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Source: *Proceedings of the Royal Society of London. Series A, Mathematical and Physical Sciences*, Vol. 202, No. 1071 (Aug. 22, 1950), pp. 466-484
Published by: The Royal Society
Stable URL: http://www.jstor.org/stable/98543
Accessed: 26/08/2010 17:05

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REFERENCES

Andrews, J. P. 1947 *Proc. Phys. Soc.* **59**, 990.
Bädeker, K. 1907 *Ann. Phys., Lpz.*, **22**, 749.
Barnard, G. P. 1935 *Proc. Phys. Soc.* **47**, 477.
Barnard, G. P. 1939 *Proc. Phys. Soc.* **51**, 222, and a number of Russian papers.
Baumbach, H. H. von & Wagner, C. 1933 *Z. phys. Chem.* **22**, 199.
Bergman, L. & Pelz, R. 1937 *Z. tech. Phys.* **18**, 178.
Billig, E. & Landsberg, P. T. 1950 *Proc. Phys. Soc.* A, **63**, 101.
Billig, E. & Plessner, K. W. 1949 *Phil. Mag.* **40**, 568.
Borelius, G. 1949 *Ark. Fys.* **1**, 305 (includes bibliography).
Ditchburn, R. W. 1933 *Proc. Roy. Soc.* A, **141**, 169.
Eckart, F. & Gudden, B. 1941 *Naturwissenschaften*, **29**, 575.
Eckart, F. & Schmidt, A. 1941 *Z. Phys.* **118**, 199.
Görlich, P. 1935 *Z. tech. Phys.* **16**, 268.
Görlich, P. 1939 *Z. Phys.* **112**, 490.
Görlich, P. & Lang, W. 1938 *Z. phys. Chem.* B, **41**, 23.
Hamaker, H. C. & Beezhold, W. F. 1934 *Physica*, **1**, 119.
Lovell, B. 1947 *Electronics*, p. 49 (references). Pilot Press.
Overbeck, C. J. 1933 *J. Opt. Soc. Amer.* **23**, 109.
Preston, J. S. 1936 *J. Instn Elect. Engrs*, **79**, 424.
Preston, J. S. 1948 *Rev. Opt.* (*théor. instrum.*), **27**, 520.
Sandström, A. E. 1946 *Phil. Mag.* **37**, 347.

The Bloch integral equation and electrical conductivity

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(*Communicated by E. C. Stoner, F.R.S.—Received* 7 *February* 1950—
Revised 11 *April* 1950)

An account is given of the solution, for effectively the whole temperature range, of the Bloch (1928) integral equation for the electron momentum distribution in a metal in an electric field. Solutions of this equation, from which the temperature variation of the electrical conductivity of the metal may be immediately calculated, have previously been obtained only in the limiting cases of 'high- and low-temperatures', corresponding to $(T/\theta_D) \gg 1$ and $\ll 1$, where θ_D is the Debye characteristic temperature.

As a preliminary to its solution by numerical methods the integral equation is expressed in a non-dimensional form (§2). Solutions are obtained by deriving a high-temperature approximation which is valid over a much wider temperature range than that previously known, and by means of a method of successive approximations (§3). The temperature variation of conductivity is calculated from these solutions, and it is shown that there are significant differences between the results and those obtained from the semi-empirical formula of Grüneisen (1930) (§4).

A comparison is made between the calculated and observed temperature variation of conductivity for a number of metals. There are deviations in detail, and a brief discussion is given of secondary factors from which they may arise, but in general the agreement is good, and it is concluded that the theoretical treatment covers satisfactorily the main features of the observed variation (§5).

In an appendix it is shown that the approximate relations obtainable by the variational method developed by Kohler (1949) are consistent with the more exact results obtained here.

1. Introduction

The theoretical treatment of the electrical conductivity of metals, developed by Bloch (1928, 1930), leads to an integral equation for the electron momentum distribution in a metal in an electric field. The temperature variation of conductivity may be estimated directly from the solution of this equation. Up to the present,† however, the Bloch integral equation, or transport equation as it is sometimes called, has been solved only for the special cases of 'high- and low-temperatures', corresponding to $(T/\theta_D) \gg 1$ and $\ll 1$, where θ_D is the Debye characteristic temperature of the metal. In this paper consideration is given to the solution of the transport equation for intermediate temperatures, and so to the estimation of the temperature variation of electrical conductivity over effectively the whole temperature range.

A number of simplifying assumptions are made in the Bloch treatment, and in order to test its applicability to actual metals it is desirable to make as detailed a comparison as possible with experimental results. At high temperatures the theoretical treatment may require modification to take into account the anharmonicity of the lattice vibrations and the effects of thermal expansion; at low temperatures the 'residual' resistance due to impurities and strains may be relatively large, and a large, and uncertain, 'correction' may be required to determine the 'ideal' resistance from that observed. Consequently it is at intermediate temperatures that comparison between theory and experiment would be most significant.

Solution of the transport equation by numerical methods, such as those adopted here, is necessarily carried out for particular values of the parameters involved. By considering the physical significance of these parameters, however, it is possible to select values for them which are appropriate to a wide range of actual metals, and to solve the equation for intermediate temperatures for these values (§3). The associated temperature variation of conductivity may then be calculated (§4) and compared with the experimental results (§5).

Full accounts of the theoretical treatment of electrical conductivity, based largely on Bloch's original papers, are given by Brillouin (1931), Sommerfeld & Bethe (1933), Wilson (1936) and others, and it is unnecessary to go over the long arguments in detail here; but a brief outline of the treatment is essential to introduce the various quantities involved (§2). Reference may also be made to the simplified treatment given by Mott & Jones (1936), which shows in a very direct way the relation between conductivity and temperature; since this treatment is valid only at high temperatures, however, it is not considered in detail here.

2. The Bloch treatment of electrical conductivity

In the absence of an applied field the distribution of the electrons in a metal among the available momentum states is determined by the equilibrium, Fermi-Dirac, distribution function

$$f_0(\boldsymbol{k}) = f_0(\epsilon) = \left\{\exp\left(\frac{\epsilon-\zeta}{kT}\right)+1\right\}^{-1}, \tag{2·1}$$

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† After this paper had been completed a paper by Kohler (1949) dealing with the solution of the Bloch integral equation became available; its relation to the present paper is considered in an appendix.

where $\boldsymbol{k}$ is the electron wave-vector, and ϵ and ζ are respectively the energy and chemical potential per electron. In an applied field the distribution is modified by the field and by 'collisions'. In an electric field parallel to the x-axis the steady-state, non-equilibrium, distribution function, $f(\boldsymbol{k})$, may be expressed in the form (Wilson 1936, pp. 204, 206)

$$f(\boldsymbol{k}) = f_0(\boldsymbol{k}) - k_x \mu(\epsilon) \frac{df_0}{d\epsilon}, \tag{2·2}$$

where k_x is the x-component of $\boldsymbol{k}$, and $\mu(\epsilon)$ is a function to be determined.

Since the steady-state distribution function is independent of time it satisfies the Boltzmann equation

$$\frac{df}{dt} = \left(\frac{\partial f}{\partial t}\right)_{\text{field}} + \left(\frac{\partial f}{\partial t}\right)_{\text{coll.}} = 0. \tag{2·3}$$

To obtain an explicit equation for f from (2·3), expressions are required for $(\partial f/\partial t)_{\text{field}}$ and $(\partial f/\partial t)_{\text{coll.}}$ in terms of f. A general expression for $(\partial f/\partial t)_{\text{field}}$ may be readily obtained (see, for example, Wilson 1936, p. 63). For $(\partial f/\partial t)_{\text{coll.}}$ the problem is much more complicated, and the approximate expressions derivable are dependent on the particular collision mechanism presumed to be involved. In the treatment of 'collisions' associated with thermal lattice vibrations, the case considered here, two different simplifying assumptions have been adopted (Bloch 1928, cf. Sommerfeld & Bethe 1933; Nordheim 1931, cf. Wilson 1936). Both approximations lead to formally similar results; the essential difference lies in the physical significance of a function, depending on the potential field of the lattice ions and on the electron wave-functions, and usually denoted by C, which occurs in the final expression for $(\partial f/\partial t)_{\text{coll.}}$. As will be seen later, the two treatments lead to the same calculated temperature variation of conductivity, though the calculated absolute values would be different.

