THE SECOND ORDER ELECTRICAL EFFECTS IN METALS

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1. Introduction

The theory of transport phenomena in metals depends upon the solution of an integral equation for the velocity distribution function f of the conduction electrons. This integral equation is formed by equating the rate of change in f due to external fields and temperature gradients to the rate of change in f due to the mechanism which produces the resistance. If this latter rate of change is denoted by $[\partial f/\partial t]_{\text{coll}}$, it happens with some mechanisms that

$$\left[\frac{\partial f}{\partial t}\right]_{\text{coll}} = -\frac{f-f_0}{\tau}, \tag{1}$$

where f_0 is the equilibrium distribution, and τ is the time of relaxation which does not depend on the external fields. When equation (1) is true, the problem is comparatively simple, but in general $[\partial/\partial t]_{\text{coll}}$ is an integral operator and it is not possible to define a time of relaxation and a free path. It is known that at high temperatures, such that $(\Theta/T)^2$ can be neglected, where Θ is the Debye temperature, a free path exists; but, in general, special methods have to be used to solve the integral equation.

The methods which have been given hitherto for including the terms involving $(\Theta/T)^2$ are not satisfactory. Brillouin* has used a complicated method in which f is expanded as an infinite series. The approximations are so difficult to control that Brillouin obtained a result which is in conflict with the thermodynamic relations between the thermoelectric effects†. It is, however, possible to obtain a solution, neglecting only terms of order $(\Theta/T)^3$, by a simple method of successive approximations, and this is given in § 2. The new terms are small and probably not of much physical significance, since we are reaching the limit of validity of the theory in pushing the calculations so far. However, the problem of determining these correction terms is interesting mathematically, and it is highly desirable to verify the thermodynamic relations, since otherwise Brillouin's result might suggest that the theory is wrong.

The electrical effects at low temperatures present considerable difficulties, since a free path cannot be defined at all. A method of obtaining the electrical conductivity of a pure metal was given by Bloch‡, but this cannot be extended to deal with the second-order effects such as the thermal conductivity and the

* *Die Quantenstatistik* (Springer, 1931), p. 357.

† *Conductibilité électrique et thermique des métaux* (Hermann, 1934), p. 50.

‡ *Zeit. f. Physik*, 59 (1930), 208.

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thermoelectric phenomena. A more general method* involves the use of infinite determinants, which is troublesome, and its convergence cannot be investigated. None of these methods, moreover, can be applied to the more interesting and practical problems concerning Matthiessen's rule. The resistance in a metal is produced partly by the heat vibrations of the lattice and partly by irregularities due to strains and impurities or to alloying. Matthiessen's empirical rule is that the electrical resistance of a metal is the sum of an ideal resistance, characteristic of the pure metal, and a residual resistance due to impurities. This means that the reciprocal free paths are additive, and it can only be true when free paths can be defined for both of the processes which produce the resistance.

In § 3 we give a very simple method for determining the conductivity in an impure solid. The results are expressed as series in descending powers of the residual resistance. Since we stop at the second term in the series it is not possible to verify Matthiessen's rule directly, but the expression we obtain for the ideal resistance is the same as that obtained by neglecting the impurities entirely, and hence the rule must be a good approximation. The non-existence of a free path entails the breakdown of the Wiedemann-Franz law at low temperatures, and so we might expect the thermal resistance of an impure solid to show some peculiarities. To the approximation used here, the thermal resistance must consist of a part depending on the impurities and a part independent of them, but it is not obvious that the part independent of the impurities is the same as in an ideal crystal. Actually we find that the leading term is the same, and that it is highly probable that the remaining terms are the same also. Finally, an expression for the thermoelectric power is found, which, like the expression for the thermal conductivity, could not have been obtained by the formal theory which assumes the existence of a free path.

