually perpendicular. There is as yet no satisfactory explanation of the change of resistance of a metal when a magnetic field is applied parallel to the direction of the current flow. It is possible that the effect of the binding of the electrons in the metal lattice, and the consequent nonseparability of the stationarity equation will suffice to explain this phenomenon. Another possibility which may play an important role is the effect of the exchange (Austausch) phenomena among the electrons which may considerably increase the spin effect. At present, however, it is impossible to decide if these proposed explanations will suffice to account for the observations.

IV. The adiabatic case. Before closing this paragraph, we shall show that

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[9] Compare R. Peierls, Zeits. f. Physik **53**, 265 (1929).

$\Delta\rho/\rho$ vanishes in second approximation when a strictly adiabatic arrangement is employed. We have from (51):

$$\frac{\Delta\rho}{\rho} = \frac{K_2}{H_2}\left[1 + \mu^2\left(\frac{K_1D_1}{K_2D_0} - \frac{K_3'D_2}{K_2D_0}\right)\right].$$

As we are interested here only in the effect for weak fields, we shall place $\mu = 0$ in the calculation of the terms multiplying μ^2. We shall need D_0 and D_1 in second approximations, which means calculating the individual integrals involved to a third approximation. From the appendix we take the following values:

$$\left(\alpha = \frac{2\pi^2k^2T}{3m^2}\right)$$

$$H_1 = l^2\bar{v}\left(1 - \frac{\alpha T}{2\bar{v}^4}\right)$$

$$H_2 = l\bar{v}^2\left(1 - \frac{\alpha T}{2\bar{v}^4}\right)$$

$$D_0 = \alpha l^2\bar{v}^4\left(1 - \frac{3\alpha T}{\bar{v}^4}\right)$$

$$D_1 = \alpha l^3\bar{v}^3\left(1 - \frac{5}{2}\frac{\alpha T}{\bar{v}^4}\right)$$

$$K_2 = l\bar{v}^2\left(1 - \frac{\mu^2l^2}{\bar{v}^2} - \frac{\alpha T}{2\bar{v}^4}\right)$$

$$H_3' = 0.$$

We find then:

$$\frac{K_2}{H_2} = 1 - \frac{\mu^2l^2}{\bar{v}^2}\left(1 + \frac{\alpha T}{2\bar{v}^4}\right)$$

and

$$\frac{K_1D_1}{K_2D_0} = \frac{H_1D_1}{H_2D_0} = \frac{l^2}{\bar{v}^2}\left(1 + \frac{\alpha T}{2\bar{v}^4}\right)$$

and hence:

$$\frac{\sigma}{\sigma_0} = \left(1 - \frac{\mu^2l^2}{\bar{v}^2}\left[1 + \frac{\alpha T}{2\bar{v}^4}\right]\right)\left(1 + \frac{\mu^2l^2}{\bar{v}^2}\left[1 + \frac{\alpha T}{2\bar{v}^4}\right]\right) = 1.$$

which was to be shown. The fact that the adiabatic change of resistance is smaller than the isothermal is of no practical consequence, as we have seen that the magnitude of the actual effect is determined by the fluctuations of l/v among the electrons, and those due to the Fermi distribution which we have here alone taken into account are not essential.

(6). The galvanomagnetic effects.

In this paragraph we shall examine the results obtained for the two galvanomagnetic effects, *viz.* the Hall and Ettinghausen effects, more in detail. We have found (Eq. (39)) the value of the isothermal Hall constant as:

$$R_i = \frac{e}{m} \cdot \frac{1}{\sigma} \frac{K_1}{K_2} \cdot \tag{68a}$$

From Eq. (55), we see that in first approximation:

$$\frac{K_1}{K_2} = \frac{l}{(2kTu_0/m)^{1/2}} = \frac{l}{\bar{v}} = \frac{ml\lambda}{h} \tag{69}$$

and using the value of $\sigma = (8\pi/3)(e^2 l/h\lambda^2)$, we find, as before:

$$R_i = \frac{3}{8\pi} \frac{\lambda^3}{e} = \frac{1}{ne} \tag{70}$$

as the value of the isothermal Hall constant, independent of the magnetic field. That this latter conclusion is unaffected by the introduction of the spin, we see at once from the values of K_1 and K_2 with spin as given in the appendix:

$$K_1^s = K_1\left[1 - \left(\frac{\mu_0 H}{2kT \log A}\right)^2\right]$$

$$K_2^s = K_2\left[1 - \left(\frac{\mu_0 H}{2kT \log A}\right)^2\right].$$

In fact no dependence of the Hall constant on the strength of the magnetic field has been found for the normal metals, which is in accordance with our theoretical conclusions.

Turning to the adiabatic Hall effect, we find from (43) with the help of (45):

$$R_a = \frac{e}{m\sigma} \cdot \frac{K_1 K_8' - K_5 K_4'}{K_2 K_8' - K_6 K_4'} \cdot \tag{71}$$

If we insert the values of the integrals in first approximation, we find that both numerator and denominator vanish, leaving the value of R_a indeterminate in this approximation. This is in accord with our previous remark that for an adiabatic effect, all integrals have to be evaluated to a second approximation. Using the values of the integrals as given in the appendix in second approximation, we find:

$$R_a = \frac{e}{m\sigma} \cdot \frac{l}{\bar{v}} = R_i. \tag{72}$$

We thus find that the adiabatic Hall effect is equal to the isothermal effect, if we assume, as is done throughout, that the number of free electrons does not depend on the temperature. The equality of R_a and R_i is not surprising, as it holds in first approximation (the quotient of the two second order quantities is in itself a quantity of the first order), and in this approximation the heat conductivity vanishes.[10] A numerical calculation of the Hall constant for Ag at room temperature gives $R = 10.4 \times 10^{-4}$ and the experimentally determined value is $R = 8.4 \times 10^{-4}$, a most satisfactory agreement. In this connection, we must point out that the classical theory, i.e. when one uses the Maxwell instead of the Fermi distribution law, leads to the following values of R:

$$R_i = 3\pi/8en$$

$$R_a = 27\pi/64en$$

the numerical values of which differ but little from that obtained by the new theory.

