THE ELECTRICAL AND THERMAL CONDUCTIVITIES OF MONOVALENT METALS

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Summary

The experimentally determined values of the high and low temperature electrical and thermal conductivities of pure sodium, copper, silver, and gold are such that the ratios of these quantities for each of these metals do not agree with the values expected from the Bloch free electron theory, except for the high temperature Wiedemann-Franz ratio. Reasonable agreement can be achieved by assuming (i) that the conduction electrons can interact directly with transverse lattice vibrations, and (ii) that the Fermi surface departs significantly from spherical shape in all these metals, and touches the boundary of the Brillouin zone in the case of copper, silver, and gold.

I. INTRODUCTION

The thermal conductivity of a pure metal at low temperatures, assuming energy transport by quasi-free electrons (electron energy E a function of the wave number k only) interacting with lattice vibrations having a Debye spectrum, has been calculated by the author (Klemens 1954*b*) by solving numerically the appropriate transport equation. The conductivity thus obtained is about 11 per cent. larger than the value previously obtained by Sondheimer (1950), and its accuracy was estimated to be better than 0·5 per cent. This does not substantially alter the well-known discrepancy between the predictions of the theory and the observed thermal conductivity. In this paper the discrepancy will be re-examined and modifications of the quasi-free electron model which offer an explanation will be considered.

In all theoretical expressions for the thermal and electrical conductivities of pure metals there enter two constants, always in the same combination, which are difficult to calculate but can be combined and treated as an empirical constant. They are the effective number of free electrons and the electron-phonon interaction constant C. When comparing experimental results with theoretical predictions, the empirical constant is eliminated by forming the ratio of two conductivities. Of the four quantities used, namely, the electrical and thermal conductivities at high and at low temperatures, the high temperature electrical and thermal conductivities are related by the Wiedemann-Franz law, so that only two independent ratios can be formed. The Wiedemann-Franz law holds at high temperatures irrespective of particular assumptions about the band structure and the electron-phonon interaction, and it is therefore not a sufficient test of the Bloch theory. It is in fact well obeyed at high temperatures

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for all metals, except where there is an appreciable lattice component of thermal conduction.

By the quasi-free electron theory if W is the thermal resistance and T_1 and T_2 are two temperatures such that $T_1 \ll \theta < T_2$ then, according to Klemens (1954*b*),

$$\frac{W(T_1)}{W(T_2)} = 64 \cdot 0 N^{2/3} (T_1/\theta)^2, \quad \ldots\ldots\ldots\ldots\ldots (1)$$

where θ is the Debye temperature and N the number of free electrons per atom. Also the electrical resistance at high and at low temperatures is related by

$$\frac{R(T_1)}{R(T_2)} = 497 \cdot 6 \frac{T_1^5}{T_2 \theta^4}, \quad \ldots\ldots\ldots\ldots\ldots (2)$$

and, since $R(T_2) = LW(T_2)T_2$, where $L = (\pi K/e)^2/3 = 2 \cdot 45 \times 10^{-8}$ WΩ/deg^2, the high temperature conductivities can be eliminated from (**1**) and (**2**) giving

$$\frac{W(T_1)}{T_1^2} = \frac{64 \cdot 0}{497 \cdot 6} N^{2/3} \frac{\theta^2}{L} \frac{R(T_1')}{T_1'^5}, \quad \ldots\ldots\ldots\ldots (3)$$

where T_1 and $T_1' \ll \theta$. This equation could, of course, be derived without reference to the high temperature conductivities.

It has previously been assumed by various authors (see Sondheimer 1952) that N is the *effective* number of free electrons per atom, defined in terms of the current induced in the band by an electric field, and that it can be treated as an adjustable parameter. However, it arises in (**1**) from a term $q^2/2k_\zeta^2$ in the transport equation at high temperatures, q being the maximum wave number of the phonons and k_ζ the Fermi wave number. For a spherical Fermi surface $q/k_\zeta \propto N^{1/3}$, where N is the number of free electrons per atom in the conduction band, quite independently of the dependence of E on k. For a monovalent metal we must therefore take $N = 1$.