In deriving the expression for $(\partial f/\partial t)_{\text{coll.}}$ it is also assumed that the relation between electron energy, ϵ, and wave-vector, $\boldsymbol{k}$, is of the form

$$\epsilon = \frac{h^2}{8\pi^2 m^*} |\, \boldsymbol{k} \,|^2, \tag{2·4}$$

corresponding to electrons of effective mass m^* distributed in a single band of standard form.

The final expression for $(\partial f/\partial t)_{\text{coll.}}$ is an integral involving the function μ, and by combining this with (2·3) and the expression for $(\partial f/\partial t)_{\text{field}}$ the Bloch integral equation for μ (and hence for f) may be obtained in the forms given by Sommerfeld & Bethe (1933, p. 521, equation (35·19)) and Wilson (1936, p. 215, equation (345); the present case corresponds to the inclusion of only the first term on the left-hand side of that equation). In order to bring out more clearly the dimensional character of the various functions involved the Bloch equation may be conveniently re-expressed in the following non-dimensional form:

$$\chi^{\frac{3}{2}} = \int_0^y \{\Psi(z) - \Psi(-z)\}\, dz, \tag{2·5}$$

where
$$\left.\begin{aligned}\Psi(z) &= \frac{z^2(\mathrm{e}^{\xi}+1)}{(1-\mathrm{e}^{-z})(\mathrm{e}^{\xi+z}+1)}\left\{\left(\chi+\frac{pz}{2r}-\frac{z^2}{y}\right)\phi(\xi+z)-\chi\phi(\xi)\right\};\\ \phi(\xi\pm z) &= \mu(\epsilon\pm kTz)/\{bMk\theta_D(h/m^*C)^2y^{\frac{5}{2}}eF\};\\ \xi &= (\epsilon-\zeta)/kT = x-\eta;\\ y &= \theta_D/T;\quad z = h\nu/kT;\\ r &= \epsilon_0/k\theta_D = \theta_F/\theta_D;\quad p = (2q^2)^{\frac{1}{3}};\\ \chi &= \frac{p}{r}\frac{\epsilon}{kT} = py\left\{\frac{\zeta}{\epsilon_0}+\frac{\xi}{ry}\right\};\\ 1/b &= 3(2^{\frac{1}{2}}\pi)^3.\end{aligned}\right\} \tag{2·6}$$

In these equations the symbols have the following significance: F, applied field; $-e$, electron charge; M, mass of atom; ν, frequency of lattice vibration; θ_D, Debye characteristic temperature; ϵ_0, Fermi zero energy; q, number of electrons per atom outside full bands. The function C, which is assumed to be independent of electron energy and of temperature, may be taken as equal to that given by Wilson (1936, p. 201) or, apart from a numerical factor of $\frac{2}{3}$, that given by Sommerfeld & Bethe (1933, p. 513). In the derivation of (2·5) use has been made of the relation between ϵ_0 and the number of electrons per unit volume, n (see Stoner 1939, p. 267):

$$\epsilon_0 = \frac{h^2}{8m^*}\left(\frac{3n}{\pi}\right)^{\frac{2}{3}} = \frac{h^2}{8m^*a^2}\left(\frac{3q}{\pi}\right)^{\frac{2}{3}}, \tag{2·7}$$

where a^3 = volume of atomic cell.

The electric current density associated with the steady-state distribution (2·2) is

$$\begin{aligned}J_x &= -(e/4\pi^3)\int v_x f\,dk_x\,dk_y\,dk_z\\ &= \frac{e}{4\pi^3}\int\frac{2\pi}{h}\left(\frac{\partial\epsilon}{\partial k_x}\right)k_x\mu(\epsilon)\frac{df_0}{d\epsilon}\,dk_x\,dk_y\,dk_z,\end{aligned}$$

which with (2·4) may be expressed as

$$J_x = \frac{16\pi^2(2m^*)^{\frac{3}{2}}e}{3h^4}\int_0^\infty \epsilon^{\frac{3}{2}}\mu(\epsilon)\frac{df_0}{d\epsilon}\,d\epsilon. \tag{2·8}$$

Using this expression and (2·6), (2·7) the conductivity, σ, is given by

$$\left.\begin{aligned}\sigma = J_x/F &= \alpha y\int_{-\eta}^{\infty}\chi^{\frac{3}{2}}\phi(\xi)\frac{df_0}{d\xi}\,d\xi,\\ \text{where}\qquad \alpha &= \{Mhk\theta_D e^2\}/\{6a^3(\pi m^*C)^2\}.\end{aligned}\right\} \tag{2·9}$$

In order to calculate the absolute conductivity from (2·9) it would be necessary to determine the function C, while to calculate the temperature variation of conductivity it is sufficient to solve the transport equation, (2·5), for $\phi(\xi)$ for a range of values of y.

High-temperature approximation

Bloch (1928) obtained a solution of (2·5) for $y \ll 1$ effectively by taking the first term in a Taylor series expansion of $\phi(\xi\pm z)$ and the first term in the expansion of the remainder of the integrand in ascending powers of z. The right-hand side of (2·5) then involves the function ϕ only in the form $\phi(\xi)$, and (2·5) is reduced from an integral equation to a linear algebraic equation. Neglecting the small terms $\pm(pz/2r)$ (cf. § 3), the solution of this equation is given by

$$\phi(\xi) = -2\chi^{\frac{3}{2}}/y^3. \tag{2·10}$$

The corresponding value of the conductivity from (2·9) is

$$\sigma = -\frac{2\alpha}{y^2}\int_{-\eta}^{\infty} \chi^{\frac{3}{2}} \frac{df_0}{d\xi} d\xi. \tag{2·11}$$

The Fermi-Dirac integral in this expression cannot be evaluated analytically, but since in many metals the conduction electrons form a highly degenerate 'electron gas' at ordinary temperatures it is sufficient to use the first term in the 'low-temperature' approximation to the integral. From (2·6), (2·11) and the Fermi-Dirac approximation,

$$\sigma = 2\alpha(py)^3/y^2 = 4\alpha q^2 y. \tag{2·12}$$

This expression indicates that the conductivity at high temperatures varies inversely as the absolute temperature, corresponding to a specific resistance, $\rho_T = 1/\sigma$, proportional to T. Rough calculations show that this relationship is not appreciably affected by using more exact values for the Fermi-Dirac integral in (2·11) provided $(T/\theta_F) < 0{\cdot}1$.

Low-temperature approximation

Accounts of the method used by Bloch (1930) to obtain an approximate solution of (2·5) for $y \gg 1$ have been given by Sommerfeld & Bethe (1933, p. 526), Wilson (1936, p. 212) and others. The method is also discussed in § 3, and it will suffice here to quote the expression obtained for the conductivity,

$$\sigma = \frac{\alpha q^2}{5\,!\,\zeta(5)} y^5, \tag{2·13}$$

where $\zeta(5)$ is a Riemann function. Equation (2·13) indicates a variation of specific resistance, ρ_T, with T^5.

3. Solution of the transport equation for intermediate temperatures

Two methods of obtaining solutions of the transport equation for intermediate temperatures are considered in this section. First, a modified form of high-temperature solution, valid over a much wider temperature range than that previously given, is obtained. Secondly, a numerical method of successive approximations for testing the validity of the new first approximation and for obtaining higher approximations is described. For both of these the expression of the transport equation in the non-dimensional form, (2·5), introduced in § 2 was an essential preliminary.

Numerical values of parameters

Equation (2·5) contains parameters, ξ, y, z, which are reduced variables appropriate to any metal, and others, p and r, which may be regarded as specifying a particular metal. The function χ depends upon both kinds of parameter and upon ζ and ϵ_0.

As (2·5) is to be solved numerically, it is desirable to select values of p and r which will give the solution as wide a range of applicability as possible.