For the Ettinghausen effect, we have from (44) and (45):

$$P = \frac{e^2}{m^2\sigma} \frac{K_1K_6 - K_2K_5}{K_2K_8' - K_6K_4'} \cdot \tag{73}$$

Here again both numerator and denominator are different from zero only when the second approximation is carried out, but the quotient is of the first order. We find upon inserting the values given in the appendix:

$$P = \frac{e^2}{m^2\sigma} \cdot \frac{lT}{\bar{v}^3} \cdot \tag{74}$$

We thus find that the Ettinghausen constant, just as the Hall constant, is independent of the magnetic field in this approximation. If the value of σ is inserted into (74) along with the de Broglie wave-length λ, the final expression for P becomes

$$P = \frac{mT}{n} \cdot \left(\frac{\lambda}{h}\right)^2 . \tag{75}$$

A numerical estimation for the case of Ag at room temperature leads to the value 0.3×10^{-9} as compared to the measured value of 1.6×10^{-9}. The predicted value is thus found to be of the correct order of magnitude, but about five times too small, a discrepancy which is not to be looked upon as serious in view of the assumptions made in deriving (75). For example, the dependence of the electron free path on velocity has been consistently neglected, as not much can be said about it. It is not unreasonable to suppose, however, that discrepancies, such as that which is here found, are due to the dependence of l on v. The classical theory yields for P:

$$P = \frac{3\pi}{32} \cdot \frac{1}{kn}$$

an expression whose numerical value for Ag is about 3.7×10^{-8}. This value is no longer of the correct order of magnitude, (about 20 times too large), and here we find the new theory predicting a somewhat better value.

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[10] Compare p. 11.

Summarizing the results, we can say that the new theory affords a somewhat better explanation of the galvanomagnetic effects than the classical theory gave. In both theories, however, fails completely an explanation of the fact that these effects, and also the thermomagnetic effects, show variations in sign among different metals. It seems that the solution of this problem is to be found in the departure of the electrons from complete freedom, thus involving a more rigorous wave mechanical treatment of the problem. We return to this point in §9.

(7). The thermomagnetic effects.

The thermomagnetic effects, comprising the Nernst and Righi-Leduc effects, form the subject of discussion of this paragraph. We see that the actual calculation of these effects shall prove somewhat more troublesome than the corresponding calculation of the galvanomagnetic effects, as we now have 3-rowed determinants to evaluate instead of 2-rowed ones as hitherto, except for the case of the isothermal Nernst coefficient, which we write according to (41) as:

$$Q_i = \frac{K_1K_4' - K_2K_3'}{K_2^2\left(1 + \mu^2\frac{K_1^2}{K_2^2}\right)}\cdot \tag{76}$$

With (69) and the values of the integrals given in the appendix we obtain easily:

$$Q_i = \frac{\alpha l}{2\bar{v}^3}\left(1 - \frac{\mu^2 l^2}{\bar{v}^2}\right); \quad \alpha = \frac{2\pi^2 k^2 T}{3m^2} \tag{77}$$

which is an effect of second order. (Only the numerator of (76) vanishes in first approximation). At room temperature the term depending on the magnetic field, which can be written as $(el\lambda/h)^2H^2$ is exceedingly small compared to unity for all field strengths which can easily be obtained. This fact has already been assumed in the evaluation of the integrals. We can write with an exceedingly good degree of approximation:

$$Q_i = \frac{\pi^2k^2mlT}{3}\left(\frac{\lambda}{h}\right)^3. \tag{77a}$$

Turning now to the adiabatic effects, Eq. (49) and (50) become, with the help of (48) and a simple algebraic reduction:

$$Q_a = \frac{(K_1K_4' - K_2K_3')(K_1K_8' - K_5K_4') + (K_2K_4' + \mu^2K_1K_3')(K_1K_7' - K_5K_3')}{(K_2^2 + \mu^2K_1^2)(K_1K_8' - K_5K_4') - (K_2K_4' + \mu^2K_1K_3')(K_1K_6 - K_2K_5)}$$

and

$$\frac{m}{e}S = \frac{(K_2^2 + \mu^2K_1^2)(K_1K_7' - K_5K_3') + (K_1K_6 - K_2K_5)(K_1K_4' - K_2K_3')}{(K_2^2 + \mu^2K_1^2)(K_1K_8' - K_5K_4') - (K_2K_4' + \mu^2K_1K_3')(K_1K_6 - K_2K_5)}\cdot$$

The evaluation of these expressions including the dependence on the magnetic field is rather complicated, so we shall restrict ourselves to the case of weak fields (which is sufficient for all practical purposes). The rather unwieldly expressions (78) can be then simplified by means of the following consideration: the denominators ($\mu=0$) can be written in the following form:

$$H_2^2(H_1H_8' - H_5H_4')\left[1 - \frac{H_4'}{H_2}\left(\frac{H_1H_6 - H_2H_5}{H_1H_8' - H_5H_4'}\right)\right].$$

With the help of (71) and (73) the second term in the square brackets is easily shown to be equal to

$$\frac{m}{e}\,\frac{H_4'}{H_2}\cdot\frac{P}{R}\,.$$

H_4' vanishes in first approximation, but H_2 and R do not (see appendix). Hence this term can be neglected in comparison to unity. The expressions (78) thus reduce to the simpler forms:

$$Q_a = \frac{H_1H_4' - H_2H_3'}{H_2^2} + \frac{H_4'}{H_2}\left(\frac{H_1H_7' - H_5H_3'}{H_1H_8' - H_5H_4'}\right) \tag{79}$$

and

$$\frac{m}{e}S = \frac{H_1H_7' - H_5H_3'}{H_1H_8' - H_5H_4'} + \frac{(H_1H_6 - H_2H_5)(H_1H_4' - H_2H_3')}{H_2^2(H_1H_8' - H_5H_4')}\,. \tag{80}$$

The second term of (80) is clearly to be neglected in comparison with the first, as it is of the second order and the first term is of the first order. (The second term is equal to PQ_i/R.) Accordingly, the value of S becomes:

$$S = \frac{e}{m}\,\frac{H_1H_7' - H_5H_3'}{H_1H_8' - H_5H_4'} \tag{81}$$

and that of Q_a, with the help of (81) and (76):

$$Q_a = Q_i + \frac{m}{e}\,\frac{H_4'}{H_2}S. \tag{82}$$

Introducing the Thomson potential gradient coefficient μ_P as defined by Eq. (15) (Sec. A); (82) becomes:

$$Q_a = Q_i + \mu_P S. \tag{83}$$

The evaluation of (81) with the help of the integrals tabulated in the appendix gives for S:

$$S = \frac{e}{m}\,\frac{l}{\bar{v}} = \frac{el\lambda}{h} \tag{84}$$

and for Q_a:

$$Q_a = 2Q_i = \frac{2\pi^2 mlk^2T}{3}\left(\frac{\lambda}{h}\right)^3. \tag{85}$$