2. HIGH TEMPERATURES

We adopt the usual notation by which the electronic states are classified by a wave vector $\mathbf{k}$. If there is an electric field $\mathscr{E}$ and a temperature gradient parallel to the x axis, the distribution function is

$$f = f_0 - k_1 c(E) \frac{\partial f_0}{\partial E}, \tag{2}$$

where f_0 is the Fermi function, and the integral equation† is

$$-4\Lambda\left(\frac{h^2}{8\pi^2 m}\right)^{\frac{1}{2}}\left(\frac{\Theta}{T}\right)^3 E^{\frac{1}{2}}\left\{e\mathscr{E} + T\frac{\partial}{\partial x}\frac{\zeta}{T} + \frac{E}{T}\frac{\partial T}{\partial x}\right\} = \int_0^{\Theta/T}\frac{z^2 dz}{e^z - 1}$$
$$\times\left[\left\{Ec(\eta) - c(\eta+z)\left(E + \tfrac{1}{2}kTz - D\left(\frac{T}{\Theta}\right)^2 z^2\right)\right\}\frac{e^\eta + 1}{e^\eta + e^{-z}}\right.$$
$$\left. + \left\{Ec(\eta) - c(\eta-z)\left(E - \tfrac{1}{2}kTz - D\left(\frac{T}{\Theta}\right)^2 z^2\right)\right\}\frac{e^\eta + 1}{e^{\eta-z} + 1}\right]. \tag{3}$$

* Kroll, *Zeit. f. Physik*, 80 (1933), 50, and 81 (1933), 425.

† This and the other formulae required are given by A. H. Wilson, *The theory of metals* (Cambridge, 1936), pp. 215–18.

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Here A and D are constants characteristic of the metal, $-\epsilon$ is the charge of the electron, ζ is the Fermi energy of the conduction electrons and $\eta = (E-\zeta)/kT$. Further, we are restricting the discussion to monovalent elements and assuming that $E = h^2|\mathbf{k}|^2/(8\pi^2 m)$. If we replace the left-hand side of (3) by E^n and denote the corresponding solution by $c^{(n)}$, the electric current is

$$J = \mathscr{K}_1\left\{\epsilon^2\mathscr{E} + \epsilon T\frac{\partial}{\partial x}\left(\frac{\zeta}{T}\right)\right\} + \mathscr{K}_2\frac{\epsilon}{T}\frac{\partial T}{\partial x}, \tag{4}$$

and the heat current is

$$w = \mathscr{K}_2\left\{-\epsilon\mathscr{E} - T\frac{\partial}{\partial x}\left(\frac{\zeta}{T}\right)\right\} - \mathscr{K}_3\frac{1}{T}\frac{\partial T}{\partial x}, \tag{5}$$

where

$$\mathscr{K}_1 = -\frac{8A}{3\pi h}\left(\frac{\Theta}{T}\right)^3\int_{-\infty}^{\infty} E^{\frac{3}{2}}c^{(\frac{1}{2})}(\eta)\frac{\partial f_0}{\partial\eta}d\eta, \tag{6a}$$

$$\mathscr{K}_2 = -\frac{8A}{3\pi h}\left(\frac{\Theta}{T}\right)^3\int_{-\infty}^{\infty} E^{\frac{3}{2}}c^{(\frac{1}{2})}(\eta)\frac{\partial f_0}{\partial\eta}d\eta = -\frac{8A}{3\pi h}\left(\frac{\Theta}{T}\right)^3\int_{-\infty}^{\infty} E^{\frac{3}{2}}c^{(\frac{1}{2})}(\eta)\frac{\partial f_0}{\partial\eta}d\eta, \tag{6b}$$

$$\mathscr{K}_3 = -\frac{8A}{3\pi h}\left(\frac{\Theta}{T}\right)^3\int_{-\infty}^{\infty} E^{\frac{3}{2}}c^{(\frac{1}{2})}(\eta)\frac{\partial f_0}{\partial\eta}d\eta. \tag{6c}$$

The equality of the two expressions for $\mathscr{K}_2$ is known to be the condition for the validity of the thermodynamic relations between the thermoelectric effects, and is a consequence of the fact that the nucleus of the integral equation is symmetrical. In its present form the integral equation is not obviously symmetrical, and Brillouin has suggested that his failure to prove the identity of the two forms of $\mathscr{K}_2$ may be due to the approximations used in deriving the integral equation. We therefore transform (3) and show that this conjecture is wrong.