For metals in which the electrons satisfy the degeneracy criterion, $(kT/\epsilon_0) \ll 1$, ζ is closely equal to ϵ_0, and it is sufficiently accurate to express χ (cf. (2·6)) as

$$\chi = py\left\{1+\frac{\xi}{ry}\right\}. \tag{3·1}$$

In order to deal with electrons in a narrow band, i.e. for which ϵ_0 is comparable with kT, it would be necessary to take into account the dependence of ζ on T. This would not involve any insuperable difficulty, since Stoner (1939) has given numerical tables and series expressions which show the dependence of ζ on T for effectively the whole temperature range, but in what follows χ is taken to be of the form (3·1) so as to avoid an inessential complication of the central problem.

The number of electrons per atom, q, outside full bands, which determines p (cf. (2·6)), is taken as equal to unity, so that the results are immediately applicable to the alkali and noble metals (cf. §4).

TABLE 1. DEBYE TEMPERATURES, ESTIMATED FERMI-DIRAC CHARACTERISTIC TEMPERATURES AND RELATED DATA FOR REPRESENTATIVE METALS

A, atomic weight;
d, density, g.cm.$^{-3}$;
θ_D, Debye characteristic temperature;
θ_F, Fermi-Dirac characteristic temperature, ϵ_0/k (see equation (3·2));
$r = \theta_F/\theta_D$.

	A	d	θ_D	$\theta_F \times 10^{-4}$	$r \times 10^{-2}$
Li	6·94	0·534	(400)	5·46	(1·36)
Na	23·00	0·97	(150)	3·66	(2·44)
K	39·10	0·86	100	2·37	2·37
Rb	85·48	1·52	(70)	2·06	(2·94)
Cs	132·91	1·87	(50)	1·76	(3·52)
Cu	63·57	8·93	315	8·15	2·59
Ag	107·88	10·50	215	6·38	2·97
Au	197·2	19·3	170	6·41	3·77

In table 1 values of r, equal to θ_F/θ_D, and of the data used in estimating θ_F, are given for some representative metals. The Debye temperatures, θ_D, are from Borelius (1935, p. 252) and Seitz (1940, p. 110). Values enclosed in brackets are less certain than the others. The Fermi-Dirac characteristic temperatures, θ_F, have been determined from (2·7), which, for electrons to the number q per atom in a metal of density d, atomic weight A, may be written (cf. Stoner 1939, p. 279)

$$\theta_F = \epsilon_0/k = 3·017 \times 10^5 (m/m^*)\,(qd/A)^{\frac{2}{3}}, \tag{3·2}$$

using the Birge (1941) values of the fundamental constants. The values are calculated for $q = 1$, $m^* = m$. Values of A and d are from standard tables.

The values of r in table 1 are all of the same order of magnitude, and much greater than unity, the mean value being $2·7_4 \times 10^2$. As will be seen later, the solution of (2·5) for $r \gg 1$ does not depend critically upon r. A value of $r = 3 \times 10^2$ is adopted in the numerical work. This value is sufficiently close to all those listed in table 1 for the results of the calculations to be directly applicable to at least all those metals.

Strictly, $\phi(\xi)$ is to be determined from (2·5) for all values of ξ from $-\eta$ to ∞ (corresponding to values of ϵ from 0 to ∞), but it can be seen from (2·9) that in order to calculate the conductivity accurately it is necessary to obtain $\phi(\xi)$ accurately only for a limited range of values of ξ. From (2·1), (2·6),

$$\frac{df_0}{d\xi} = -\frac{1}{(e^{\xi}+1)(e^{-\xi}+1)}, \tag{3·3}$$

so $|df_0/d\xi|$ decreases exponentially for large values of $|\xi|$. Consequently the only appreciable contribution to the integral in (2·9) comes from the region of small values of $|\xi|$; $|df_0/d\xi|$ decreases to 1 % of its value at $\xi = 0$ when $|\xi| \doteqdot 6$. In order to obtain an accurate value of σ it is sufficient therefore to obtain a solution of (2·5) of comparable accuracy only for small values of $|\xi|$; for larger values of $|\xi|$ a lower degree of accuracy in the values of $\phi(\xi)$ is adequate.

First approximation

Using the Taylor series expansion for $\phi(\xi \pm z)$ in (2·5), the part of the integrand involving ϕ becomes

$$\left[\left\{\left(\frac{pz}{2r}-\frac{z^2}{y}\right)\phi(\xi)+z\left(\chi+\frac{pz}{2r}-\frac{z^2}{y}\right)\phi'(\xi)+\dots\right\}\frac{e^z}{e^{\xi+z}+1}\right.$$
$$\left.+\left\{\left(-\frac{pz}{2r}-\frac{z^2}{y}\right)\phi(\xi)-z\left(\chi-\frac{pz}{2r}-\frac{z^2}{y}\right)\phi'(\xi)+\dots\right\}\frac{1}{e^{\xi-z}+1}\right],$$

where a dash denotes differentiation with respect to ξ. Examination of (2·5) suggests that a modified high-temperature solution, valid over a wider range of y, may be obtained by neglecting $\phi', \phi'', \dots$ and the small terms $\pm(pz/2r)$, but leaving the remainder of the integrand unaltered. The tentative new first approximation to $\phi(\xi)$, say $\phi_1(\xi)$, is then

$$\phi_1(\xi) = -y\chi^{\frac{3}{2}}/I(\xi, y), \tag{3·4}$$

where

$$I(\xi, y) = (e^{\xi}+1)\int_0^y \frac{z^4\,dz}{e^z-1}\left\{\frac{e^z}{e^{\xi+z}+1}+\frac{1}{e^{\xi-z}+1}\right\}. \tag{3·5}$$

Values of $I(\xi, y)$, determined by numerical integration and by series expansion, are shown in figure 1 in the reduced form $I(\xi, y)/I(0, y)$ for $y = 1, 2, 3, 5$. The corresponding asymptotic values, determined from

$$I(\infty, y) = \int_0^y \frac{z^4(e^z+1)\,dz}{e^z-1}, \tag{3·5a}$$

are also shown.

For $y < 1$, expansion of the integrand of (3·5) in ascending powers of z and term-by-term integration gives

$$I(\xi, y) = \tfrac{1}{2}y^4 + \tfrac{1}{36}\{1-12e^{\xi}(e^{\xi}+1)^{-2}\}y^6 + \dots.$$

Substituting the first term of this series for I in (3·4), the expression for ϕ_1 becomes the same as the previously known high-temperature approximation, (2·10), which is thus a special case of (3·4) for $y^2 \ll 1$. For larger values of y it is not possible to estimate *a priori* the error introduced in (3·4) by the neglect of $\phi', \phi'', \dots$. The most direct method of determining the range of validity of (3·4) is to substitute $\phi_1(\xi)$ in (2·5) and to test whether or not that equation is satisfied. The details of this method may best be considered in conjunction with the discussion of the method of successive approximations used to obtain higher approximations in the temperature range for which ϕ_1 is not sufficiently accurate.

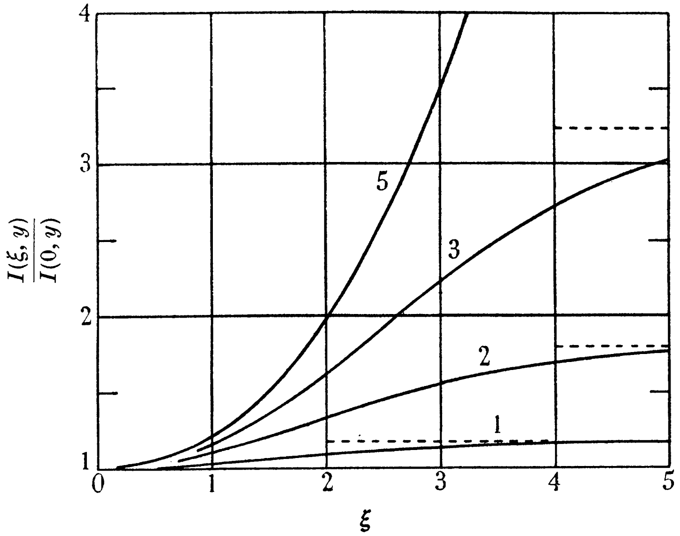

FIGURE 1. The reduced function $I(\xi, y)/I(0, y)$; see equation (3·5). The figures on the curves give the values of y. The values of $I(0, y)$ for $y = 1, 2, 3, 5$ are 0·4490, 5·376, 18·15, 54·15 respectively. The broken lines show the values of $I(\infty, y)/I(0, y)$ for $y = 1, 2, 3$ calculated from (3·5a); the corresponding value for $y = 5$ is 12·07.