The numerical values for these expressions for Ag at room temperature are

$$Q_a = 2Q_i = 1.0 \times 10^{-4}$$
$$S = 6.7 \times 10^{-7}.$$

The values measured are:

$$Q = 1.8 \times 10^{-4}$$
$$S = 2.7 \times 10^{-7}$$

and we find the agreement quite satisfactory. The classical theory gives the following values for Ag at room temperature:

$$Q_a = \frac{15\pi}{32}\frac{lk}{(2\pi mkT)^{1/2}} = 68 \times 10^{-4}$$
$$Q_i = \frac{\pi}{4}\frac{lk}{(2\pi mkT)^{1/2}} = 36.4 \times 10^{-4}$$
$$S = \frac{7\pi}{16}\frac{le}{(2\pi mkT)^{1/2}} = 7.2 \times 10^{-7}.$$

The value of S agrees essentially with the value obtained by the new theory. Q, however, is 20 to 30 times too large, and here we see that the new theory is in better agreement with experiment than the classical theory.

We shall not enter into a detailed discussion of the change of thermal conductivity in a magnetic field as the effect is so small that it has never been observed for normal metals. It turns out that in the adiabatic arrangement (i.e. no heat flow perpendicular to the direction of the primary heat current) the predicted change is smaller than that due to the effect of the electron spin.

(8). The relations among the transverse effects.

There are a number of relations which have been found among the four transverse galvano- and thermomagnetic effects, some of which are purely empirical and others with more or less of a theoretical foundation. We shall now see that these relations can be theoretically established on the basis of the foregoing values for the various effects.

I. Hall and Leduc effects. We have found for the Hall constant the value

$$R = \frac{1}{\sigma}\frac{el\lambda}{h} \qquad (Eq.\ 36)$$

and for the Leduc-Righi coefficient the value:

$$S = el\lambda/h. \qquad (Eq.\ (84)$$

A comparison of these two expressions shows that

$$S = \sigma R. \qquad (86)$$

The appearance of σ in this equation is due to the following fact. The Hall constant is defined per unit primary current, the Leduc coefficient on the other hand per unit temperature gradient. Were the Hall constant defined as the transverse potential gradient per unit primary potential gradient, this asymmetry would disappear and Eq. (86) would then simply be $S=R$. The other relations among these effects would also be somewhat simplified. The historical reason for such an asymmetry is closely connected with our remarks in section A concerning the quantities which are experimentally controllable. The relation (86) is well obeyed experimentally. The following table shows the results for a number of metals as given by Bridgman:[11]

TABLE IV.

Metal	Ag	Al	Cd	Co	Cu	Fe	Ni	Zn	Au	Sb	Bi
$\sigma R \times 10^7$	−5.0	−1.4	+1.2	+2.5	−3.0	+7.2	−2.5	+1.2	−2.7	+48	−400
$S \times 10^7$	−2.7	−0.62	+0.89	+1.1	−2.1	+5.2	−2.5	+1.1	−2.5	−20.1	−20.5

Bismuth, which is decidedly abnormal in regard to all magnetic effects, shows a departure from the law, but all the other metals obey it within the experimental uncertainty. One must remember that the Leduc effect is extremely difficult to measure and that fluctuations of 100 percent in the measured values are found. The Hall effect can be relied upon on the average with a precision of some 30 percent.

II. Nernst and Ettinghausen coefficients. Bridgman and Lorentz have derived the following relation:

$$Q_i = \kappa P/T. \tag{87}$$

We have inserted the subscript i to denote the isothermal Nernst coefficient. The difference between the isothermal and adiabatic Nernst effects is not made in the original papers, but is clear from the following derivation of this law due to Bridgman. We consider a primary electric current flowing in the x direction. (Fig. 3) Because of the Ettinghausen effect this produces a temperature gradient $\partial T/\partial y$ in the y direction (T_2, T_1). If we now imagine that we let a heat current flow in the external (dotted) circuit and do work, then this energy must be supplied by the primary current. The heat current which flows in the external circuit is

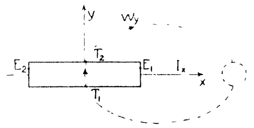

Fig. 3.

$$W_y = \kappa \partial T/\partial y = \kappa P I_x H$$

using the definition of P. The power delivered by this heat current is obviously (per cm in the y direction):

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[11] P. W. Bridgman, Phys. Rev. **24,** 644 (1924).

$$W_y\frac{1}{T}\,\frac{\partial T}{\partial y} = \frac{\kappa P I_x H}{T}\,\frac{\partial T}{\partial y}.$$

As this energy must be supplied by the primary current, the heat current W_y must produce an electric F_x in the x direction against which the current must flow by virtue of the Nernst effect (E_1, E_2). The power thus expended by the primary current is:

$$I_x F_x = I_x Q_i H \partial T/\partial y.$$

It is clear that the isothermal value of Q_i must be used here, as we must suppose that the x direction in which a primary electric current flows is at constant temperature for the same reasons which are given in paragraph 4. Equating these two expressions for the energy expended per unit time, we find exactly the desired relation $Q_i = \kappa P/T$.

As this relation is derived from purely energetic considerations, we should expect that it is exactly obeyed by the expressions we have found. This is indeed so, and we proceed to give the proof for small magnetic fields. We have the following expressions for weak fields: (76), (73), (11b):

$$Q_i = \frac{H_1 H_4' - H_2 H_3'}{H_2^2}$$

$$P = \frac{e^2}{m^2\sigma}\,\frac{H_1 H_6 - H_2 H_5}{H_2 H_8' - H_6 H_4'}$$

$$\kappa = \frac{4\pi m G}{6}\left(\frac{m}{h}\right)^3 \frac{H_2 H_8' - H_6 H_4'}{H_2} = \frac{m^2\sigma}{2e^2}\left(\frac{H_2 H_8' - H_6 H_4'}{H_2^2}\right).$$

We must then show that

$$H_1 H_4' - H_2 H_3' = \frac{1}{2T}(H_1 H_6 - H_2 H_5). \tag{88}$$

The integrals H_3' and H_4' are, by definition (38):

$$\left.\begin{aligned} H_3' &= \int_0^\infty \frac{\partial f_0}{\partial T} l^2 v^2 dv \\ H_4' &= \int_0^\infty \frac{\partial f_0}{\partial T} l v^3 dv \end{aligned}\right\} \tag{89}$$