If we put $-z$ for z in the second curly bracket on the right-hand side of (3) and use a new variable $\eta' = \eta + z$, the right-hand side becomes

$$-\left(\frac{\partial f_0}{\partial\eta}\right)^{-1}\int_{\eta-\Theta/T}^{\eta+\Theta/T}\left[Ec(\eta) - c(\eta')\left\{\frac{E+E'}{2} - D\left(\frac{T}{\Theta}\right)^2(\eta'-\eta)^2\right\}\right]\frac{(\eta-\eta')^2 d\eta'}{|e^{-\eta}-e^{-\eta'}|(e^{\eta}+1)(e^{\eta'}+1)}.$$

Hence, if we put

$$c(\eta)\,H(\eta)^{\frac{1}{2}} = \phi(\eta),$$

where

$$H(\eta) = \int_{\eta-\Theta/T}^{\eta+\Theta/T}\frac{E(\eta-\eta')^2 d\eta'}{|e^{-\eta}-e^{-\eta'}|(e^{\eta}+1)(e^{\eta'}+1)},$$

the integral equation is of the form

$$\chi(\eta) = \phi(\eta) - \int_{\eta-\Theta/T}^{\eta+\Theta/T}\frac{(\eta-\eta')^2}{|e^{-\eta}-e^{-\eta'}|(e^{\eta}+1)(e^{\eta'}+1)}\frac{1}{\{H(\eta)H(\eta')\}^{\frac{1}{2}}} \times\left\{\frac{E+E'}{2} - D\left(\frac{T}{\Theta}\right)^2(\eta-\eta')^2\right\}\phi(\eta')\,d\eta'. \tag{7}$$

This is a symmetrical equation of Volterra's type, and can be solved by the method of successive approximations.

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When solving the integral equation approximately it is essential to take a form for the solution which is consistent with the symmetry of the nucleus. It is easy to do this when the equation is written in the form (7), but the original form is the more convenient to work with, although more care must then be taken in carrying the approximations to the required degree of accuracy.

The solution of the equation

$$E^n = \int_{-\Theta/T}^{\Theta/T} \left[Ec(\eta) - c(\eta+z)\left\{E + \tfrac{1}{2}kTz - D\left(\frac{T}{\Theta}\right)^2 z^2\right\}\right] \frac{e^\eta + 1}{e^{\eta+z}+1} \frac{z^2 dz}{|1-e^{-z}|} \qquad (8)$$

depends on the fact* that, if terms of order $(\Theta/T)^2$ compared with the leading term are neglected, the right-hand side is

$$\frac{D}{2}\left(\frac{\Theta}{T}\right)^2 c(\eta) = \frac{(6\pi^2)^{\frac{2}{3}} h^2}{32\pi^2 ma^2}\left(\frac{\Theta}{T}\right)^2 c(\eta).$$

We can therefore easily obtain the zero order solution $c_0^{(n)}$. We then substitute $c^{(n)} = c_0^{(n)} + c_1^{(n)}$, and on using the above approximation for the terms in c_1 we obtain a simple equation for c_1. This process can be repeated, but the calculations become very complicated. We have

$$c_1^{(n)} = \frac{2}{D}\left(\frac{T}{\Theta}\right)^2 \left\{E^n - \frac{2}{D}\left(\frac{T}{\Theta}\right)^2 \int_{-\Theta/T}^{\Theta/T} \left[E^{n+1} - (E+kTz)^n \left\{E + \tfrac{1}{2}kTz - D\left(\frac{T}{\Theta}\right)^2 z^2\right\}\right] \frac{e^\eta+1}{e^{\eta+z}+1} \frac{z^2 dz}{|1-e^{-z}|}\right\}. \qquad (9)$$

The integrals $\mathscr{K}_1, \mathscr{K}_2, \mathscr{K}_3$ are somewhat simpler to evaluate than is c_1, and it can be verified, by using the identity

$$\int_{-\infty}^{\infty} \left\{\frac{F(\eta+z)}{e^{\eta+z}+1} - \frac{F(\eta)}{e^\eta + e^z}\right\} \frac{d\eta}{e^{-\eta}+1} = 0 \qquad (10)$$

and then putting $-z$ for z, that the two expressions for $\mathscr{K}_2$ are the same.