II. Thermal Conductivities at High and at Low Temperatures

The thermal conductivities of pure sodium and copper have been measured by Berman and MacDonald (1951, 1952) and that of pure gold and silver by White (1953*a*, 1953*b*), who also repeated the measurements on copper (White 1953*c*). Subtracting the residual resistance, they obtained the ideal thermal resistance, which at low temperatures is indeed approximately proportional to T^2. The values of $W(T_1)/T_1^2$ so obtained, together with $W(T_2)$, the thermal resistance at room temperatures, are given in Table 1. Taking for θ the value θ_R, which is derived by fitting the ideal electrical resistance to (**2**), and putting $N = 1$, the ratio $W(T_1)/T_1^2 W(T_2)$ was calculated from (**1**) and compared with the corresponding ratio of the measured values. As seen in the table, these two ratios are not equal, so that (**1**) is not satisfied.

It has not been made clear whether this discrepancy arises from a failure of the theory in respect of $W(T_1)$ or of $W(T_2)$, or because of a wrong choice of the θ-value. The last two effects are not independent, for a failure of the theory to give the correct expression for $W(T_2)$—and hence for $R(T_2)$—would affect the

value of θ_R. The theoretical expressions for $W(T_2)$ and $R(T_2)$ may not be correct because the Bloch theory neglects the following effects which should be considered at high temperatures even for the quasi-free electron model:

(i) A lowering of the effective vibration frequencies due to the dispersion of the lattice waves, and due to each high frequency wave being neither purely longitudinal nor purely transverse.

(ii) The occurrence of Umklapp-processes. These are processes which conserve energy but change the total wave-vector by an inverse lattice vector. On the quasi-free electron model these processes cannot occur at low temperatures, but must occur at high temperatures. Since they are not considered in

TABLE 1

Metal	Sodium	Copper	Silver	Gold
$W(T_1)/T_1^2$ (W^{-1} cm deg^{-1})	$3{\cdot}8\times10^{-4}$	$2{\cdot}55\times10^{-5}$	$6{\cdot}4\times10^{-5}$	$1{\cdot}3\times10^{-4}$
$W(T_2)$ (W^{-1} cm deg) ..	0·73	0·26	0·24	0·64
$R(T_1)/T_1^5$ (Ω cm deg^{-5}) ..	$5{\cdot}3_7\times10^{-15}$	$2{\cdot}6_4\times10^{-16}$	$1{\cdot}11\times10^{-15}$	$3{\cdot}9\times10^{-15}$
θ_R (°K)	202	330	220	170
θ_D (°K)	150	315	215	170
θ_L (°K)	260	505	340*	270*
$\theta_{(3)}$ (°K)	117	136	105	80
Ratio of calculated to observed values of $W(T_1)/T_1^2W(T_2)$				
using θ_R	3·0	6·0	5·0	5·8
θ_L	1·8	2·6	2·1	2·3
$(\theta_L/\theta_R)^4$	2·8	5·4	5·8	6·3
$(\theta_L/\theta_{(3)})^2$	5·0	13·7	10·5	11·4
$(\theta_D/\theta_{(3)})^2$	1·7	5·4	4·2	4·5

* Taking the same ratio of θ_L/θ_D as for copper.

the Bloch theory, they form an additional source of resistance, also proportional to T at high temperatures. The magnitude of this resistance, which is difficult to calculate accurately, is sensitive to the shape of the zone boundary and to its position relative to the Fermi surface. However, it can never greatly exceed the Bloch resistance, and would only be about 30 per cent. of the Bloch resistance for $N=1$ and a spherical Brillouin zone.

(iii) A possible variation at high frequencies of the electron-phonon interaction parameter C, assumed in the Bloch theory to be constant for all interaction processes. Such a variation would follow from Nordheim's assumption of a rigid ion, in contrast to Bloch's deformable ion, and would also occur in intermediate cases. But even for a deformable ion a decrease of C with increasing phonon frequency would be obtained if proper account were taken of the partial interference of electron wave-functions in calculating the transition matrix. This point is discussed by Bethe (see Sommerfeld and Bethe 1933, p. 517).