We have:

$$\begin{aligned} \frac{\partial f_0}{\partial T} &= \frac{\partial}{\partial T}\left(\frac{1}{(1/A)e^{m2v^2/2kT} + 1}\right) = -f_0^2\frac{\partial}{\partial T}\left(\frac{1}{A}e^{mv^2/2kT}\right) \\ &= \frac{1}{A} f_0^2 e^{mv^2/2kT}\left(\frac{mv^2}{2kT^2} + \frac{1}{A}\,\frac{dA}{dT}\right). \end{aligned}$$

On the other hand:

$$\frac{\partial f_0}{\partial v} = -\frac{mv}{kT}\cdot\frac{1}{A}f_0{}^2 e^{mv^2/2kT}$$

so that

$$\frac{\partial f_0}{\partial T} = -\frac{\partial f_0}{\partial v}\left[\frac{v}{2T} + \frac{kT}{m}\,\frac{d\log A}{dT}\cdot\frac{1}{v}\right] \tag{90}$$

Inserting the value of $\partial f_0/\partial T$ as given by (90) in the integrals (89), they become

$$H_3{}' = \frac{1}{2T}\int_0^\infty f_0\frac{\partial}{\partial v}(l^2v^3)dv + \frac{kT}{m}\,\frac{d\log A}{dT}\int_0^\infty f_0\frac{\partial}{\partial v}(l^2v)dv$$

$$H_4{}' = \frac{1}{2T}\int_0^\infty f_0\frac{\partial}{\partial v}(lv^4)dv + \frac{kT}{m}\,\frac{d\log A}{dt}\int_0^\infty f_0\frac{\partial}{\partial v}(lv^2)dv.$$

A comparison of these integrals with those defined in (38) now shows that:

$$H_3{}' = \frac{H_5}{2T} + H_1\frac{kT}{m}\,\frac{d\log A}{dT}$$

and

$$H_4{}' = \frac{H_6}{2T} + H_2\frac{kT}{m}\,\frac{d\log A}{dT}$$

and therefore

$$H_1H_4{}' - H_2H_3{}' = \frac{1}{2T}(H_1H_6 - H_2H_5)$$

which was to be proved. A comparison of the measured values of Q and of $\kappa P/T$ is given the following table:[12]

TABLE V.

Metal	Ag	Al	Cd	Co	Cu	Fe	Ni	Zn	Au	Sb	Bi
$Q\times10^4$	-1.8	$+0.42$	-1.2	$+7.8$	-1.9	-9.5	$+10$	-0.73	-1.7	$+176$	$+1780$
$(\kappa P/T)\times10^4$	-2.2	$+0.74$	-0.90	$+4.3$	-2.0	-8.5	$+6.1$	-0.99	-0.93	$+110$	$+950$

The agreement is certainly all that can be expected.

III. Bridgman's relation among the four effects. Equations (86) and (87) lead immediately to another relation proposed by Bridgman, namely:

$$\frac{PR}{Q_iS} = \frac{T}{\kappa\sigma} \tag{90}$$

which also agrees very well with experiment. It is interesting to note that the isothermal value of Q appears in this equation, a point which is not stressed

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[12] P. W. Bridgman, reference 11.

by Bridgman. We can combine Eqs. (86) and (87), however, in a somewhat neater manner by dividing the latter by the former. This leads to the relation:

$$\frac{RQ_i}{PS} = \frac{\kappa}{\sigma T} = \frac{\pi^2}{3}\left(\frac{k}{e}\right)^2 \tag{91}$$

which is course equivalent to (90). In this way we find a law among the four coefficients analogous to the Wiedemann-Franz law; in fact, the constant on the right hand side of (91) is the Wiedemann-Franz constant. The following table gives the values of RQ_i/PS taken from measurements.

TABLE VI.

Metal	Ag	Al	Cd	Co	Cu	Fe	Ni	Zn	Au	Sb	Bi
$RQ_i/PS\times 10^{-8}$	3.4	2.6	4.1	8.0	3.1	3.7	3.8	1.9	4.6	9.9	155

The numerical value predicted by (91) is 2.45×10^8. The agreement is worthy of notice and surely within the experimental error, except in the case of bismuth and perhaps antimony. According to the classical theory

$$\frac{RQ_i}{PS} = \frac{16}{7}\left(\frac{k}{e}\right)^2 = 1.7\times 10^8.$$

Here the isothermal value of R is used. If we use the adiabatic value, a factor of 9/8 must be introduced. Although the values in the table check the new theoretical result somewhat better than the old one, the experimental uncertainty is so large that no such difference can be looked upon as convincing. Much more convincing is the fact that the four individual effects are better given by the new theory than by the classical theory.

IV. Moreau's relation. We come finally to a relation proposed by Moreau,[13] which is well confirmed by experiment:

$$Q = \mu R\sigma. \tag{92}$$

Here Q denotes the Nernst coefficient and μ the Thomson coefficient (both not more exactly defined). If we consult Eq. (83), we find

$$Q_a - Q_i = \mu_P S$$

and using (86), this becomes:

$$Q_a - Q_i = \mu_P R\sigma. \tag{93}$$

We thus see that the relation of Moreau can be theoretically deduced, if we interpret Q as the difference between the adiabatic and isothermal Nernst coefficients, and μ as the Thomson potential gradient coefficient, and not as the measured energy coefficient μ_E. The reason that (92) is well confirmed by experiment is that $Q_a=2Q_i$, and hence $Q_a-Q_i=Q_i$ and that according to

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[13] G. Moreau, Comptes Rendus **130**, 120, 412, 562 (1900).

Eq. (22d), $\mu_P = \mu_E/2$. Since not more than an agreement in order of magnitude can be expected (the measurements of μ_E are hardly reproducible), Eq. (93) agrees with experiment fully as well as (92).

(9). Wave mechanical refinements.

We have seen that the results of our theoretical considerations have, on the whole, been quite satisfactory and have the advantage of being relatively simple. We must now, however, discuss the weaknesses therein and shall try to give a general idea of how these remaining questions are to be solved. In the case of the change of resistance of a metal in a magnetic field, we encountered a defect in the theory, and of course the fact that the theory offers only a possibility of one sign for the galvano- and thermomagnetic effects (corresponding to the negative charge of the electron) is very disturbing. This difficulty, which existed in the classical theory, has given rise to many speculations about the existence of positive carriers of electricity in the process of electrical conduction. Another very unsatisfactory phase of our theory is the necessity of treating the free path of the electrons as a more or less phenomenological quantity, and to a less extent the more or less plausible assumptions (which are introduced concerning the number of free electrons are not wholly free from criticism.