Since our expressions are only correct to the order $(\Theta/T)^2$, it is natural to approximate by expanding the integrand in powers of z. There are two kinds of approximation possible which must be carefully distinguished: expansions in powers of z and expansions in powers of η. The latter is in general not justified, and the error in Brillouin's method is in expanding expressions such as $(e^\eta+1)/(e^{\eta+z}+1)$ and neglecting terms of higher order than η^2. A preliminary transformation simplifies the integrals. Putting

$$G(E) = \frac{1}{kT}\int^E F(E)\,dE,$$

* Wilson, *loc. cit.* p. 208.

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we have

$$\frac{1}{e^z-1}\int_{-\infty}^{\infty}\frac{G(E)-G(E-kTz)}{(e^\eta+1)(e^{-\eta}+1)}d\eta$$

$$=\frac{1}{e^z-1}\int_{-\infty}^{\infty}G(E)\left\{\frac{1}{(e^\eta+1)(e^{-\eta}+1)}-\frac{1}{(e^{\eta+z}+1)(e^{-\eta-z}+1)}\right\}d\eta$$

$$=\int_{-\infty}^{\infty}\frac{F(E)}{(e^{-\eta}+1)(e^{\eta+z}+1)}d\eta, \tag{11}$$

on integrating by parts, provided that $e^{-\eta}G(\zeta\pm kT\eta)\to 0$ as $\eta\to\infty$. If we use (11) and expand expressions such as $(E+kTz)^n$ in powers of z, we have, since

$$\mathscr{J}_n\equiv\int_0^{\Theta/T}\frac{z^n dz}{(e^z-1)(1-e^{-z})}=\frac{1}{n-1}\left(\frac{\Theta}{T}\right)^{n-1}-\frac{1}{12(n+1)}\left(\frac{\Theta}{T}\right)^{n+1}+\ldots, \tag{12}$$

the following expressions:

$$\mathscr{K}_1=-\frac{16\Lambda}{3\pi hD}\frac{\Theta}{T}\int_{-\infty}^{\infty}E^3\left[1+\left(\frac{\Theta}{T}\right)^2\left\{\frac{1}{18}+\frac{1}{12}\frac{k^2T^2}{E^2}-\frac{15}{8}\frac{k^2T^2}{DE}\right\}\right]\frac{\partial f_0}{\partial\eta}d\eta, \tag{13a}$$

$$\mathscr{K}_2=-\frac{16\Lambda}{3\pi hD}\frac{\Theta}{T}\int_{-\infty}^{\infty}E^4\left[1+\left(\frac{\Theta}{T}\right)^2\left\{\frac{1}{18}-\frac{1}{12}\frac{k^2T^2}{E^2}-\frac{23}{8}\frac{k^2T^2}{DE}\right\}\right]\frac{\partial f_0}{\partial\eta}d\eta, \tag{13b}$$

$$\mathscr{K}_3=-\frac{16\Lambda}{3\pi hD}\frac{\Theta}{T}\int_{-\infty}^{\infty}E^5\left[1+\left(\frac{\Theta}{T}\right)^2\left\{\frac{1}{18}-\frac{5}{36}\frac{k^2T^2}{E^2}-\frac{35}{8}\frac{k^2T^2}{DE}\right\}\right]\frac{\partial f_0}{\partial\eta}d\eta. \tag{13c}$$

If a free path existed, the coefficients of $(\Theta/T)^2$ would be the same in these three expressions.