Solution by successive approximations

The method of successive approximations adopted may be indicated by rewriting (2·5) in the form

$$\chi K(\xi, y)\,\phi_{\nu+1}(\xi) = -\chi^{\frac{3}{2}} + \int_0^y \{F(z) - F(-z)\}\,dz, \tag{3·6}$$

where

$$F(z) = \frac{z^2(e^{\xi}+1)}{(1-e^{-z})(e^{\xi+z}+1)}\left(\chi + \frac{pz}{2r} - \frac{z^2}{y}\right)\phi_\nu(\xi+z), \tag{3·7}$$

and $K(\xi, y)$ is of the same form as $I(\xi, y)$, (3·5), but with the factor z^4 in the integrand replaced by z^2. The subscripts to the ϕ's have been added in (3·6), (3·7) for convenience in discussing the method of successive approximations. The 'solution' of (3·6) is to be understood to mean the solution, $\phi(\xi)$, of the equation obtained by omitting the subscripts.

If a particular function ϕ_ν is a solution of (3·6) then obviously the function $\phi_{\nu+1}$, obtained by inserting ϕ_ν in the right-hand side, will be equal to ϕ_ν. This test for consistency provides a check on any approximate solution which may be obtained. In the present connexion, agreement to within 1 % between $\phi_{\nu+1}$ and ϕ_ν was regarded as sufficient, and this condition need be satisfied only for small values of $|\xi|$, up to 5 say, since the main contribution to the integral in the expression for the conductivity, (2·9), arises from such values of ξ.

In order to obtain higher approximations in the range of y values for which ϕ_1 does not satisfy the consistency condition the following method has been used. Values of

ϕ_2 are determined from (3·6) in the process of checking ϕ_1, and values of ϕ_3 are determined in the same way from ϕ_2. If ϕ_3 agrees with ϕ_2 to within the required accuracy for the relevant values of ξ, then ϕ_2 is a satisfactory solution; if not, the process is repeated until a function, ϕ_ν, is obtained such that $\phi_{\nu+1}$ agrees with ϕ_ν to within the required limits. In practice this procedure involves extensive computational work, since, for each value of y, numerical integration of the integral on the right-hand side of (3·6) gives a value of $\phi_{\nu+1}$ for only one value of ξ, and computation of $\phi_{\nu+2}$ from $\phi_{\nu+1}$ requires $\phi_{\nu+1}$ for a whole range of values of ξ.

Examination of (3·6) indicates that the solution is such that $\phi(-\xi)$ is approximately equal to $\phi(\xi)$. In obtaining successive approximations it was assumed that ϕ_ν is an even function at all stages. The final approximation was then tested for consistency in (3·6) for both negative and positive values of ξ, and in all cases it was found that the final value of $\phi_{\nu+1}(-\xi)$ agreed to within 1 % with $\phi_{\nu+1}(\xi)$. This considerably reduced the necessary computation.

From (3·4), (3·1), ϕ_1 may be written as

$$\phi_1(\xi) = -\frac{(p^3y^5)^{\frac{1}{2}}\{1+(\xi/ry)\}^{\frac{3}{2}}}{I(\xi,y)}. \tag{3·8}$$

For small values of ξ, and values of y of order unity, $(\xi/ry) \ll 1$. Consequently from (3·8) $\phi_1', \phi_1'', \ldots$ are determined largely by the corresponding differential coefficients of I. Further, the method of derivation indicates that ϕ_1 is a good approximation to ϕ if $\phi', \phi'', \ldots$ are small compared with ϕ. The function ϕ_1 may therefore be expected to be a good approximation to the solution of (3·6) if the differential coefficients of I with respect to ξ are small compared with I. The rate of change of I with ξ increases with y (cf. figure 1), so if ϕ_1 is a satisfactory approximation for a particular value of y it may be concluded that it is also satisfactory for smaller values of y.

For $y = 1$ it is found that ϕ_1 is a sufficiently accurate approximation, since ϕ_2 agrees with ϕ_1 to within 1 % for $|\xi| \leqslant 5$. For $y = 2$ higher approximations are required. In order to determine the largest value of y for which ϕ_1 is a sufficiently accurate solution it would be necessary to test the validity of this solution for a number of values of y in the range 1 to 2. This is unnecessary, however, since in the calculation of the conductivity associated with ϕ it is found that for $y \leqslant 2$ it is sufficient to consider only ϕ_1 (see §4).

Detailed application of the method of successive approximations has been restricted to $y = 2, 3, 5$ (cf. §§4, 5). The shape of the curves representing the successive approximations are similar for all these values of y, but more approximations are required as y increases. In illustration the successive approximations, ϕ_ν, to the solution of (3·6) for $y = 5$ are shown in figure 2. The curve showing ϕ_4, which lies between those for ϕ_3, ϕ_5, has been omitted for clarity. The values of ϕ_6, indicated by circles, agree to within 1 % with the corresponding values of ϕ_5, which is taken as the final approximation.

For $y = 2$ and 3 it is the second and third approximations, respectively, which constitute sufficiently accurate approximations to the solution of (3·6). In what follows it will be convenient to denote this final approximation in each case by ϕ.

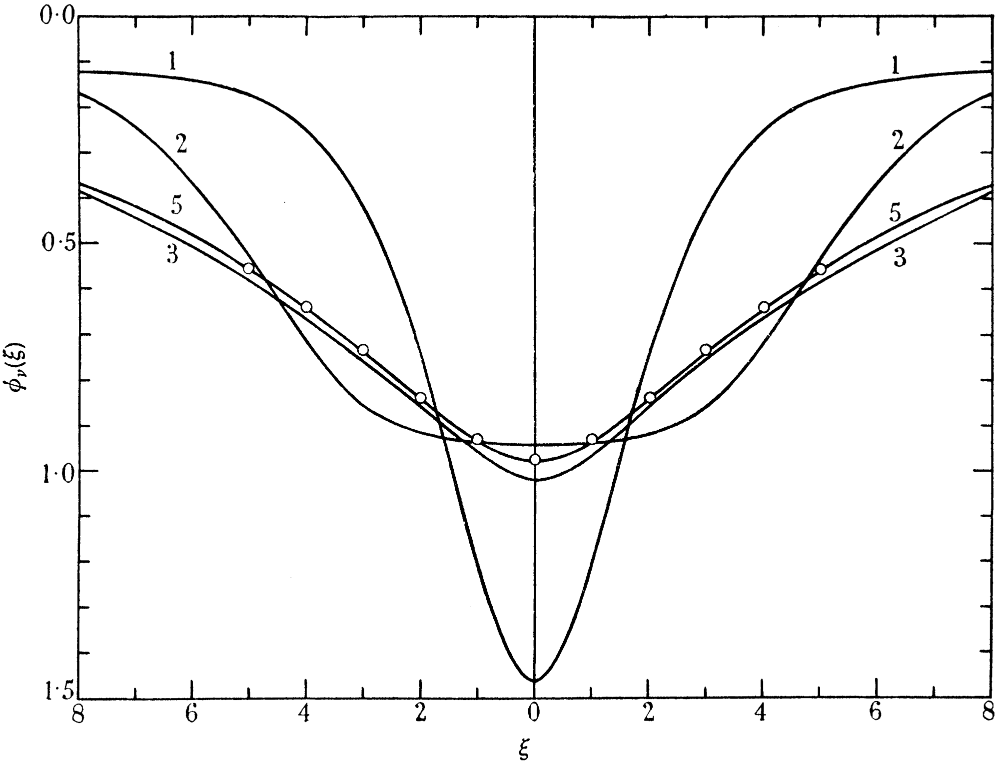

FIGURE 2. Successive approximations to the solution, $\phi(\xi)$, of the transport equation for $y = 5$; see equation (3·6). The numbers on the curves denote the stage of approximation, ν. The circles show the values of $\phi_6(\xi)$.

Orthogonality condition

A further check on the solutions of the transport equation has been made by a method which is essentially an adaptation of that used by Bloch (1930) to obtain an approximate solution for low temperatures.

