

THE LATTICE COMPONENT OF THE THERMAL CONDUCTIVITY OF METALS AND ALLOYS

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Summary

Makinson's (1938) theory of the lattice component of the thermal conductivity of metals and alloys, when limited at low temperatures by interaction with the conduction electrons, is re-examined, and the magnitude of the lattice conductivity is related to the electronic thermal conductivity at low temperatures, thus avoiding uncertainties in the theory at high temperatures. The result depends on whether transverse lattice waves can interact with the electrons.

The variation of the lattice conductivity with electron concentration is discussed, and the theory is applied to the systems copper-nickel, copper-zinc, silver-palladium, and silver-cadmium. At present only the first system has been measured, and the results can be reconciled qualitatively to the theory if it is assumed that holes appear in the $3d$ band for nickel concentrations greater than 10–20 per cent. It also appears that for copper there is direct interaction between electrons and transverse waves. Qualitative predictions are made for the other three systems.

I. INTRODUCTION

In addition to the thermal conduction in metals due to the free electrons, there is heat transport by the lattice. Since the free electrons, interacting with the lattice waves, limit the phonon mean free path, this lattice conductivity is much smaller than the conductivity of a dielectric solid and forms only a small part of the total thermal conductivity of a good electronic conductor. However, the lattice component becomes appreciable for metals and alloys of smaller electronic conductivity, and in some cases it has been possible to identify the lattice component.

The theory of the thermal conductivity of dielectric solids has been formulated by Peierls (1929) and extended by Klemens (1951). The same theory can be used in the presence of free electrons, except that the interaction between electrons and lattice waves must be considered as an additional scattering process. The relaxation time for this interaction has been worked out by Bethe (see Sommerfeld and Bethe 1933), and his result was used by Makinson (1938), who obtained an expression for the lattice conductivity in terms of electron interaction, boundary scattering, scattering by lattice defects, and phonon-phonon interaction and gave a qualitative discussion of the overall temperature dependence of the lattice conductivity.

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In the special case when the only processes contributing significantly to the thermal resistance are electron interactions, Makinson obtained for the thermal conductivity

$$\kappa_g = 7 \cdot 18 G \left(\frac{T}{\theta} \right)^2, \quad \text{for } T \ll \theta, \quad \dots \dots \dots (1)$$

where it can be shown that

$$G = \frac{8\pi^2 \theta^2 K^3 M}{h^3 a^3 C_j^2} \left(\frac{1}{k} \frac{dE}{dk} \right)_\zeta^2 \dots \dots \dots (2)$$

Here θ is the Debye temperature, K the Boltzmann constant, M the mass, and a^3 the volume, of a unit cell, and E and k the energy and wave number of an electron state. The constant C_j is the usual coupling constant, of the dimensions of energy.

In order to eliminate the coupling constant C_j^2 , Makinson expressed κ_g in terms of $\kappa_e(\infty)$, the electronic thermal conductivity at high temperatures. He treated modes of all three polarizations as interacting equally with the conduction electrons, so that the constant C_j^2 in (2) is one-third of the corresponding constant appearing in the expression for electronic conductivity. With this assumption he obtained

$$\kappa_g = \frac{27}{4\pi^2 N^2} 7 \cdot 18 \left(\frac{T}{\theta} \right)^2 \kappa_e(\infty), \quad \dots \dots \dots (3)$$

where N is the number of free electrons per atom. It should be emphasized that (3) depends on the assumption of a free electron gas, and also that $\kappa_e(\infty)$ is not the observed conductivity but the ideal conductivity (i.e. after subtracting the residual thermal resistance) of the same material on the assumption that the Bloch theory is obeyed at high temperatures.

Now it is well known that the Bloch theory neglects Umklapp-processes, which are certainly significant at high temperatures, that it disregards the dispersion of the velocity of sound, and that it does not allow for a possible frequency variation of the interaction constant C . Furthermore, the theory does not give the observed relation between the high temperature and the low temperature thermal conductivity. It seems thus more advantageous to eliminate the high temperature conductivity and to compare κ_g to the ideal electronic thermal conductivity at low temperatures. There still remains an uncertainty due to different possible coupling schemes. We shall discuss this point in Section II.

From (3) it appears at first sight that a variation of κ_g with the concentration of free electrons is accounted for by the factor N^2 in the denominator. It must be remembered, however, that $\kappa_e(\infty)$ itself varies with electron concentration. Unfortunately the ideal electronic thermal conductivity is generally unobservable for those substances whose lattice conductivity can be determined. The variation of κ_g with electron concentration must be determined directly from (2). This variation will be discussed in Section III. In Section IV the theory will be applied to the alloy systems copper-nickel, copper-zinc, silver-palladium, and silver-cadmium.