2·1. We can evaluate these integrals by the usual approximate methods, but it should be noted that, since we have not used an expansion in powers of kT/ζ, it is consistent to evaluate these integrals exactly, which may be necessary for moderately high temperatures. For many purposes the approximate values are sufficiently accurate. If we retain terms of order $(kT/\zeta)^2$ and $(\Theta/T)^2$, the electrical conductivity is

$$\sigma=\epsilon^2\mathscr{K}_1=\frac{16\epsilon^2\zeta^3\Lambda}{3\pi hD}\left(\frac{\Theta}{T}\right)\left[1+\left(\frac{\pi kT}{\zeta}\right)^2+\frac{1}{18}\left(\frac{\Theta}{T}\right)^2\right]. \tag{14}$$

If we wish to retain all the terms written, it is necessary to take into account the dependence of ζ on T. We have*

$$\zeta=E_0-\frac{\pi^2k^2T^2}{12E_0}$$

approximately, where E_0 is the value of ζ for $T=0$. Hence

$$\sigma=\frac{16\epsilon^2E_0^3\Lambda}{3\pi hD}\frac{\Theta}{T}\left[1+\frac{3}{4}\frac{\pi^2h^2T^2}{E_0^2}+\frac{1}{18}\left(\frac{\Theta}{T}\right)^2\right]. \tag{15}$$

* Wilson, *loc. cit.* equation (250).

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The effect of the correction term involving $(kT/E_0)^2$ is to make the resistance increase less rapidly than T, while the term involving $(\Theta/T)^2$ has the opposite effect. This latter term is, however, unimportant at temperatures above room temperature. This agrees with the experimental results on certain metals such as Pd and Pt, whereas the resistance of Cu, Ag and Au increases more rapidly than T. This increase in the resistance is presumably due to the increasing importance of the anharmonic lattice forces, and for the monovalent metals it must outweigh the decrease given by (15). Mott* has ascribed the decrease of the resistance of the transition elements to the peculiar shape of the curve giving the density of the states occupied by the conduction electrons. The present theory, however, shows that the same type of temperature variation occurs when the density of states behaves normally, and Mott's speculation concerning the *special* behaviour of the transition elements has no theoretical basis. A small value of E_0 is all that is required to explain the results. However, it has not so far been possible to find the distribution function when the energy levels in the metal are not those of a free electron, and, although it is probable that the first order effects are roughly the same for all metals, it is rather dangerous to assume that the same is true of the second order correction terms. These depend very sensitively on the energy variation of the integrands of $\mathscr{K}_1$, $\mathscr{K}_2$, $\mathscr{K}_3$, and it is impossible to be sure of obtaining the correct generalization of these integrals without re-solving the integral equation.

2·2. To determine the thermal conductivity and the thermoelectric effects it is necessary to approximate more closely to the integrals. We use the formula

$$-\int \phi(E)\frac{\partial f_0}{\partial E}dE = \phi(\zeta)+\frac{\pi^2}{6}k^2T^2\frac{d^2\phi}{d\zeta^2}+\frac{7\pi^4}{360}k^4T^4\frac{d^4\phi}{d\zeta^4}+\ldots. \tag{16}$$

The thermal conductivity is given by

$$\kappa = \frac{\mathscr{K}_1\mathscr{K}_3-\mathscr{K}_2^2}{\mathscr{K}_1 T} = \frac{16\pi k^2\zeta^3 A}{9hD}\Theta\left[1+\frac{6}{5}\left(\frac{\pi kT}{\zeta}\right)^2+\left(\frac{\Theta}{T}\right)^2\left(\frac{1}{18}+\frac{1}{3\pi^2}-\frac{3}{2\pi^2}\frac{\zeta}{D}\right)\right]. \tag{17}$$

The correction term in $(\Theta/T)^2$ is small and negative, since $E_0/D = 2^{\frac{1}{3}}$ for a monovalent metal.

The absolute thermoelectric force per degree is $-\mathfrak{S}/e$, where

$$\mathfrak{S} = \frac{\mathscr{K}_2-\zeta\mathscr{K}_1}{\mathscr{K}_1 T} = \frac{\pi^2k^2T}{\zeta}\left[1-\frac{8}{15}\left(\frac{\pi kT}{\zeta}\right)^2-\left(\frac{\Theta}{T}\right)^2\left(\frac{1}{6\pi^2}+\frac{\zeta}{\pi^2 D}\right)\right]. \tag{18}$$

The experimental results are not sufficiently accurate for any conclusions to be drawn about the correctness of the second order terms.

