DEVIATION FROM MATTHIESSEN'S RULE AND LATTICE THERMAL CONDUCTIVITY OF ALLOYS*

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The purpose of this note is to point out that the difference in the ideal electronic thermal conductivity between an alloy and a pure metal can be estimated from the corresponding difference in the ideal electrical resistivity, using the Wiedemann-Franz law. This allows the separation of the thermal conductivity into an electronic and a lattice component to be made with greater confidence, particularly at liquid oxygen temperatures.

Matthiessen's rule states that the electrical resistivity of metals is composed of an ideal and a residual resistivity

$$\rho = \rho_i + \rho_0, \quad \dots \dots \dots \dots \dots \dots \dots \quad (1)$$

where $\rho \to \rho_0$ as $T \to 0$, ρ_0 is independent of temperature T, and $\rho_i(T)$ is independent of ρ_0. The ideal resistivity ρ_i arises from the scattering of electrons by lattice waves, while ρ_0 is due to the scattering by imperfections and impurities.

On going from a metal to an alloy, the residual resistivity is substantially increased. However, this is not the only change, for the number of free electrons is generally affected, and hence the band structure. Consequent changes in ρ_0 cannot be separated from changes due to the increased number of scattering centres, but in general a change in band structure causes a change in ρ_i, which can be observed. Thus we may write for an alloy

$$\rho = \rho_0 + \rho_i + \Delta\rho_i, \quad \dots \dots \dots \dots \dots \dots \quad (2)$$

where now ρ_i is the ideal resistivity of the parent metal and $\Delta\rho_i$ the change in ideal resistivity on alloying.

In analogy to (1), the electronic thermal conductivity $\varkappa_e$ is limited by the scattering of electrons by imperfections and impurities, leading to a residual thermal resistivity W_0, and by the lattice waves, leading to an ideal thermal resistivity W_i (see, for example, Klemens 1956). Thus

$$1/\varkappa_e = W_e = W_0 + W_i. \quad \dots \dots \dots \dots \dots \dots \quad (3)$$

Furthermore, it can be shown that W_0 and ρ_0 are related by the Wiedemann-Franz-Lorenz relation

$$\rho_0 = LW_0 T, \quad \dots \dots \dots \dots \dots \dots \dots \quad (4)$$

where $L = \pi^2/3(K/e)^2$ is the Sommerfeld value of the Lorenz number (K is the Boltzmann constant, e the electronic charge). For the ideal resistivities, however,

$$\rho_i < LW_i T, \quad \dots \dots \dots \dots \dots \dots \quad (5)$$

except at high temperatures, where the two are equal (e.g. Klemens 1956).

The thermal conductivity of metals and alloys is additively composed of the electronic component $\varkappa_e$ and a lattice component $\varkappa_g$, the latter arising from the heat transport by lattice waves (Koenigsberger 1907; for proof of additivity see Klemens 1956). Thus

$$\varkappa = \varkappa_e + \varkappa_g, \quad \dots\dots\dots\dots\dots\dots \quad (6)$$

but in pure metals $\varkappa_g \ll \varkappa_e$. In alloys, where $\varkappa_e$ is small because W_0 is large, $\varkappa_e$ and $\varkappa_g$ are often of comparable magnitude, and if $\varkappa_e$ can be calculated, one can deduce $\varkappa_g$ from the measured values of $\varkappa$. To obtain $\varkappa_e$ it is necessary to measure ρ_0 and hence to deduce W_0.

In recent years a number of systematic investigations of the thermal and electrical conductivities of alloys have been undertaken so as to evaluate their lattice thermal conductivities (for reviews see Olsen and Rosenberg (1953) and Klemens (1956, 1958)). In order to deduce $\varkappa_g$ at very low temperatures (say, below 20 °K) it is usually sufficient to consider only W_0, derived from ρ_0, when calculating $\varkappa_e$ from (3), W_i being negligibly small. However, at higher temperatures W_i cannot be neglected, even in alloys. Kemp *et al.* (1954, 1956) have considered the term W_i in (3) to calculate $\varkappa_e$—and hence obtain $\varkappa_g$—at temperatures up to about 90 °K. This procedure has been followed in subsequent investigations (see Klemens 1958), and from the behaviour of $\varkappa_g$ at these higher temperatures it has been possible to obtain information concerning the scattering of lattice waves by various point defects and by anharmonicities.

Unfortunately there is no direct information about the value of W_i in alloys, for $\varkappa_e$ can be directly measured only in the pure parent metal. It has thus been assumed in all such work on the lattice thermal conductivity of alloys that in the alloy W_i is the same as in the parent metal. As long as $W_i \ll W_0$, an error in W_i will not be serious, but the higher the temperature and the more dilute the alloy, the greater will be the relative contribution of W_i to W_e and of $\varkappa_e$ to $\varkappa$, and the more important will be errors of W_i in calculating $\varkappa_g$.