While (i) and (ii) would cause the high temperature resistance to increase over the value given by the Bloch theory, (iii) would cause a decrease.

In view of these uncertainties, equation (**1**) is not a good test of the validity of the theory of thermal conduction at low temperatures.

III. Thermal and Electrical Conductivities at Low Temperatures

The uncertainties of the theory at high temperatures can be avoided by comparing the thermal and electrical conductivities at low temperatures, using equation (**3**). One can confidently expect the phonon spectrum at low frequencies to be of the form given by the simple elastic theory, so that, according to the Bloch theory, the θ-value in (**3**) should be θ_L, related to the velocity of longitudinal low frequency waves and calculated by Blackman (1951) for some metals, including sodium and copper.

Substituting the observed values of W/T^2 and R/T^5 into (**3**) and calculating a value for θ from it, denoted by $\theta_{(3)}$, we find that $\theta_{(3)}$ is too low in all cases (see Table 1). The discrepancy $(\theta_L/\theta_{(3)})^2$ is somewhat less for sodium than for the noble metals.

It should be noted that the discrepancy in (**1**) would have been reduced if θ_L had been used instead of θ_R; but this could have been done only at the expense of introducing a discrepancy $(\theta_L/\theta_R)^4$ in (**2**) (Blackman 1951). Attempts to resolve this discrepancy, by Klemens (1952) in terms of dispersion of the lattice waves, and by Bhatia (1952) in terms of Umklapp-processes, are both in error.* A full consideration of these effects would lead to an increase in the high temperature resistance, as pointed out above, so that the discrepancy in (**2**) would be increased even further.

There are thus discrepancies between theory and experiment which can be explained neither in terms of deviations of the phonon spectrum from the Debye model, nor by reasonable adjustment of the θ-values. One is therefore led to conclude that they arise as result of deviations of the electronic band structure from the quasi-free electron model.

IV. Modifications of the Quasi-Free Electron Model

It has been seen that the observed ratio of the electrical to the thermal resistance at low temperatures is greater than expected from the Bloch theory. The following explanation is offered.

It is well known that the processes responsible for electrical resistance are such as to move an electron in momentum space from a point on the Fermi surface to a point on the opposite side of it. At high temperatures this is done in large steps, each phonon interaction changing the direction of the electron by about 1·5 radians. At low temperatures the angular change at each interaction is only of order T/θ, so that the processes producing the electrical resistance

* Klemens takes the density of normal modes to be proportional to $\omega^2 d\omega$, ω being the phonon frequency, but this is correct only in the absence of dispersion. Bhatia correctly deduces that the θ-value at high temperatures is lowered because of Umklapp-processes, but does not consider that these processes increase $R(T_2)$, and hence increase the θ-value deduced from (**2**).

can be regarded as a small-step diffusion process, in which an electron wanders to the opposite side of the Fermi surface. The calculation of the resistance becomes a random walk problem on the Fermi surface. The electrical resistance is inversely proportional to the square of the distance to be covered and proportional to the number of steps per unit time and to the square of the average length of each step. It would therefore be expected that the electrical resistance of a metal having a non-spherical Fermi surface would differ from that derived on the Bloch theory, where a spherical Fermi surface is assumed.

On the other hand, the thermal resistance at low temperatures is due to a movement of electrons from a point just above the Fermi surface to one just below it, or vice versa; that is, a change of energy of order KT without an appreciable change of direction. Since in such processes the electron does not change its location on the Fermi surface but only its " height " above or below it, changes in the shape of the Fermi surface will not affect the thermal resistance, except by changing the effective number of free electrons, which does not enter the present considerations.

The possible deformations of the Fermi surface from spherical shape satisfy the following requirements: (i) the enclosed volume is kept constant, (ii) the deformation has the polyhedral symmetry of the Brillouin zone, and (iii) along the axes of symmetry the deformation is outward. Such a deformation will alter the electrical resistance relative to the thermal resistance at low temperatures. This effect will be even more pronounced, and increase the electrical resistance, if the Fermi surface touches the zone boundary, for then an electron, diffusing on the Fermi surface, can reach an opposite point not only by the usual way but also by drifting to the nearest point of contact and reappearing on the opposite side of the zone. The distance to be covered is thus approximately halved on the average, and there will be an additional resistance, about four times the ordinary resistance, due to movement via the points of contact, so that the total resistance is increased by a factor of about 5.