II. THE ABSOLUTE VALUE OF THE LATTICE CONDUCTIVITY

We shall express (2) in terms of the ideal electronic thermal conductivity $\kappa_e(T)$ at low temperatures. Sondheimer (1950) has obtained the following expression for the thermal conductivity at low temperatures according to the Bloch theory

$$\kappa_e(T) = \kappa_e(\infty) \left(\frac{\theta}{T}\right)^2 \frac{1}{71 \cdot 6 N^{2/3}}, \dots\dots\dots (4)$$

solving the Bloch equation to third order by a variational method. The author (Klemens 1954) has solved the same equation numerically and obtained, with an uncertainty less than 0.5 per cent., a numerical factor 64.0 in place of 71.6. Using this new value and substituting into (3) we obtain

$$\kappa_g = 313 \kappa_e(T) \left(\frac{T}{\theta}\right)^4 N^{-4/3}. \dots\dots\dots (5)$$

The factor $N^{-4/3}$ arises because κ_g is proportional to $k_{\zeta}^{-2} (dE/dk)_{\zeta}^2$, while κ_e is proportional to $k_{\zeta}^2 (dE/dk)_{\zeta}^2$. The factor $(dE/dk)_{\zeta}^2$ cancels in the ratio, so that in (5)

$$N^{4/3} \propto k_{\zeta}^4. \dots\dots\dots (6)$$

This is independent of the dependence of E on k and, provided the Fermi surface is spherical, N denotes the actual number of electrons in the conduction band. If the Fermi surface touches the zone boundary, the effective value of $N^{2/3}$ will be reduced and will be proportional to the area of the Fermi surface in k -space ; but for monovalent metals it is not likely to depart very much from the value $N=1$.

Formula (5) has been deduced on Makinson's assumption that electrons interact with the transverse as well as with the longitudinal waves, so that, if C^2 is the interaction constant in the expressions for the electronic conductivities, $C_j^2 = C^2/3$. In this case we must also take θ to be near the value θ_D , the Debye temperature as deduced from low temperature specific heat measurements.

However, if we adopt the Bloch model, in which electrons interact with the longitudinal lattice vibrations only, (5) must be modified. In this case $C_L^2 = C^2$, $C_T^2 = 0$. However, (1) and (2) will remain unaltered. The contribution to the thermal conductivity from the transverse phonons will not be higher than that given by Makinson's coupling model, if we assume that longitudinal and transverse phonons interact by means of three-phonon processes conserving total wave-vector. As has been pointed out elsewhere (Klemens 1951), these processes do not contribute directly to the thermal resistance, but are important in establishing thermal equilibrium and tend to equalize the effective mean free paths of phonons of the same frequency but different polarization.

In (3) we must thus replace C_j^2 by C^2 , so that an additional factor 1/3 enters into (5), the electronic conductivity being increased relative to the lattice conductivity. Thus

$$\kappa_g = 105 \kappa_e(T) \left(\frac{T}{\theta}\right)^4 N^{-4/3}, \dots\dots\dots (7)$$

for interaction of electrons with longitudinal waves only. Also, in that case the appropriate θ -value will not be θ_D but θ_L , the Debye temperature appropriate to the longitudinal lattice waves only, as introduced by Blackman (1951).

Using values of the ideal thermal resistance observed by Berman and MacDonald (1952) for copper, and by White (1953*a*, 1953*b*) for silver and gold, the lattice thermal conductivity has been calculated from (5) using θ_D for θ , and again from (7), using θ_L . The value of θ_L for copper has been taken from Blackman (1951), and the values of silver and gold were chosen in the same proportion to θ_D . The results are shown in Table 1.

TABLE 1

Metal	$T^2\kappa_e(T)$ (W cm ⁻¹ deg)	θ_D (°K)	θ_L (°K)	$\kappa_g T^{-2}$ according to Eqn. (5) (W cm ⁻¹ deg ⁻³)	$\kappa_g T^{-2}$ according to Eqn. (7) (W cm ⁻¹ deg ⁻³)
Gold	7.7×10^3	170	270	2.9×10^{-3}	1.5×10^{-4}
Silver	$1.5_6 \times 10^4$	215	340	2.3×10^{-3}	1.2×10^{-4}
Copper	$4.4_5 \times 10^4$	315	505	1.4×10^{-3}	7.2×10^{-5}

Makinson's coupling scheme (interaction between electrons and waves of all polarizations) gives a lattice conductivity higher by a factor 20 than given by Bloch's coupling scheme (electrons interacting with longitudinal waves only), and observations of the lattice component of the thermal conductivity should thus provide a method of discriminating between these two schemes. It must be emphasized, however, that intermediate coupling schemes, such that $C_L^2 > C_D^2 \neq 0$, are also possible, and these would lead to intermediate values of the lattice conductivity. Finally, there is the possibility that the transverse waves are not coupled tightly to the longitudinal waves. This would result in an additional contribution to the conductivity, of different temperature dependence, analogous to the "longitudinal" conductivity of quartz glass (Klemens 1951).