Since Matthiessen's rule (2) is not obeyed when going from a pure metal to an alloy, but ρ_i changes by $\Delta\rho_i$ due to changes in the band structure, one would expect (3) to break down similarly, so that the electronic thermal resistivity becomes

$$W_e = W_0 + W_i + \Delta W_i, \quad \dots\dots\dots\dots\dots \quad (7)$$

where W_i is now the ideal thermal resistivity of the parent metal. Since ΔW_i cannot be observed directly, there is some uncertainty in the separation of $\varkappa_g$ and $\varkappa_e$ from observations of $\varkappa$ and ρ_0. Paradoxically, uncertainties due to ΔW_i are greatest for dilute alloys, even though ΔW_i is then probably small, because of the increased necessity, as pointed out above, of knowing $W_i + \Delta W_i$ accurately.

It is the purpose of this note to point out that ΔW_i can be calculated from $\Delta\rho_i$ by means of a relation analogous to (4)

$$\Delta\rho_i = LT\Delta W_i, \quad \dots\dots\dots\dots\dots\dots \quad (8)$$

and since $\Delta\rho_i$ can be deduced from measurements of the electrical conductivity of the alloy, it is possible to calculate $\varkappa_e$ with greater confidence.

The ideal electrical and thermal resistivities arise from interactions between electrons and phonons which take electrons from a region of momentum space where there are too many electrons into a region where there are too few, relative to the equilibrium concentration. As pointed out elsewhere (Klemens 1956), the deviations g of the distribution function from the equilibrium distribution f^0 are of the form

$$g(\mathbf{k}) \propto f(\mathbf{k}_1)\, df^0/d\varepsilon, \quad \dots\dots\dots\dots \quad (9a)$$

for electrical conduction, and

$$g(\mathbf{k}) \propto f(\mathbf{k}_1)\, \varepsilon\, df^0/d\varepsilon, \quad \dots\dots\dots\dots \quad (9b)$$

for thermal conduction, where $\mathbf{k}$ is the electron wave-vector, $\mathbf{k}_1$ is a unit vector specifying the direction of $\mathbf{k}$, $f(\mathbf{k}_1)$ is some function of $\mathbf{k}_1$ depending on the shape of the Fermi surface and the zone structure, and is the same function in both cases, and ε is the reduced electron energy ($\varepsilon = (E - \zeta)/KT$, ζ being the Fermi energy).

In the case of electrical conduction the sign of g depends upon $f(\mathbf{k}_1)$ and thus on the direction of $\mathbf{k}$. Hence ρ_i is due to the motion of electrons (through interaction with phonons) to distant regions on the Fermi surface, involving substantial changes in $\mathbf{k}_1$ (horizontal movement).

In the case of thermal conduction, the sign of $g(\mathbf{k})$ can be reversed not only by changing $\mathbf{k}_1$ but also by changing ε. Thus W_i is due to two types of motion in $\mathbf{k}$-space: horizontal movement through large angles on the Fermi surface, and vertical movement through values of ε comparable to unity. To a first approximation each movement contributes to W_i in an additive manner, so that

$$W_i = W_{Hi} + W_{Vi}. \quad \dots\dots\dots\dots \quad (10)$$

Since $f(\mathbf{k}_1)$ is the same in the cases of electrical and of thermal conduction, horizontal movement is equally efficacious in both cases, so that W_{Hi} and ρ_i are related by the Wiedemann-Franz relation (4)

$$\rho_i = LTW_{Hi}. \quad \dots\dots\dots\dots \quad (11)$$

It is the occurrence of the term W_{Vi} in (10) which is responsible for the inequality (5). This term is particularly important at low temperatures.

Now W_{Vi} is relatively insensitive to changes in the band structure, being mainly governed by a local property of the Fermi surface. On the other hand W_{Hi}, being due to motion of electrons over large distances on the Fermi surface (large changes in $\mathbf{k}_1$), is sensitive to the overall shape of the Fermi surface, particularly in regard to its position relative to the zone boundaries (Klemens 1954, 1956).

The change $\Delta\rho_i$ on alloying is due to the sensitivity of the horizontal movement to changes in the band structure; it is reflected by changes in W_{Hi} which must be much larger than any change in W_{Vi}. Thus from (11) we obtain (8) as a good approximation.

Using (7) and (8), one can deduce $\varkappa_e$ for alloys with more confidence than previously, since values of ρ_0 and $\Delta\rho_i$ can be obtained from measurements of ρ.

This eliminates one source of uncertainty in the evaluation of x_g. There still remains a second limitation : since x is measured only with limited precision, x_g cannot be determined from (6) if $x_e \gg x_g$, even if x_e is accurately known. Thus studies of x_g are still confined to alloys which are not too dilute. However, the correction (7) and (8) should make possible a more reliable estimate of x_g at higher temperatures in the case of many dilute alloys which previously could be analysed only at low temperatures.

References

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