We have seen that the ratio $R(T_1)/W(T_1)$ is larger than expected from the Bloch theory, the discrepancy being $(\theta_L/\theta_{(3)})^2$ shown in Table 1. This discrepancy can be reduced by a factor of about 5 if it is assumed that the Fermi surface touches the zone boundary. Even so, for the noble metals, the discrepancy is too large to be explained in this way alone. In order to reconcile the theory to the observed values of $R(T_1)/W(T_1)$, it must be further assumed that the conduction electrons interact with the transverse waves as well as with the longitudinal waves. This would make θ_D the appropriate θ-value in equation (3) and the discrepancy in (3), now $(\theta_D/\theta_{(3)})^2$, is sufficiently reduced, as seen from Table 1, to permit an explanation in terms of the Fermi surface touching the zone boundary.

Peierls (1930*a*, 1930*b*, 1932) suggested that the Fermi surface of monovalent metals should touch the zone boundary in order to account for the absence of observable effects at low temperatures arising from quasi-equilibria between electrons and phonons, and, although Klemens (1951) showed that this was not a necessary conclusion, it remained a possibility. Smit (1952) pointed out that the effects of shear strain on the thermoelectric forces suggest strongly that the

Fermi surface touches the zone boundary in the cases of gold and silver. Measurements by Mortlock (1953) have made it appear probable that this is also the case for copper. The sign of the thermoelectric power of the noble metals, in contrast to that of the alkali metals, gives additional support to the hypothesis.

Bloch's conclusion that the conduction electrons cannot interact directly with transverse phonons is based on the assumption of a spherical Fermi surface. Since this assumption has here been discarded to explain the low temperature conductivities, it is not unreasonable to assume some interaction between the conduction electrons and transverse waves. There is also some evidence for such interaction from the study of the lattice component of the thermal conductivity of alloys (Klemens 1954*a*). The magnitude of the lattice component depends sensitively upon the degree of interaction between the conduction electrons and transverse waves. The lattice component of a pure metal cannot be determined directly but can be deduced from the thermal conductivity of dilute alloys. Measurements on copper-nickel alloys, as discussed by the author, indicate such interaction in the case of copper, and recent measurements of silver-palladium alloys (White, personal communication) indicate the same for silver.

Considering now the high temperature resistance (electrical or thermal), and remembering that for Fermi surfaces touching the zone boundary the contribution from Umklapp-processes to the resistance is roughly equal to that from ordinary processes, and also that dispersion can reduce the frequency of the shortest lattice waves by about 1·5 (Klemens 1952) and thus increase the resistance by a factor of 2 to 2·5, one can explain the discrepancies in (**1**) with $\theta=\theta_D\sim\theta_R$ for the noble metals. This would, of course, also explain the discrepancies in (**2**) noted by Blackman (1951).

With sodium the position is different, since the discrepancy from (**3**) is smaller. It can be explained either by assuming that the Fermi surface touches the zone boundary, but that the conduction electrons do not interact with transverse waves, or by assuming a Fermi surface, non-spherical but nevertheless not touching the zone boundary, and interaction between the electrons and transverse phonons. The latter explanation seems more probable, because it will also explain the observed value of the high temperature resistance, and because of the normal sign of the thermoelectric power.

V. Conclusions

The experimental value of the ratio R/W for pure metals at low temperatures is too large compared with the predictions of the Bloch theory, and deviations from the quasi-free electron model must be assumed to explain this discrepancy. Values of the high temperature resistance also indicate that the Bloch theory is not valid. It seems that in the four metals considered there is interaction between the conduction electrons and transverse lattice waves. In gold, silver, and copper the Fermi surface apparently touches the zone boundary, while in sodium it does not.

There is evidence in support of these conclusions from thermoelectric effects and from the lattice component of the thermal conductivity.

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