While it is impossible to observe the lattice conductivity of the monovalent metals directly, it should be possible to infer it from the lattice conductivity of dilute alloys.

III. VARIATION OF LATTICE CONDUCTIVITY WITH ELECTRON CONCENTRATION

It is possible to vary the number of free electrons in a band by varying the composition of some alloys. The resulting variation of the lattice conductivity can serve thus as a qualitative test of Makinson's theory. Nevertheless, for this purpose one cannot use (3), because of the unknown behaviour of $\kappa_e(\infty)$, but (1) and (2) must be used directly. If the thermal resistance of the lattice component is $W_g = 1/\kappa_g$,

$$W_g \propto (kdk/dE)\zeta^2, \dots\dots\dots (8)$$

for a spherical Fermi surface. This can be expressed also as

$$W_g \propto g(k)\zeta/(dE/dk)\zeta^2 \\ \propto G(E)\zeta/(dE/dk)\zeta, \dots\dots\dots (9)$$

where $G(E)$ is the density of states per unit energy interval and $g(k)$ is the density of states per unit wave-number. The latter quantity is proportional to the area of the Fermi surface in k -space and it is easily seen from Sommerfeld and Bethe (1933), equation 46.2, that every element of the Fermi surface contributes additively to W_g , so that (9) is a general expression, valid also if the Fermi surface is non-spherical, or extends over two zones, provided dE/dk is averaged over all elements of the Fermi surface.

For a single band of free electrons, (9) is constant and independent of electron concentration. However, as the Fermi surface approaches the zone boundary, dE/dk decreases and W_g increases until the zone is nearly full, when $g(k)$ decreases and both $g(k)$ and W_g approach zero for a full band. In Figure 1 the variation of W_g with electron concentration for an s -band is shown schematically.

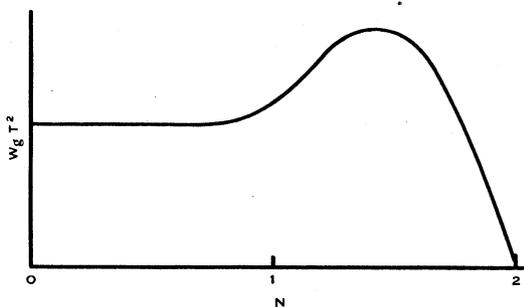


Fig. 1.—Variation of $W_g T^2$ with electron concentration for an s -band (schematic).

Such behaviour can be expected for the alloys copper-zinc and silver-cadmium. With increasing concentration of the divalent constituent the number of electrons in the s -band increases from one. A quantitative test seems impossible at present, because it is not known whether every divalent atom donates an additional electron to the conduction band or keeps a fraction of the additional electronic charge localized. Also the energy contours are not known in detail near the zone boundary and it is still an open question whether the Fermi surface of the monovalent metal touches the zone boundary.

In the case of the alloy systems copper-nickel and silver-palladium the number of electrons in the s -band is reduced with increasing concentration of the transition element. The thermal resistance due to the s -band should thus remain constant or decrease slightly. But at sufficiently high concentrations of the transition element, holes will appear in the d -band. It is seen from (9) that the resistance due to the d -band must be added to the resistance due to the s -band. The general variation of this component of W_g , at least for low concentrations of holes, will be given by a curve similar to the right-hand part of Figure 1. The total resistance will thus remain almost constant, and not more than the resistance of the monovalent metal, until that alloy composition at which holes first appear; then it will pass through a maximum and reach a constant value, above the value for the monovalent metal.

IV. COMPARISON WITH OBSERVATIONS

Apart from various technical alloys which are difficult to interpret, the only alloys whose thermal conductivity has been studied at low temperatures are the series copper-nickel, namely, 10 per cent. nickel by Estermann and Zimmerman (1952), 20 per cent. nickel by Hulm (1951), 30 per cent. nickel by Wilkinson and Wilks (1949), and 40 per cent. nickel by Berman (1951). Estermann and Zimmerman have also studied "Monel", an alloy containing 67 per cent. nickel, 30 per cent. copper, and iron, manganese, silicon, and carbon. We can regard "Monel" as approximately equivalent to 70 per cent. nickel and 30 per cent. copper.