* *Proc. Roy. Soc.* A, 153 (1936), 699.

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3. Low temperatures

The scattering of the electrons at low temperatures is mainly due to impurities and, in an alloy, to the irregular distribution of the atoms. A free path can always be defined for this process and it is independent of the energy of the electrons and the temperature. Taking into account the scattering due to both the impurities and the heat motion of the lattice, equation (8) must be replaced* by

$$E^n = \Lambda M \left(\frac{\Theta}{T}\right)^3 E^2 c(\eta) + \int_{-\Theta/T}^{\Theta/T} \left[Ec(\eta) - c(\eta+z)\left\{E + \tfrac{1}{2}kTz - D\left(\frac{T}{\Theta}\right)^2 z^2\right\}\right] \frac{e^\eta + 1}{e^{\eta+z}+1} \frac{z^2 dz}{|1-e^{-z}|}, \quad (19)$$

where M is a constant depending on the number and scattering power of the impurities. The best method of solving this equation is to transform it into the symmetrical form corresponding to (7) and to obtain a solution by successive approximations. A much simpler method which is valid at low temperatures depends on the fact that, for small values of T/Θ, the first term on the right-hand side of (19) is much larger than the second, and we can obtain a solution by treating the integral operator as small. The first two approximations are

$$c_0^{(n)} = \frac{1}{\Lambda M}\left(\frac{T}{\Theta}\right)^3 E^{n-2}, \quad (20)$$

$$c_1^{(n)} = -\frac{1}{\Lambda^2 M^2}\left(\frac{T}{\Theta}\right)^6 \int_{-\Theta/T}^{\Theta/T} \left[E^{n-3} - \frac{(E+kTz)^{n-2}}{E^2}\left\{E + \tfrac{1}{2}kTz - D\left(\frac{T}{\Theta}\right)^2 z^2\right\}\right] \frac{e^\eta+1}{e^{\eta+z}+1}\frac{z^2 dz}{|1-e^{-z}|}. \quad (21)$$

Since the maximum value of kTz, namely $k\Theta$, is small compared with ζ, it is sufficient to expand quantities such as $(E+kTz)^n$ in powers of kTz/E. Using the same methods as in the preceding section we find

$$\mathscr{K}_1 = -\frac{8}{3\pi h}\int_{-\infty}^{\infty}\left[\frac{E}{M} - \frac{1}{\Lambda M^2}\left(\frac{T}{\Theta}\right)^3\left\{\frac{D}{E}\left(\frac{T}{\Theta}\right)^2\left(2\mathscr{J}_5 + \frac{5}{12}\mathscr{J}_7\frac{k^2T^2}{E^2}\right) - \frac{1}{4}\mathscr{J}_5\frac{k^2T^2}{E^2} - \frac{55}{64}\mathscr{J}_7\frac{k^4T^4}{E^4}\right\}\right]\frac{\partial f_0}{\partial \eta}d\eta, \quad (22a)$$

$$\mathscr{K}_2 = -\frac{8}{3\pi h}\int_{-\infty}^{\infty}\left[\frac{E^2}{M} - \frac{1}{\Lambda M^2}\left(\frac{T}{\Theta}\right)^3\left\{D\left(\frac{T}{\Theta}\right)^2\left(2\mathscr{J}_5 + \frac{1}{4}\mathscr{J}_7\frac{k^2T^2}{E^2}\right) - E\left(\frac{1}{4}\mathscr{J}_5\frac{k^2T^2}{E^2} + \frac{13}{192}\mathscr{J}_7\frac{k^4T^4}{E^4}\right)\right\}\right]\frac{\partial f_0}{\partial \eta}d\eta, \quad (22b)$$

$$\mathscr{K}_3 = -\frac{8}{3\pi h}\int_{-\infty}^{\infty}\left[\frac{E^3}{M} - \frac{1}{\Lambda M^2}\left(\frac{T}{\Theta}\right)^3\left\{ED\left(\frac{T}{\Theta}\right)^2\left(2\mathscr{J}_5 - \frac{1}{4}\mathscr{J}_7\frac{k^2T^2}{E^2}\right) + E^2\left(\frac{3}{4}\mathscr{J}_5\frac{k^2T^2}{E^2} + \frac{1}{64}\mathscr{J}_7\frac{k^4T^4}{E^4}\right)\right\}\right]\frac{\partial f_0}{\partial \eta}d\eta. \quad (22c)$$

* Wilson, *loc. cit.* p. 223.