The removal of the aforementioned weaknesses can be accomplished by a more rigorous wave mechanical calculation (as we have already mentioned in the text) which treats the electrons no longer as free particles, but as material waves moving in the field of the lattice ions or atoms. This more correct model immediately frees us of the necessity of introducing the accessory quantities, free path and number of free electrons, but offers in their place quantities which demand a far more thorough knowledge of the interatomic fields than is now available. At the time of writing, the results of the wave mechanical calculations of conductivity are so complicated and contain so many unknown quantities, that one cannot use it for a quantitative discussion in most cases.

Bloch[14] has given the first complete wave mechanical calculation of conductivity. There are several points in which his results add essentially to those obtained by the more simple theory. In the first place, it is characteristic of our theory that the collisions (or interaction) between electrons and atoms (or lattice vibrations) have been considered as elastic (without change of energy). That this is only approximately true for high temperatures and not at all so for low temperatures, one can see from the following consideration; if we consider the interaction between the electron "waves" and the heat oscillations of the metal lattice, it is clear from the selection rules for the harmonic oscillator, that such interaction can take place only when the electrons gain or lose an amount of energy equal to $h\nu$ with ν the frequency of the lattice oscillation with which the electron interacts. This small but definite energy interchange is of importance because of the Pauli exclusion principle, which allows such transitions to take place only if the end state is not already

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[14] F. Bloch, Zeits. f. Physik **52**, 555 (1928).

occupied by another electron. Because of these "inelastic" collisions, the stationary condition which lies at the basis of the whole calculation must be modified. This modification becomes important at low temperatures but does not change the state of affairs much at high temperatures. In the former case most of the possible end states are already occupied, whereas in the latter, this is no longer true. This accounts for the increase of conductivity at very low temperatures, since the collisions alone prevent an infinite conductivity and insure the stationary state, so that if they are infrequent, the conductivity becomes correspondingly large.

There is another effect at very low temperatures which becomes important in limiting the number of collisions. In Bloch's work it is assumed that the oscillations of the metal lattice are always in thermal equilibrium. This equilibrium is certainly disturbed by the collisions and if the time necessary for the re-establishment of equilibrium is small compared to the time between collisions, then Bloch's assumption is essentially correct. An investigation of this point is carried out by Peierls,[15] who shows that the departure from harmonicity of the lattice oscillations is responsible for the maintenance of equilibrium (and for the heat conductivity of insulators). At low temperatures, however, due to the reduced amplitude of the lattice oscillations, departures from harmonicity are rare, and it takes a relatively long time for the lattice of itself to come to equilibrium. In this case, the electron collisions become the controlling factor in the maintenance of thermal equilibrium and the calculations of Bloch must be accordingly modified.[15]

Characteristic of the motion of the electron "waves" is the dependence of their energy on the velocity components (or more exactly, on the quantum numbers of their states of translation). This is no longer given by the simple relation $E \sim v^2$. We consider a metallic crystal and characterize the available state of translation for each electron by the quantum numbers k, l, m. The energy belonging to one of these states may be written:[16]

$$E_{klm} = E_0 - \text{const.}\ [\cos (k/k_0 + \cos (l/l_0) + \cos (m/m_0)] \tag{94}$$

and the current for the same state in the x direction

$$S_{klm} = \text{const.}\ \sin (k/k_0). \tag{95}$$

Equation (94) shows a most interesting result, in that the values of k_0, l_0 and m_0 are equal to one another only for cubic crystals. For small values of k, l and m, the energy is then given essentially by const. $(k^2+l^2+m^2)$ just as in the case of free electrons. But it is noteworthy that for non-cubic crystals in this approximation the energy does not depend simply on $(k^2+l^2+m^2)$. The so-called normal metals all have a cubic crystal structure and the abnormality which is often present in metals which display other than a cubic structure may be explained to a large extent by the "abnormal" dependence of the energy of its electrons on the quantum numbers.

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[15] R. Peierls, Ann. d. Physik (5) **4**, 121 (1930).

[16] F. Bloch, Zeits. f. Physik **52**, 555 (1928).

Equation (95) leads to a most surprising consequence. For electrons for which $k<\pi k_0/2$ the current increases with increasing k, but for those for which $k>\pi k_0/2$ it decreases. In the latter case, therefore, an electron in an electric field (the field produces an increase in k) is actually decelerated instead of accelerated. Peierls[17] had made use of this fact to try to explain the change of sign of the Hall effect. For such metals in which the values of $k<\pi k_0/2$ the Hall effect will have the normal sign (corresponding to that of bismuth) and for those in which $k>\pi k_0/2$ it will have the opposite sign.

Thus wave mechanics offers in principle the possibility of the removal of the unpleasant features of the simple theory of free electrons. There remains of course a large amount of work to be done in regard to a more complete solution of the problems of conduction than has been obtained. An important step in this direction has been recently taken by Morse,[18] who has attacked the mathematical problem of finding the exact wave functions and their eigenvalues in a metallic crystal in a systematic manner.

APPENDIX

§1. In this appendix we bring together the values of a number of integrals and combinations of them which are necessary in the text. There are the following eight integrals which primarily interest us:

$$K_1 = \int_0^\infty f_0\frac{\partial}{\partial v}\left(\frac{l^2v}{1+\mu^2l^2/v^2}\right)dv; \quad K_5 = \int_0^\infty f_0\frac{\partial}{\partial v}\left(\frac{l^2v^3}{1+\mu^2l^2/v^2}\right)dv$$

$$K_2 = \int_0^\infty f_0\frac{\partial}{\partial v}\left(\frac{lv^2}{1+\mu^2l^2/v^2}\right)dv; \quad K_6 = \int_0^\infty f_0\frac{\partial}{\partial v}\left(\frac{lv^4}{1+\mu^2l^2/v^2}\right)dv$$

$$K_3 = \int_0^\infty f_0\frac{l^2v^2dv}{1+\mu^2l^2/v^2}; \quad K_7 = \int_0^\infty f_0\frac{l^2v^4dv}{1+\mu^2l^2/v^2}$$

$$K_4 = \int_0^\infty f_0\frac{lv^3dv}{1+\mu^2l^2/v^2}; \quad K_8 = \int_0^\infty f_0\frac{lv^5dv}{1+\mu^2l^2/v^2}$$

v denotes the velocity of the electrons, l their mean free path, $\mu=eH/m$ with e the charge, m the mass of an electron, and H the magnetic field strength. f_0 is the Fermi distribution function:

$$f_0 = \frac{1}{(1/A)e^{mv^2/2kT}+1} = \frac{1}{e^{u-u_0}+1} \qquad (A1)$$

with

$$u = mv^2/2kT; \quad u_0 = \log A.$$

We shall evaluate the integrals for the case $\mu^2l^2/v^2\ll 1$ that is, for weak magnetic fields, and with l treated as independent of the velocity. These restric-

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[17] R. Peierls, reference 9.