Multiplying by $df_0/d\xi$, equation (2·5) may be rewritten as

$$\int_0^y \{G(z) - G(-z)\}\,dz = -\chi^{\frac{1}{2}}\frac{df_0}{d\xi} + \int_0^y \{H(z) - H(-z)\}\,dz, \tag{3·9}$$

where

$$G(z) = \frac{z^2\{\phi(\xi+z) - \phi(\xi)\}}{(\mathrm{e}^{-\xi}+1)(1-\mathrm{e}^{-z})(\mathrm{e}^{\xi+z}+1)}, \quad H(z) = \frac{z^3\left\{\dfrac{z}{y} - \dfrac{p}{2r}\right\}\phi(\xi+z)}{\chi(\mathrm{e}^{-\xi}+1)(1-\mathrm{e}^{-z})(\mathrm{e}^{\xi+z}+1)}. \tag{3·10}$$

Since (3·9) is satisfied for all values of ξ from $-\eta$ to $+\infty$, the integral of the left-hand side with respect to ξ over this range is equal to the corresponding integral of the right-hand side. Further, since $\eta \gg 1$, and all three terms of (3·9) decrease exponentially for large values of $|\xi|$, the lower limit of the integration with respect to ξ may be replaced by $-\infty$. The integral of the left-hand side is then zero. Consequently the integral of the right-hand side is also zero, that is,

$$\int_{-\infty}^{\infty} \chi^{\frac{1}{2}}\frac{df_0}{d\xi}\,d\xi = \int_{-\infty}^{\infty} d\xi \int_0^y \{H(z) - H(-z)\}\,dz. \tag{3·11}$$

This equation represents essentially the orthogonality condition which is satisfied if the inhomogeneous integral equation (3·9) has a finite solution (cf. Brillouin 1931, p. 374; Courant & Hilbert 1924, p. 102).

Substituting for χ from (3·1), noting that $|df_0/d\xi|$ decreases exponentially for large values of $|\xi|$, and that $(ry) \gg 1$, the left-hand side of (3·11) may be evaluated approximately as $-(py)^{\frac{1}{2}}$. Evaluation of the right-hand side in terms of an approximation to ϕ then provides a check on that approximation. Using the final approximations to ϕ it is found in all the cases considered that the right-hand side of (3·11), evaluated by numerical integration, agrees to within 1 % with the left-hand side. The integration over ξ from $-\infty$ to $+\infty$ may be carried out without undue difficulty, since the value of the integral over z decreases rapidly as $|\xi|$ increases.

Low-temperature approximation. The right-hand side of (3·9) decreases as y increases, and to obtain the low-temperature approximation (corresponding to $y \gg 1$) the left-hand side is equated to zero. The solution of this equation is $\phi(\xi)$ = constant, and the value of the constant is determined by (3·11). Assuming χ to be constant at the value corresponding to $\xi = 0$, integration with respect to ξ in (3·11) gives (cf. Wilson 1936, p. 213)

$$\phi(\xi) = -\frac{(p^3y^5)^{\frac{1}{2}}}{2J_5}, \tag{3·12}$$

where

$$J_5 = \int_0^y \frac{z^5 dz}{(\mathrm{e}^z-1)(1-\mathrm{e}^{-z})}. \tag{3·13}$$

Since the derivation of (3·12) is valid only for $y \gg 1$, the upper limit of the integral in (3·13) may be replaced by ∞, and J_5 evaluated as $5!\,\zeta(5)$. With this value of J_5, equation (3·12) with (2·9) and the Fermi-Dirac approximation gives the low-temperature approximate expression for σ quoted in §2.

4. Calculation of conductivity

The conductivity, σ, may be expressed from (2·9), (3·1) in the reduced form

$$\sigma' = \sigma/\beta = y^{\frac{5}{2}} \int_{-\eta}^{\infty} \left\{1 + \frac{\xi}{ry}\right\}^{\frac{3}{2}} \phi(\xi) \frac{df_0}{d\xi} d\xi, \tag{4·1}$$

where

$$\beta = p^{\frac{3}{2}}\alpha. \tag{4·2}$$

For a given metal β is a constant, and in particular is independent of temperature. From (3·3), $|df_0/d\xi|$ decreases exponentially for $|\xi| \gg 1$; further, $\eta \gg 1$, $(ry) \gg 1$. Consequently, (4·1) may be written, to a sufficient approximation, as

$$\sigma' = y^{\frac{5}{2}} \int_{-\infty}^{\infty} \phi(\xi) \frac{df_0}{d\xi} d\xi + \frac{3}{2} \frac{y^{\frac{5}{2}}}{ry} \int_{-\infty}^{\infty} \xi \phi(\xi) \frac{df_0}{d\xi} d\xi. \tag{4·3}$$

Now, as indicated in §3, $\phi(\xi)$ is, to within the required accuracy, an even function of ξ, and $df_0/d\xi$ is also an even function (cf. (3·3)), so (4·3) may be reduced to

$$\sigma' = 2y^{\frac{5}{2}} \int_0^{\infty} \phi(\xi) \frac{df_0}{d\xi} d\xi. \tag{4·4}$$

For convenience in evaluating the integral in (4·4) the range of integration may be divided into two parts: $\xi = 0$ to 5, and $\xi = 5$ to ∞. The contribution to the integral from the first part may be determined by numerical integration using the final approximations to ϕ. The contribution from the second part is relatively small, and ϕ may be replaced by a constant value, say ϕ_c, limits to which are determined by $\phi_1(5) > \phi_c > \phi(5)$. This part of the integral is then given by

$$\int_5^\infty \phi(\xi)\frac{df_0}{d\xi}d\xi = -\phi_c/(e^5+1). \tag{4·5}$$

For small values of $|\xi|$, $|\phi| < |\phi_1|$, and for large values, $|\phi| > |\phi_1|$ (see figure 2). This relation between ϕ_1 and ϕ, which is general, and which applies not only to $y = 5$, suggests, in conjunction with (4·4), that for the smaller values of y, for which ϕ does not differ greatly from ϕ_1, the value of σ' may be approximately the same when calculated from ϕ_1 as when calculated from ϕ. For $y = 2$ the two values of σ' calculated in this way agree to within 1 %. For $y = 3$ and 5 the values calculated with ϕ_1 are greater than those calculated with ϕ by about 4 and 16 % respectively. It may be concluded that for $y < 2$ it is sufficiently accurate in calculating σ' to replace ϕ by ϕ_1 in (4·4).

Values of σ' have been calculated from (4·4) for $y = 0·5(0·1)\,2, 3, 5$, using the values of ϕ and ϕ_1 determined as described in § 3. By interpolation in the σ', y table values of σ' have been determined for $T/\theta_D = 1/y = 0·2(0·1)\,1·0,\ 1·2(0·2)\,2·0$. The results are shown in table 2 in the reduced form $\sigma'_1/\sigma'_y = \rho_T/\rho_\theta$, where ρ_T, ρ_θ are the specific electrical resistance at $T°$ K, $\theta_D°$ K, respectively. This reduced form is convenient for comparison with experimental results. Values shown in brackets are somewhat less certain than the others owing to the difficulty of interpolation.

Table 2 also contains values of $(T^5/\rho_\theta)(\rho_T/T^5)_0$ and $(T/\rho_\theta)(\rho_T/T)_\infty$, where $(\rho_T/T^5)_0$ and $(\rho_T/T)_\infty$ are limiting values corresponding to $(T/\theta_D) \to 0$ and $(T/\theta_D) \to \infty$, respectively (cf. equations (2·13), (2·12)). It may be noted that although the values of $(T^5/\rho_\theta)(\rho_T/T^5)_0$ and $(T/\rho_\theta)(\rho_T/T)_\infty$ correspond to the low- and high-temperature approximations they could not be obtained from those alone, since neither of the approximations is valid at $T = \theta_D$, and so ρ_θ could not be determined from them.

The values shown in table 2 are considered in relation to the experimental results in § 5. Although values of ρ_T/ρ_θ cannot be determined accurately from the table for $0·2 > (T/\theta_D) > 0·05$, the values given show the temperature variation of resistance over practically the whole of the temperature range of particular interest (cf. § 1, and figures 3 and 4).