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Remembering that a higher degree of accuracy is required for κ and $\mathfrak{S}$ than for σ, we have

$$\sigma = \sigma_0\left[1-\sigma_0\frac{3\pi hD}{4\epsilon^2\zeta^3\Lambda}\left(\frac{T}{\Theta}\right)^5\mathscr{J}_5\left\{1-\frac{1}{8}\frac{\zeta}{D}\left(\frac{k\Theta}{\zeta}\right)^2\right\}\right], \tag{23}$$

$$\kappa = \kappa_0 T\left[1-\kappa_0 T\frac{27h}{8\pi^3k^2\zeta^2\Lambda\Theta}\left(\frac{T}{\Theta}\right)^2\left\{\mathscr{J}_5+\frac{D}{\zeta}\left(\frac{T}{\Theta}\right)^2\left(\frac{2\pi^2}{3}\mathscr{J}_5-\frac{1}{3}\mathscr{J}_7\right)\right.\right.$$
$$\left.\left.-\frac{k^2T^2}{\zeta^2}\left(\frac{\pi^2}{12}\mathscr{J}_5+\frac{17}{24}\mathscr{J}_7\right)\right\}\right], \tag{24}$$

and $$\mathfrak{S} = \frac{\pi^2k^2T}{3\zeta}\left[1+\frac{D}{\Lambda M\zeta^2}\left(\frac{T}{\Theta}\right)^5\left\{4\mathscr{J}_5+\frac{1}{2\pi^2}\mathscr{J}_7-\frac{k^2\Theta^2}{D\zeta}\left(\frac{5}{8}\mathscr{J}_5+\frac{19}{8\pi^2}\mathscr{J}_7\right)\right\}\right], \tag{25}$$

where $1/\sigma_0 = 3\pi hM/(8\epsilon^2\zeta)$ is the residual electrical resistance, and

$$\kappa_0 T = \tfrac{1}{3}(\pi k/\epsilon)^2\sigma_0 T$$

is the corresponding thermal conductivity.

3·1. If σ_i is the conductivity of a pure metal, and if the resistances are additive, then for an impure metal

$$\frac{1}{\sigma} = \frac{1}{\sigma_0}+\frac{1}{\sigma_i}.$$

Comparing this with (23), which only holds for small values of σ_0/σ_i, we see that

$$\frac{1}{\sigma_i} = \frac{3\pi hD}{4\epsilon^2\zeta^3\Lambda}\left(\frac{T}{\Theta}\right)^3\mathscr{J}_5\left\{1-\frac{1}{8}\frac{\zeta}{D}\left(\frac{k\Theta}{\zeta}\right)^2\right\}. \tag{26}$$

If the quantity in the curly bracket is replaced by 1, this expression for σ_i is the same as that found by neglecting the impurities altogether. Since the additional factor only differs from 1 by about $10^{-4}-10^{-5}$, the non-existence of a free path at low temperatures has a negligible effect on the electrical conductivity. It is interesting to note that the coefficient of the term in $(T/\Theta)^7$ in $\mathscr{K}_1$, and hence in σ, is about $10(k\Theta/\zeta)^2$ times the coefficient of $(T/\Theta)^5$. This is quite negligible, and the ideal resistance should be very accurately proportional to T^5.