[18] P. M. Morse, Phys. Rev. 35, 1310 (1930).

tions are not necessary, but are sufficient for obtaining the order of magnitude of the results. The case for which K_1 and K_2 are needed without approximation in μ i.e. H, is treated in detail in the text. In all the above integrals, we write

$$\frac{1}{1+\mu^2l^2/v^2} = 1 - \frac{\mu^2l^2}{v^2} \qquad (A2)$$

and in the following (as in the text) H_i is to denote the value of K_i for $\mu=0$.

Introducing the variable u and the abbreviation $w=m\mu^2/2kT$ in the integrals, we can now write:

$$\left.\begin{aligned}
K_1 &= l^2\left(\frac{2kT}{m}\right)^{1/2}\int_0^\infty f_0\frac{d}{du}\left(u^{1/2}-\frac{wl^2}{u^{1/2}}\right)du\\
K_2 &= l\frac{2kT}{m}\int_0^\infty f_0\frac{d}{du}(u-wl^2)du\\
K_5 &= l^2\left(\frac{2kT}{m}\right)^{3/2}\int_0^\infty f_0\frac{d}{du}(u^{3/2}-wl^2u^{1/2})du\\
K_6 &= l\left(\frac{2kT}{m}\right)^2\int_0^\infty f_0\frac{d}{du}(u^2-wl^2u)du
\end{aligned}\right\} \qquad (A3)$$

It is convenient to write the remaining integrals in the form:

$$\left.\begin{aligned}
K_3 &= \frac{H_5}{3} - \mu^2l^2H_1 = H_3 - \mu^2l^2H_1\\
K_4 &= \frac{H_6}{4} - \frac{\mu^2l^2}{2}H_2 = H_4 - \frac{\mu^2l^2}{2}H_2\\
K_7 &= H_7 - \frac{\mu^2l^2}{3}H_5 = H_7 - \mu^2l^2H_3\\
K_8 &= H_8 - \frac{\mu^2l^2}{4}H_6 = H_8 - \mu^2l^2H_4
\end{aligned}\right\} \qquad (A4)$$

The integrals H_7 and H_8 are given by:

$$\left.\begin{aligned}
H_7 &= \frac{l^2}{5}\left(\frac{2kT}{m}\right)^{5/2}\int_0^\infty f_0\frac{d}{du}(u^{5/2})du\\
H_8 &= \frac{l}{6}\left(\frac{2kT}{m}\right)^3\int_0^\infty f_0\frac{d}{du}(u^3)du
\end{aligned}\right\} \qquad (A6)$$

The method for the evaluation of integrals of the type $\int_0^\infty f_0(d\phi i/du)du$ is given in the paper cited on the first page. We shall carry through the evaluation here to the third approximation, retaining the dependence on the magnetic field only in the first two approximations, and obtain:

$$\int_0^\infty f_0 \frac{d\phi_i}{du} du = \phi_i(u_0) + \frac{\pi^2}{6}\left(\frac{d^2\phi_i}{du^2}\right)_{u=u_0} + \frac{7\pi^4}{360}\left(\frac{d^4\phi_i}{du^4}\right)_{u=u_0} \tag{A7}$$

Carrying out the indicated differentiations, we find:

$$\left.\begin{aligned} K_1 &= \left(\frac{2kTu_0}{m}\right)^{1/2} l^2\left\{1 - \frac{wl^2}{u_0} - \frac{\pi^2}{24u_0^2}\left(1 + \frac{3wl^2}{u_0}\right) - \frac{7\pi^4}{384u_0^4}\right\} \\ K_2 &= \frac{2kTu_0}{m} l\left\{1 - \frac{wl^2}{u_0}\right\} \\ K_5 &= \left(\frac{2kTu_0}{m}\right)^{3/2} l^2\left\{1 - \frac{wl^2}{u_0} + \frac{\pi^2}{8u_0^2}\left(1 + \frac{wl^2}{u_0}\right) + \frac{7\pi^4}{640u_0^4}\right\} \\ K_6 &= \left(\frac{2kTu_0}{m}\right)^2 l\left\{1 - \frac{wl^2}{u_0} + \frac{\pi^2}{3u_0^2}\right\} \end{aligned}\right\} \tag{A8}$$

and

$$\left.\begin{aligned} H_7 &= \frac{l^2}{5}\left(\frac{2kTu_0}{m}\right)^{5/2}\left\{1 + \frac{5\pi^2}{8u_0^2} - \frac{7\pi^4}{384u_0^4}\right\} \\ H_8 &= \frac{l}{6}\left(\frac{2kTu_0}{m}\right)^3\left\{1 + \frac{\pi^2}{u_0^2}\right\} \end{aligned}\right\} \tag{A9}$$

From these equations all the desired results can be obtained. We must first, however, determine the value of $u_0 = \log A$ in the third approximation. The condition which fixes u_0 is the constancy of the number of free electrons. This is expressed by the equation:[19]

$$n = \frac{4\pi}{3} G\left(\frac{m}{h}\right)^3\left(\frac{2kT}{m}\right)^{3/2}\int_0^\infty f_0 \frac{d}{du}(u^{3/2})du$$

or

$$n = \frac{4\pi G}{3}\left(\frac{m}{h}\right)^3 \frac{H_5}{l^2} \tag{A10}$$

Using (A8) we find immediately:

$$\left(\frac{3n}{4\pi G}\right)^{2/3} = \left(\frac{m}{h}\right)^2\left(\frac{2kTu_0}{m}\right)\left\{1 + \frac{\pi^2}{8u_0^2} + \frac{7\pi^4}{640u_0^4}\right\}^{2/3}.$$

If we now introduce the de Broglie wave-length λ defined by:

$$\lambda^3 = 4\pi G/3n \tag{A11}$$

and the corresponding velocity

$$\bar{v} = h/m\lambda \tag{A12}$$

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[19] Compare Zeits. f. Physik **47**, 1 (1928) Eq. (18).