The values of $(\rho_T/\rho_\theta)_G$ in table 2 are from the semi-empirical formula suggested by Grüneisen (1930), which may be expressed in the form

$$\left(\frac{\rho_T}{\rho_\theta}\right)_G = \left(\frac{T}{\theta_D}\right)^5 \frac{J_5(\theta_D/T)}{J_5(1)}, \tag{4·6}$$

where $J_5(\theta_D/T)$ is given by (3·13). Tables of values of J_5 are given by Grüneisen (1933). Equation (4·6) may be obtained by assuming that the approximate expression for the conductivity derived from (3·12) is valid over the whole temperature range. The derivation of (3·12) provides no justification for this assumption. Although (4·6) reduces to the theoretical approximations for $y \gg 1$ and $\ll 1$, for intermediate temperatures it can only be regarded as an empirical interpolation formula. The Grüneisen values agree with the calculated values to within 1 % for $(T/\theta_D) \geqslant 0{\cdot}7$ and $\leqslant 0{\cdot}05$, but for temperatures between these limits there are significant differences (see table 2).

TABLE 2. SPECIFIC ELECTRICAL RESISTANCE AS A FUNCTION OF TEMPERATURE

ρ_T, ρ_θ, calculated specific resistance at T° K, $\theta_D{}^\circ$K;
$(\rho_T/T^5)_0$, value from the low-temperature approximation (see equation (2·13));
$(\rho_T/T)_\infty$, value from the high-temperature approximation (see equation (2·12));
$(\rho_T/\rho_\theta)_G$, values from Grüneisen's (1933) semi-empirical formula (see equation (4·6));
θ_D, Debye characteristic temperature.

$\dfrac{T}{\theta_D}$	$\dfrac{\rho_T}{\rho_\theta}$	$\dfrac{T^5(\rho_T/T^5)_0}{\rho_\theta}$	$\dfrac{T(\rho_T/T)_\infty}{\rho_\theta}$	$\left(\dfrac{\rho_T}{\rho_\theta}\right)_G$
0·05	—	$0{\cdot}000\,164_6$	—	$0{\cdot}000\,164_3$
0·10	—	0·005 27	—	0·004 92
0·15	—	0·040 01	—	0·026 62
0·2	0·060 2	0·168 6	0·212	0·068 0
0·3	(0·169)	—	0·318	0·181 2
0·333	$0{\cdot}210_5$	—	0·353	0·222 1
0·4	(0·295)	—	$0{\cdot}423_5$	0·304 5
0·5	0·419	—	0·529	0·426 5
0·6	0·539	—	0·635	0·545 4
0·7	0·658	—	0·741	0·661 7
0·8	0·774	—	0·847	0·775 9
0·9	0·888	—	0·953	0·888 5
1·0	1·000	—	$1{\cdot}05_9$	1·000
1·2	$1{\cdot}22_2$	—	$1{\cdot}27_1$	1·220
1·4	$1{\cdot}44_1$	—	$1{\cdot}48_2$	1·438
1·6	$1{\cdot}65_7$	—	$1{\cdot}69_4$	1·654
1·8	$1{\cdot}87_3$	—	$1{\cdot}90_6$	1·869
2·0	$2{\cdot}08_8$	—	$2{\cdot}11_8$	2·084

Range of validity of results

Solutions of the transport equation, (2·5), on which are based the calculation of conductivity, have been obtained for particular values of the parameters p and r, and the limitations which this imposes on the applicability of the results must be considered.

Examination of the derivation shows that the form of the solution of (2·5) does not depend critically upon the value of r, equal to θ_F/θ_D, provided that $r \gg 1$. The Debye temperatures of most metals are such that a small value of r could arise only from a value of θ_F corresponding to electrons distributed in a narrow band, and this case is not treated here. Moreover, an unfilled narrow band is ordinarily superposed on an unfilled wide band, and the relative contribution to the conductivity from the narrow band is then usually very small. The use of the particular value $r = 300$ thus imposes no serious limitation on the range of applicability of the results.

The solution of (2·5) is more sensitive to the value of $p = (2q^2)^{\frac{1}{2}}$, due to the fact that $\chi(2{\cdot}6)$ is proportional to p. Although no detailed calculations have been made of the conductivity for values of p other than $2^{\frac{1}{3}}$ (corresponding to one conduction electron per atom), examination of the derivation and of the general run of the results suggests that the temperature variation of conductivity would not be very different from that for $p = 2^{\frac{1}{3}}$.

One further general point may also be noted. Reference has been made only to conduction by electrons, but the results obtained apply equally well to conduction by 'holes' in an otherwise full band, provided that the density of states curve is of standard form at the top of the relevant band.

5. COMPARISON WITH EXPERIMENT AND CONCLUSION

The experimental results to be considered are taken from data given by Grüneisen (1928), Onnes & Tuyn (1929) and Meissner (1935). The results are usually given as the ratio, R_T/R_0, of the resistance of a specimen at the temperature to the resistance of the same specimen at 0° C. This approximates sufficiently closely to the ratio of the specific resistances, ρ_T/ρ_0. The values considered here have been 'corrected' by Matthiessen's rule for the temperature-independent 'residual' resistance, and therefore correspond to the 'ideal' resistance. In general the results are for specimens of a high degree of purity and the residual resistance is small compared with the observed resistance except at very low temperatures. Consequently, at intermediate and high temperatures deviations from Matthiessen's rule, such as have been observed by Grüneisen (1933) and considered theoretically by Dube (1938), would have only a slight effect on the ideal resistance.

The experimental and theoretical results may be conveniently compared by using the reduced form ρ_T/ρ_θ. In order to determine this quantity from the given values of ρ_T/ρ_0, values of ρ_θ/ρ_0 have been determined by graphical interpolation, using values of θ_D from Borelius (1935, p. 252) and Seitz (1940, p. 110). The experimental values of ρ_T/ρ_θ as a function of T/θ_D and the corresponding theoretical curve (cf. table 2) are shown in figure 3. It may be noted that errors in the somewhat uncertain values of θ_D have only a slight effect on the experimental (ρ_T/ρ_θ), (T/θ_D) relation, since a change in the value adopted for θ_D affects both quantities in approximately the same way.

The most striking feature of figure 3 is the good agreement between the experimental points and the theoretical curve over practically the whole temperature range considered. An alternative method of representation, which brings out more clearly the deviations between the theoretical and experimental results, is suggested by the theoretical linear relation between ρ_T/ρ_θ and T/θ_D at high temperatures. In figure 4 the reduced specific resistance $(\rho_T/\rho_\theta)/(T/\theta_D)$ is shown as a function of T/θ_D.

In figures 3 and 4 the agreement between the theoretical curves and the experimental points for the noble metals, copper, silver and gold, is very good except at high temperatures, where the experimental values lie above the curves. The observed ρ_T, T curves are convex to the T-axis in this region, and this deviation from a linear relation between ρ_T and T has been ascribed by Mott & Jones (1936, p. 268) to a decrease of the effective Debye characteristic temperature with increasing temperature. No accurate theoretical estimate of this effect has been made, but Mott & Jones (1936,

p. 17) give a simplified treatment of the effect of thermal expansion on the characteristic vibration frequencies of a lattice. From this they show (1936, p. 269) that the variation of the characteristic temperature is of the right order of magnitude to account for the observed curvature in the ρ_T, T curves for the noble metals, assuming that $(\rho_T/T) \propto 1/\theta_D^2$ (cf. equation (2·12)).