If κ_i is the ideal thermal conductivity, then

$$\frac{1}{\kappa} = \frac{1}{\kappa_0 T}+\frac{1}{\kappa_i}.$$

Comparing this with (24), we have, omitting small terms,

$$\frac{1}{\kappa_i} = \frac{27h}{8\pi^3k^2\zeta^2\Lambda\Theta}\left(\frac{T}{\Theta}\right)^2\left\{\mathscr{J}_5+\frac{D}{\zeta}\left(\frac{T}{\Theta}\right)^2\left(\frac{2\pi^2}{3}\mathscr{J}_5-\frac{1}{3}\mathscr{J}_7\right)\right\}. \tag{27}$$

The thermal resistance in the absence of impurities has not been calculated accurately, but Kroll's method gives the term in T^2, which is the same as that found here. It is probable that the expression (27), and (26) also, has a much greater validity than we should expect from our method of solution, since for small values of Θ/T the term involving $D\mathscr{J}_5$ becomes dominant, and (27) gives

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the correct thermal resistance at high temperatures, including the correction terms involving $(\Theta/T)^2$. The experimental evidence about the behaviour of the thermal resistance at low temperatures is meagre. $1/\kappa_i$ seems to behave like T^n, where n lies between 2 and 3, while $1/\kappa$ has a minimum at liquid helium temperatures. This is in qualitative agreement with the theory, but no exact comparison is possible.

The Wiedemann-Franz ratio for an impure metal is a rather complicated expression which has the constant value $\frac{1}{3}(\pi k/\epsilon)^2$ at very high and very low temperatures, and has a minimum in between. For an ideal metal

$$\frac{\kappa_i}{\sigma_i T} = \frac{1}{3}\left(\frac{\pi k}{\epsilon}\right)^2 \Big/ \left\{1 - \frac{\mathscr{J}_7}{2\pi^2 \mathscr{J}_5} + \frac{3\zeta}{2\pi^2 D}\left(\frac{\Theta}{T}\right)^2\right\}. \tag{28}$$

When a free path exists, it can be shown that

$$\mathfrak{S} = \frac{\pi^2 k^2 T}{3}\left[\frac{1}{\zeta} + \frac{\sigma_0}{\sigma_0 + \sigma_i}\left(\frac{\partial}{\partial E}\log l_i\right)_{E=\zeta}\right]. \tag{29}$$

From (25) we have $$\mathfrak{S} = \frac{\pi^2 k^2 T}{3\zeta}\left[1 + \frac{2\sigma_0}{\sigma_i}\left(1 + \frac{\mathscr{J}_7}{8\pi^2 \mathscr{J}_5}\right)\right]. \tag{30}$$

At high temperatures l_i exists and is proportional to E^2, so that (29) and (30) give the same result. (Note that (30) is only valid for small values of σ_0/σ_i. The general expression for $\mathfrak{S}$ is probably obtained from (30) by substituting $\sigma_0 + \sigma_i$ for σ_i.) At low temperatures the factor $1 + \mathscr{J}_7/(8\pi^2 \mathscr{J}_5)$ is introduced owing to the non-existence of a free path. This factor is about $\frac{3}{2}$.

The experimental results on the thermoelectric forces of alloys at low temperatures are very complicated*. For some alloys $\mathfrak{S}$ seems to be proportional to T, but for others there are wide divergences. On the whole, however, (30) with $\sigma_0 + \sigma_i$ substituted for σ_i gives reasonable qualitative agreement with the less abnormal results. To find the variation with composition, let us suppose that the normal metal has n_0 impurities per unit volume, and that Δn_0 foreign atoms per unit volume are added by alloying. If we assume that Δn_0 is so small that the number of free electrons is unaltered, and hence ζ is unchanged, we have

$$\Delta\mathfrak{S} \propto \frac{T\Delta n_0}{n_0 + \Delta n_0 + \beta T^5}.$$

This agrees quite well with the observations on dilute solutions of cobalt in gold for concentrations up to about 2 %. The most anomalous alloys are those for which $\mathfrak{S}$ changes sign at liquid helium temperatures. Such a behaviour might be explained by assuming that the density of states and the free path (or rather what replaces it at low temperatures) have different energy variations. Since, however, we have no formula for $\mathfrak{S}$ whose validity in such circumstances is unquestionable, the subject is too speculative to pursue.

* Keesom and Matthijs, *Physica*, 2 (1935), 623.

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