then we can write

$$\frac{2kTu_0}{m} = \left(\frac{h}{m\lambda}\right)^2 \left\{1 + \frac{\pi^2}{8u_0^2} + \frac{7\pi^4}{640u_0^4}\right\}^{-2/3}$$

or

$$\frac{2kTu_0}{m} = \bar{v}^2\left(1 + \frac{\pi^2}{8u_0^2} + \frac{7\pi^4}{640u_0^4}\right)^{-2/3}. \tag{A13}$$

This equation can be solved by successive approximations. Introducing the abbreviation:

$$\alpha = 2\pi^2k^2T/3m^2 \tag{A14}$$

we obtain the following series of equations, which are later needed:

$$\left.\begin{aligned}
\frac{2kTu_0}{m} &= \bar{v}^2\left(1 - \frac{\alpha T}{2\bar{v}} - \frac{9}{20}\,\frac{\alpha^2T^2}{\bar{v}^8}\right)\\
\frac{wl^2}{u_0} &= \frac{\mu^2l^2}{\bar{v}^2}\left(1 + \frac{\partial T}{2\bar{v}^4}\right)\\
\frac{1}{u_0^2} &= \frac{6\alpha T}{\pi^2\bar{v}^4}\left(1 + \frac{\alpha T}{\bar{v}^4}\right)\\
\frac{1}{u_0^4} &= \frac{36\alpha^2T^2}{\pi^4\bar{v}^8}\\
\frac{d}{dT}\left(\frac{1}{u_0^2}\right) &= \frac{12\alpha}{\pi^2\bar{v}^4}\left(1 + \frac{2\alpha T}{\bar{v}^4}\right)\\
\frac{d}{dT}\left(\frac{1}{u_0^4}\right) &= \frac{144\alpha^2T}{\pi^4\bar{v}^8}
\end{aligned}\right\} \tag{A15}$$

It is to be emphasized that the quantities λ and $\bar{v}$ depend only on n and are assumed to be independent of the temperature. $\bar{v}$ is the critical velocity of the Fermi distribution function for $T=0$. It is not to be confused with $\bar{v}$ for other temperatures which can readily calculated by means of (A10).

We now introduce the values of u_0 as given by (A15) in the equations (A8) and obtain as final formulas:

$$\boxed{\begin{aligned}
K_1 &= l^2\bar{v}\left[1 - \frac{\mu^2l^2}{\bar{v}^2} - \frac{\alpha T}{2\bar{v}^4}\left(1 + \frac{2\mu^2l^2}{\bar{v}^2}\right) - \frac{11}{10}\,\frac{\alpha^2T^2}{\bar{v}^8}\right]\\
K_2 &= l\bar{v}^2\left[1 - \frac{\mu^2l^2}{\bar{v}^2} - \frac{\alpha T}{2\bar{v}^4} - \frac{9}{20}\,\frac{\alpha^2T^2}{\bar{v}^8}\right]\\
K_5 &= l^2\bar{v}^3\left[1 - \frac{\mu^2l^2}{\bar{v}^2}\left(1 - \frac{\alpha T}{2\bar{v}^4}\right)\right]\\
K_6 &= l\bar{v}^4\left[1 - \frac{\mu^2l^2}{\bar{v}^2} + \frac{\alpha T}{\bar{v}^2}\left(1 + \frac{\mu^2l^2}{\bar{v}^2}\right) - \frac{13}{20}\,\frac{\alpha^2T^2}{\bar{v}^8}\right]
\end{aligned}} \tag{A16}$$

and for the remaining integrals of interest, using ($A4$), ($A8$) and ($A9$), and the definition $K_i' = dK_i/dT$:

$$\boxed{\begin{aligned} K_3' &= \frac{\mu^2 l^2}{\bar{v}^2} \cdot \frac{\alpha l^2}{\bar{v}} \\ K_4' &= \frac{\alpha l}{2}\left(1 + \frac{\mu^2 l^2}{\bar{v}^2}\right) - \frac{13}{20}\,\frac{\alpha^2 l T}{\bar{v}^4} \\ K_7' &= \alpha l^2 \bar{v} - \frac{9}{5}\,\frac{\alpha^2 l^2 T}{\bar{v}^3} \\ K_8' &= \frac{3}{2}\alpha l \bar{v}^2\left(1 - \frac{\mu^2 l^2}{3\bar{v}^2}\right) - \frac{12}{5}\,\frac{\alpha^2 l T}{\bar{v}^2} \end{aligned}} \tag{A17}$$

From ($A16$) and ($A17$) follow the values of the expressions appearing in the text.

$$\boxed{\begin{aligned} K_1 K_8' - K_5 K_4' &= \alpha l^3 \bar{v}^3\left(1 - \frac{2\mu^2 l^2}{\bar{v}^2}\right) - \frac{5}{2}\,\frac{\alpha^2 l^3 T}{\bar{v}} \\ K_1 K_6 - K_2 K_5 &= \alpha l^3 \bar{v} T\left(1 - \frac{2\mu^2 l^2}{\bar{v}^2}\right) - \frac{9}{5}\,\frac{\alpha^2 l^3 T^2}{\bar{v}^3} \\ K_2 K_8' - K_6 K_4' &= \alpha l^2 \bar{v}^4\left(1 - \frac{2\mu^2 l^2}{\bar{v}^2}\right) - 3\alpha^2 l^2 T \\ K_1 K_4' - K_2 K_3' &= \frac{\alpha l^3 \bar{v}}{2}\left(1 - \frac{2\mu^2 l^2}{\bar{v}}\right) - \frac{9}{10}\,\frac{\alpha^2 l^3 T}{\bar{v}^2} \\ K_1 K_7' - K_5 K_3' &= \alpha l^4 \bar{v}^2\left(1 - \frac{2\mu^2 l^2}{\bar{v}^2}\right) - \frac{23}{10}\,\frac{\alpha^2 l^4 T}{\bar{v}^4} \end{aligned}} \tag{A18}$$

It is to be noticed that in first approximation the following holds:

$$K_i' = 0.$$

This follows from the fact that in first approximation all the integrals depend only on the number of electrons per unit volume and not on the temperature. One sees easily that if the expressions in the curled brackets in ($A8$) and ($A9$) are disregarded, as must be done in first approximation, the temperature dependence of the integrals is removed. The reader can easily convince himself that the expressions ($A18$) vanish in this approximation even if one assumes that the number of free electrons varies with the temperature.

§2. The effect of the electron spin.

We shall in this paragraph show how the effect of the spin is to be taken into account in the calculation of the preceding integrals. We here give the method for the case of the integrals H_i. The extension to the general case is obvious, and is not treated here because it leads to effects which are vanishingly small in comparison to those here obtained.