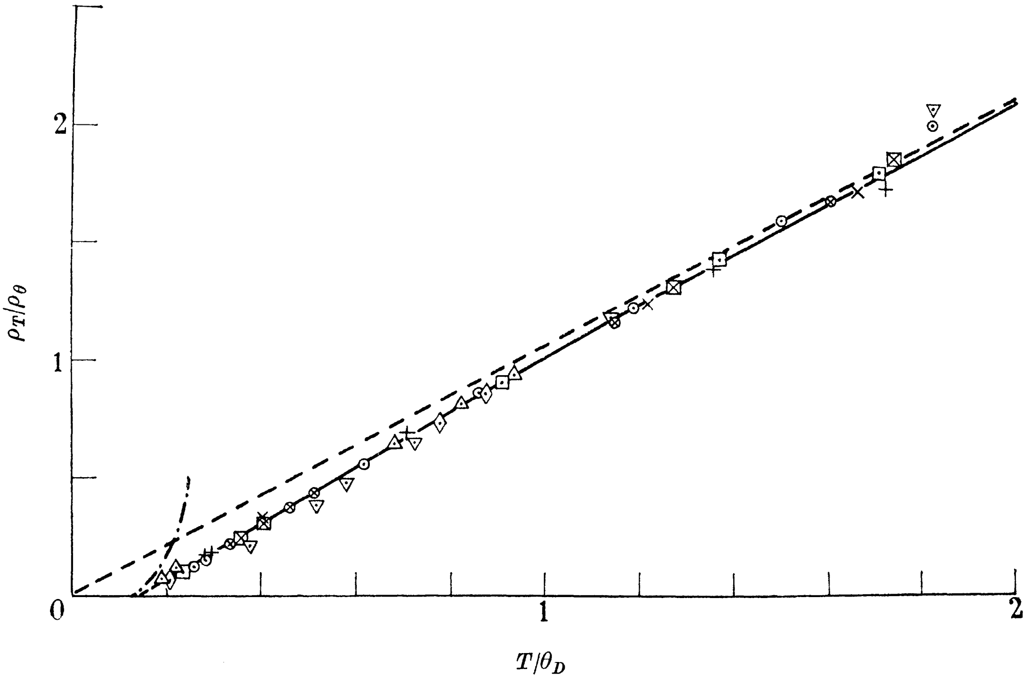

FIGURE 3. Specific electrical resistance as a function of temperature. Theoretical curve and experimental points. For sources of the experimental values see text. The broken line gives $\frac{T(\rho_T/T)_\infty}{\rho_\theta}$, and the dot-dash curve $\frac{T^5(\rho_T/T^5)_0}{\rho_\theta}$; cf. table 2 and related text. The dotted curve is interpolated. ρ_T, ρ_θ, specific resistance at T° K, θ_D° K; θ_D, Debye characteristic temperature.

		θ_D			θ_D			θ_D
△	Li	400	⊙	Cu	315	⊡	Pb	88
▽	Na	150	⊠	Ag	215	×	Pt	225
◇	K	100	⊗	Au	170	+	Pd	275

The agreement between experimental and theoretical results in figures 3 and 4 is not so good for the alkali as for the noble metals. For sodium, in particular, there are significant deviations. It is possible, however, to obtain fairly close agreement with the theoretical curves by adopting a value for θ_D of about 200° K, as compared with the mean value of about 150° K determined from specific heat measurements. This disagreement is surprising, but it is noteworthy that low-temperature specific heat measurements by Pickard & Simon (1948) indicate that, in addition to an anomaly in the specific heat-temperature curve at about 7° K, the effective value of θ_D increases with temperature at least up to 25° K; the value at 2° K is given as $\theta_D = 88^\circ$ K, and at 25° K as $\theta_D = 156$ °K. On the basis of evidence similar to this

Mott & Jones (1936, p. 11) have suggested that for the alkali metals 'the divergence between the true vibration spectrum and the Debye form is particularly great'.

For the transition metals, platinum and palladium, the experimental and theoretical values agree well except at high temperatures, for which the experimental points lie below the theoretical curves. There is strong evidence to indicate that in these metals the electrons outside full bands are distributed in two overlapping bands, the *s* and *d* bands. The current is carried mainly by the electrons in the *s* band, since the effective mass of the 'holes' in the *d* band is much larger (cf. Mott & Jones 1936, p. 267). It has been suggested by Mott (1935, 1936*a*, *b*) that transitions of electrons from the *s* band to the *d* band, due to 'collisions', may play an important part in determining the conductivity of these metals, and it is shown that in this case the estimated ρ_T, T curve is concave to the T-axis, as is observed (cf. Mott & Jones 1936, p. 269). This treatment has, however, been criticized by Wilson (1938), and it cannot be said that a completely satisfactory solution of the problem has yet been attained. Detailed discussion of this particular question is outside the scope of this paper, but two points may be noted. First, it may be shown from (4·1) and the preceding considerations that the temperature variation of resistance of a metal in which the electrons (or 'holes') outside full bands are distributed in two or more bands of standard form is the same as in the case of electrons distributed in a single band, provided that θ_F for each of them is much greater than θ_D, that the numbers of electrons (or 'holes') in the various bands are independent of temperature, and that

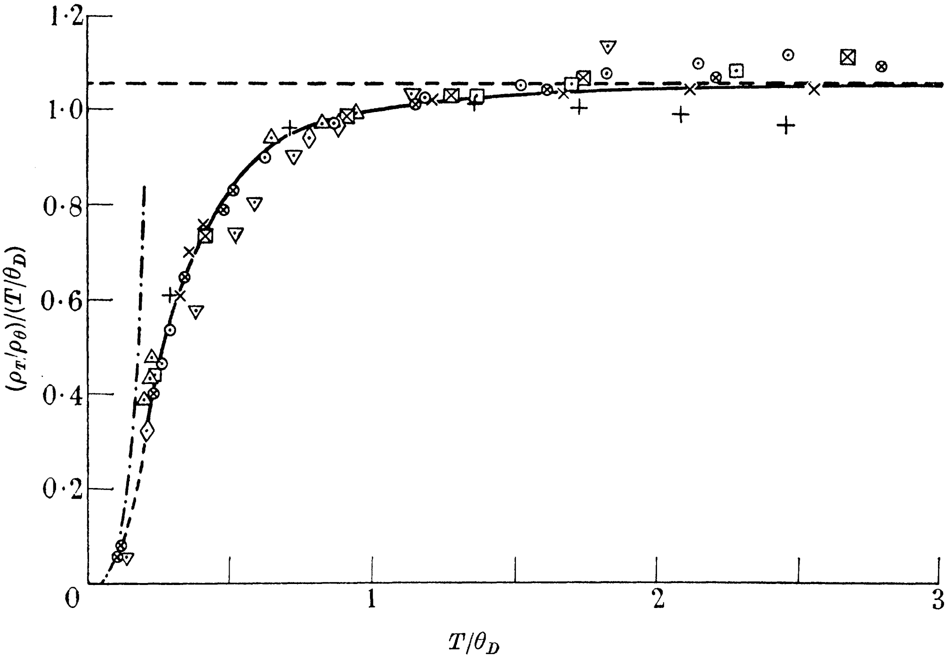

FIGURE 4. Reduced specific electrical resistance as a function of temperature. Theoretical curve and experimental points. For sources of the experimental values see text. The broken, dot-dash and dotted curves correspond to those similarly shown in figure 3. For symbols see figure 3.

there are no transitions between the bands due to 'collisions'. Secondly, in actual metals in which there are overlapping bands there may be a redistribution of electrons among the bands with increasing temperature. This 'transfer effect', which has been considered in detail in relation to the associated magnetic and thermal properties by Wohlfarth (1949), may lead to a relative increase in the conductivity with temperature, and consequently the ρ_T, T curve may be concave to the T-axis.

The principal reason for including the experimental points for lead in figures 3 and 4 is that this metal is representative of a large number of metals for which the temperature variation of electrical resistance agrees well with the theoretical curves of figures 3 and 4, although there is no evidence to suggest that their electronic structures are such as to satisfy the basic assumptions involved in the theoretical treatment; in particular, that the 'conduction' electrons are distributed in a band of standard form (cf. (2·4)). To avoid confusion the experimental points for only a few metals are included in figures 3 and 4 (although even so there is some overlap of the points for different metals). However, since the calculated curves agree fairly well with the Grüneisen curves over most of the temperature range, the comparisons which have been made between experimental values for a large number of metals and the Grüneisen curves (see, for example, Grüneisen 1933; Meissner 1935) serve as a rough comparison between the theoretical curves and experimental values. The good agreement which is found in many cases indicates that in general the temperature variation of electrical conductivity in metals depends only slightly on the electronic structure of the metal, and is determined primarily by the temperature variation of the lattice vibrations.