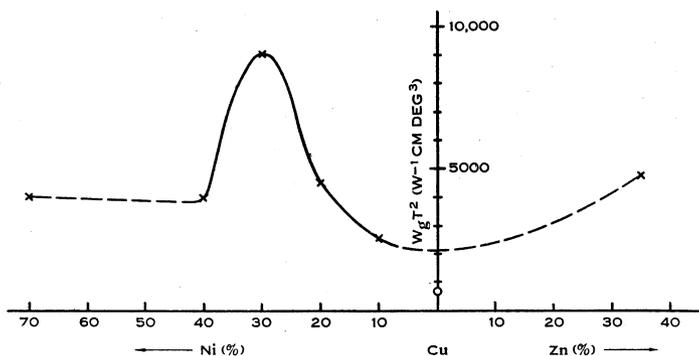


Fig. 2.—Variation of $W_g T^2$ with alloy composition for the series nickel-copper-zinc. Observed values \times , value expected for copper from equation (5) \circ . The value for copper-35 per cent. zinc is surmised from German silver (Berman 1951).

In Figure 2 the observed values of $W_g T^2$ are plotted against alloy composition, and the value calculated for pure copper according to Makinson's coupling scheme (equation (5)) is also shown. According to Bloch's coupling scheme (equation (7)) $W_g T^2$ is 20 times higher, and, unless there are unsuspected and violent variations between copper-10 per cent. nickel and pure copper, the experimental evidence seems to favour an intermediate coupling scheme, that is, electrons interacting with transverse phonons, but not as strongly as with longitudinal phonons.

An interesting feature of Figure 2 is the apparent appearance of an observable number of holes in the $3d$ -band at low nickel concentrations of about 15 per cent. This is in disagreement with the usual band theory, which predicts holes to first appear at 40 per cent. nickel (Mott 1935). On the other hand, there is other evidence for the anomalous appearance of holes at low nickel concentrations (Coles 1952), which confirms this interpretation.

The dotted line in Figure 2 indicates qualitatively the probable variation, inferred from the above considerations, of $W_g T^2$ with alloy composition for higher electron concentrations. It would be desirable to measure copper-nickel alloys of still lower nickel concentration (say 5 and 2 per cent.) and various copper-zinc alloys to test this behaviour. It may be that an examination of these alloys

will reveal a decrease of $W_g T^2$ below the value of 10 per cent. nickel. This would indicate better agreement with Makinson's coupling scheme and also the presence of holes for still lower nickel concentrations.

According to Coles the system silver-palladium behaves in agreement with the simple band theory. It would thus be of interest to study this system, as well as silver-cadmium, in order to test whether $W_g T^2$ is substantially constant from silver to silver-40 per cent. palladium (when holes should first appear) and whether $W_g T^2$ rises gradually with increasing concentration of cadmium for silver-cadmium, as expected. Such a study would clarify also the question of the interaction of transverse phonons with electrons, and possibly the departure from a spherical Fermi surface.

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VI. REFERENCES

- BERMAN, R. (1951).—*Phil. Mag.* **42** : 642.
BERMAN, R., and MACDONALD, D. K. C. (1952).—*Proc. Roy. Soc. A* **211** : 122.
BLACKMAN, M. (1951).—*Proc. Phys. Soc. Lond. A* **64** : 681.
COLES, B. R. (1952).—*Proc. Phys. Soc. Lond. B* **65** : 221.
ESTERMANN, I., and ZIMMERMAN, J. E. (1952).—*J. Appl. Phys.* **23** : 578.
HULM, J. K. (1951).—*Proc. Phys. Soc. Lond. B* **64** : 207.
KLEMENS, P. G. (1951).—*Proc. Roy. Soc. A* **208** : 108.
KLEMENS, P. G. (1954).—*Aust. J. Phys.* **7** : 64.
MAKINSON, R. E. B. (1938).—*Proc. Camb. Phil. Soc.* **34** : 474.
MOTT, N. F. (1935).—*Proc. Phys. Soc. Lond.* **47** : 571.
PEIERLS, R. E. (1929).—*Ann. Phys. Lpz.* (5) **3** : 1055.
SOMMERFELD, A., and BETHE, H. (1933). Elektronentheorie der Metalle. In "Handbuch der Physik." (Ed. H. Geiger and K. Scheel.) Vol. 24, Pt. 2. p. 333. (J. Springer : Berlin.)
SONDHEIMER, E. H. (1950).—*Proc. Roy. Soc. A* **203** : 75.
WHITE, G. K. (1953a).—*Proc. Phys. Soc. Lond. A* **66** : 559.
WHITE, G. K. (1953b).—*Proc. Phys. Soc. Lond. A* **66** : 844.
WILKINSON, K. R., and WILKS, J. (1949).—*J. Sci. Instrum.* **26** : 19.