In a homogeneous magnetic field of strength H, the Fermi distribution function becomes:

$$f(E) = f(\epsilon + \mu_0 H) = \frac{1}{(1/A')e^{(\epsilon+\mu_0 H)/kT} + 1}\cdot \tag{A19}$$

Here $\mu_0 = eh/4\pi m$ is the magnetic moment of the electron and $\epsilon = \frac{1}{2}mv^2 = \frac{1}{2}m(\xi^2+\eta^2+\zeta^2)$ is the kinetic energy. The constant A' is determined as usual by the number of free electrons, the condition that this matter stay constant takes the form:

$$n = \left(\frac{2\pi mkT}{h^3}\right)^{3/2}\left[\int_0^\infty \frac{u^{1/2}du}{(1/A'')e^u + 1} + \int_0^\infty \frac{u^{1/2}du}{(1/A''')e^u + 1}\right]. \tag{A20}$$

Here the following abbreviations are employed:

$$\left.\begin{aligned} A'' &= A'e^{\mu_0 H/kT} \text{ or } u_0'' = \log A'' = \log A' + \mu_0 H/kT \\ A''' &= A'e^{-\mu_0 H/kT} \text{ or } u_0''' = \log A''' = \log A' - \mu_0 H/kT \end{aligned}\right\} \tag{A21}$$

The integration of the equation (A20) can be performed according to the formula (A7), and yields in second approximation:

$$\frac{3nh^3}{8\pi} = (2mkT \log A')^{3/2}\left[1 + \frac{\pi^2 + 3\gamma^2}{8(\log A')^2}\right] \tag{A22}$$

with $\gamma = \mu_0 H/kT$. Here terms containing higher powers of $(\gamma/\log A)^2$ than the first have been neglected. For $\gamma = 0$, we have obviously:

$$\frac{3nh^3}{8\pi} = (2mkT \log A)^{3/2}\left[1 + \frac{\pi^2}{8(\log A)^2}\right]. \tag{A22a}$$

Dividing (A22) by (22a), and replacing $\log A' = u_0'$ by u_0 inside the square brackets of (A22), there follows:

$$1 = \left(\frac{u_0'}{u_0}\right)^{3/2}\left(\frac{1 + \pi^2/8u_0^2 + 3\gamma^2/8u_0^2}{1 + \pi^2/8u_0^2}\right) = \left(\frac{u_0'}{u_0}\right)^{3/2}\left(1 + \frac{3\gamma^2}{8u_0^2}\right)$$

or we can write

$$\frac{u_0'}{u_0} = \left(1 - \frac{3\gamma^2}{8u_0^2}\right)^{2/3} = 1 - \frac{\gamma^2}{4u_0^2} \tag{A23}$$

with the help of (A21), we find:

$$\begin{aligned} u_0'' &= u_0 + \gamma - \frac{\gamma^2}{4u_0^2} = u_0 + \gamma - \delta \\ u_0''' &= u_0 - \gamma - \frac{\gamma^2}{4u_0^2} = u_0 - \gamma - \delta \end{aligned} \qquad (A24)$$

The values of the integrals H_i can now be written without further calculation. We shall denote these integrals by H_i^s, the upper index s showing that they are calculated with spin. For example, H_1 becomes (in 2nd approx):

$$H_1^s = l^2\left(\frac{2kT}{m}\right)^{1/2}\left(1 - \frac{\pi^2}{24u_0^2}\right)\frac{1}{2}\left[(u_0'')^{1/2} + (u_0''')^{1/2}\right] \text{ [compare } (A8)\text{]}:$$

with the help of $(A24)$ and the definition of H_1 (without spin) there follows:

$$\begin{aligned} H_1^s &= H_1(1 - \gamma^2/4u_0^2) & H_5^s &= H_5 \\ H_2^s &= H_2(1 - \gamma^2/4u_0^2) & H_6^s &= H_6(1 + \gamma^2/2u_0^2) \end{aligned} \qquad (A25)$$

and also:

$$\begin{aligned} H_3^s &= H_3 & H_7^s &= H_7(1 + 5\gamma^2/4u_0^2) \\ H_4^s &= H_4(1 + \gamma\ /2u_0^2) & H_8^s &= H_8(1 + 9\gamma^2/4u_0^2). \end{aligned}$$

From these last equations follow by means of differentiation with respect to T:

$$\left.\begin{aligned} (H_3^s)' &= H_3' \\ (H_4^s)' &= H_4'\left(1 + \frac{\gamma^2}{2u_0^2}\right) + \frac{\gamma^2 H_4}{2}\frac{d}{dT}\left(\frac{1}{u_0^2}\right) \\ (H_7^s)' &= H_7'\left(1 + \frac{5\gamma^2}{4u_0^2}\right) + \frac{5\gamma^2 H_7}{4}\frac{d}{dT}\left(\frac{1}{u_0^2}\right) \\ (H_8^s)' &= H_8'\left(1 + \frac{9}{4}\frac{\gamma^2}{u_0^2}\right) + \frac{9\gamma^2 H_8}{4}\frac{d}{dT}\left(\frac{1}{u_0^2}\right) \end{aligned}\right\} \qquad (A25)$$

and finally with the help of $(A18)$ and $(A15)$:

$$\left.\begin{aligned} (H_1H_8' - H_5H_4')^s &= \alpha l^3\bar{v}^3\left(1 + \frac{3\gamma^2}{\pi^2} + \frac{11\gamma^2}{4u_0^2}\right) \\ (H_1H_6 - H_2H_5)^s &= \alpha l^3\bar{v}T \\ (H_2H_3' - H_6H_4')^s &= \alpha l^2\bar{v}^4\left(1 + \frac{3\gamma^2}{\pi^2} + \frac{5}{2}\frac{\gamma^2}{u_0^2}\right) \\ (H_1H_4' - H_2H_3')^s &= \frac{\alpha l^3\bar{v}}{2}\left(1 + \frac{3\gamma^2}{\pi^2} + \frac{\gamma^2}{4u_0^2}\right) \\ (H_1H_7' - H_5H_3')^s &= \alpha l^4\bar{v}^2\left(1 + \frac{3\gamma^2}{\pi^2} + \frac{\gamma^2}{u_0^2}\right) \end{aligned}\right\} \qquad (A26)$$

These formulas have been used in obtaining the conclusions discussed in the text, and suffice to allow the evaluation of those effects for which we have omitted such details.