Concluding remarks

The primary aim in this paper has been to extend the detailed development of the Bloch treatment of the temperature variation of electrical conductivity, so as to cover a much wider temperature range than previously, and to test the applicability of the treatment to actual metals. It will be clear from the preceding discussion that in the main the agreement between calculated and observed values is good over the whole temperature range. Although the agreement is in no case perfect the deviations may in general be ascribed to factors of secondary importance, and it may be concluded that the theoretical treatment covers satisfactorily the main features of the observed temperature variation of conductivity.

In this paper attention has been restricted to the consideration of electrical conductivity, but the Bloch treatment may be readily generalized to deal with more complex transport effects, such as thermal conductivity and thermoelectric power. In these cases integral equations arise analogous to that treated here, and both the methods and the detailed results considered here may be of value in the treatment of these more complex effects.

I am indebted to Professor E. C. Stoner, F.R.S., for his constant guidance and encouragement in this and other work. My thanks are also due to Dr E. P. Wohlfarth for many helpful discussions; to Mr B. A. Lilley for criticism of the draft manuscript; and to the Department of Scientific and Industrial Research for grants.

APPENDIX

A variational treatment of the Bloch equation

Kohler (1949) develops a variational treatment by which successive approximations to the electrical conductivity may be determined from the transport equation without the distribution function being obtained explicitly (see also Kohler 1941, 1948). This method is widely different from that adopted in the present paper, but since both treatments are based on essentially the same initial equation (cf. Kohler 1949, p. 681), they should lead to the same calculated temperature variation of conductivity. Kohler concludes from his variational treatment that the calculated conductivity is, to a close approximation, equal to that given by Grüneisen's empirical formula over the whole temperature range. This result is significantly different from the results of the present paper (cf. table 2).

The fact that the two treatments lead to different results may arise either from inadequacies in one or other of the methods, or from errors in their application. Careful examination of Kohler's paper indicates that there is an algebraical error in the derivation of the expression given for the conductivity (Kohler 1949, pp. 686, 688). This expression may be written in the form

$$\sigma = \sigma_G(1+\lambda_1+\lambda_2+\lambda_3+\dots), \tag{A.1}$$

where σ_G is the Grüneisen value. It is implied that λ_3 and subsequent terms are negligible, and for λ_1 and λ_2 Kohler obtains

$$\left.\begin{aligned}\lambda_1 &= \left(\frac{\pi^2}{2}-a\right)^2\left\{\frac{\pi^2}{3}+2a-\frac{1}{6}\left(\frac{J_7}{J_5}\right)\right\}^{-1}\gamma^2,\\ \lambda_2 &= \frac{1}{18}\left(\frac{J_7}{J_5}\right)\gamma^2,\end{aligned}\right\} \tag{A.2}$$

where $J_n = \int_0^y \frac{z^n dz}{(e^z-1)(1-e^{-z})}$; $a = 2^{-\frac{5}{3}}y^2$; $y = \theta_D/T$; $\gamma = kT/\zeta \doteqdot T/\theta_F$.

For the relevant temperature range $\gamma \ll 1$ (cf. table 1, § 3), so both λ_1 and λ_2 are small for all values of y, and σ is closely equal to σ_G. The derivation of (A.2) is not given in detail. On working through the derivation along the lines indicated by Kohler, the same expression is obtained for λ_1, but for λ_2 a different expression, namely,

$$\lambda_2 = \left(\frac{J_7}{J_5}\right)^2\left\{24\pi^2a+\tfrac{16}{5}\pi^4+(6a-2\pi^2)\left(\frac{J_7}{J_5}\right)-\left(\frac{J_7}{J_5}\right)^2+\frac{3}{10}\left(\frac{J_9}{J_5}\right)\right\}^{-1}, \tag{A.3}$$

is obtained. (Thanks are due to Mr B. A. Lilley for kindly checking the derivation of (A.3).) The numerical value of λ_2 from (A.3) (of order 10^{-2}) is generally much greater than that from Kohler's expression (of order 10^{-7}), since (A.3) does not contain γ as a factor. Values of λ_1 and λ_2, calculated from (A.2) and (A.3) with values of J_7 and J_9 determined by numerical integration and values of J_5 from Grüneisen (1933), are shown in table 3 for a number of values of y. In evaluating (A.2) the ratio θ_F/θ_D has been taken as 300 (cf. § 3).

For comparison with the results of the variational treatment the results obtained by numerical successive approximations (cf. table 2) may be represented in the form

$$\sigma = \sigma_G(1+L). \tag{A.4}$$

The corresponding values of L are shown in table 3. It is to be noted that the form of (A. 4) gives a false impression of the method of derivation of the values in table 2; (A. 4) is only introduced to facilitate comparison between the two sets of results.

Since λ_2 is not negligible for a wide range of values of y (cf. table 3) further terms in (A. 1) may also have to be taken into account in evaluating σ accurately by the variational method. Moreover, Kohler indicates that all the λ_i are positive, and since L may be written formally as $\Sigma\lambda_i$, it may be concluded from table 3 that the results of the treatment in the present paper are at least not incompatible with those of the variational treatment.

Table 3. Comparison of reduced conductivities calculated by a variational method (third approximation) and by numerical successive approximations. (For explanation see text)

λ_1, λ_2(A. 2), values from (A. 2) (cf. (A. 1));
λ_2(A. 3), values from (A. 3);
L, values calculated from (A. 4) and table 2, §4; $y = \theta_D/T$.

y	1	2	3	5
$\lambda_1 \times 10^6$	62	7·0	0·68	0·23
$\lambda_2 \times 10^6$ (A. 2)	0·41	0·40	0·39	0·35
$\lambda_2 \times 10^2$ (A. 3)	0·1	1·2	3·4	8·1
$L \times 10^2$	<1	1·8	5·5	13

References

Birge, R. T. 1941 *Phys. Soc. Rep. Progr. Phys.* **8**, 90.
Bloch, F. 1928 *Z. Phys.* **52**, 555.
Bloch, F. 1930 *Z. Phys.* **59**, 208.
Borelius, G. 1935 *Handbuch der Metallphysik*, **1/1**. Leipzig: Akad. Verlags.
Brillouin, L. 1931 *Die Quantenstatistik*. Berlin: Springer.
Courant, R. & Hilbert, D. 1924 *Methoden der mathematischen Physik*, **1**. Berlin: Springer.
Dube, G. P. 1938 *Proc. Camb. Phil. Soc.* **34**, 559.
Grüneisen, E. 1928 *Handbuch der Physik*, **13**, 1. Berlin: Springer.
Grüneisen, E. 1930 *Leipziger Vorträge*, p. 46.
Grüneisen, E. 1933 *Ann. Phys., Lpz.*, **16**, 530.
Kohler, M. 1941 *Ann. Phys., Lpz.*, **40**, 601.
Kohler, M. 1948 *Z. Phys.* **124**, 772.
Kohler, M. 1949 *Z. Phys.* **125**, 679.
Meissner, W. 1935 *Handbuch der Experimentalphysik*, **11/2**. Leipzig: Akad. Verlags.
Mott, N. F. 1935 *Proc. Phys. Soc.* **47**, 571.
Mott, N. F. 1936*a* *Proc. Roy. Soc.* A, **153**, 699.
Mott, N. F. 1936*b* *Proc. Roy. Soc.* A, **156**, 368.
Mott, N. F. & Jones, H. 1936 *The theory of the properties of metals and alloys*. Oxford: Clarendon Press.
Nordheim, L. 1931 *Ann. Phys., Lpz.*, **9**, 607.
Onnes, H. K. & Tuyn, W. 1929 *International Critical Tables*, **6**, 124.
Pickard, G. L. & Simon, F. E. 1948 *Proc. Phys. Soc.* **61**, 1.
Seitz, F. 1940 *The modern theory of solids*. New York and London: McGraw-Hill.
Sommerfeld, A. & Bethe, H. 1933 *Handbuch der Physik*, **24/2**, 333. Berlin: Springer.
Stoner, E. C. 1939 *Phil. Mag.* **28**, 257.
Wilson, A. H. 1936 *The theory of metals*. Cambridge University Press.
Wilson, A. H. 1938 *Proc. Roy. Soc.* A, **167**, 580.
Wohlfarth, E. P. 1949 *Proc. Roy. Soc.* A, **195**, 434.