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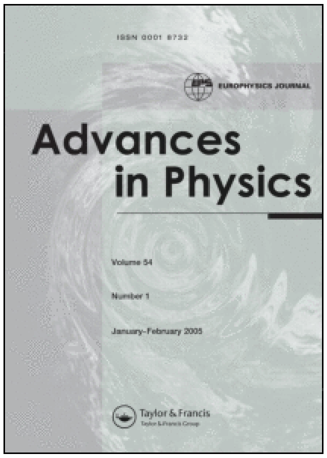

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The thermal conductivity of metals at low temperatures

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The Thermal Conductivity of Metals at Low Temperatures

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CONTENTS

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§1. INTRODUCTION

THE recent wide access to simple cryogenic equipment has produced a new interest in the thermal conductivity of metals at low temperatures and a very great deal of experimental work has been done in this field in the last few years. It is the aim of this article to provide a review of this work from an experimental point of view. The results must necessarily be compared with theory, but no effort is made to examine the basis of the theory critically or in any detail.

The situation in a metal is somewhat more complicated than in a non-conductor, since in a metal there are two mechanisms conducting the heat. As in non-conductors there is a transfer of heat by the lattice waves, but in metals there is in addition a transfer of heat by the electrons. The total heat conductivity is thus made up of two components: K_g the lattice conduction (with which another article in this volume is concerned), and K_e the electronic conduction. We may write

$$K = K_e + K_g . \qquad \qquad (1)$$

It is of course well known that the electronic thermal conductivity is closely connected with the electrical conductivity of the metal (Wiedemann–Franz law). As a not unexpected consequence such effects as magneto-resistance, anisotropies of various sorts, and superconductivity have their counterparts in K_e. The existence of free electrons in a metal also has an effect on the lattice conductivity by supplying a scattering mechanism which is not present in the non-conductors and which in the case of reasonably pure metals reduces the lattice conduction to an insignificant value compared with the electronic thermal conductivity.

In this article we shall deal first with the variation with temperature of K_e in normal metals and with the effect on it of a small impurity content, of a magnetic field and of crystalline anisotropy. When the impurity content is very large, K_g does become important and K_e and K_g in alloys are therefore dealt with together. The effects of superconductivity and the behaviour of the thermal conductivity below 1° K are dealt with in the last sections.

§2. THE THEORY OF THE ELECTRONIC THERMAL CONDUCTIVITY

2.1. *General Remarks*

The calculation of the thermal conductivity, like that of the electrical conductivity, depends upon the solution of the Boltzmann equation to give the velocity distribution function of the electrons in the presence of an external field. This solution is complicated in general, and has so far only been carried out for the simplest case: that of quasi-free electrons where the energy is of the form

$$E = \frac{h^2}{8\pi^2 m} |\mathbf{k}|^2 . \qquad \qquad (2)$$

where $\mathbf{k}$ is the wave vector and m the effective mass of the electron. This is not such a rigid restriction as it seems, since by choosing a suitable value for m we can take account of quite complicated potential distributions.

It is also necessary to assume that the distribution function of the lattice waves is unaffected by the temperature gradient. This appears to be justified except in exceptional cases where the theory is in any case of very doubtful validity (e.g. bismuth: Makinson 1938, and Sondheimer 1952 a, b).

At high temperatures where $(\theta/T)^2$ may be neglected a solution may easily be obtained (Wilson 1936). The case of an impure metal at low temperatures may be dealt with by a method of successive approximations, but the higher order approximations become very complicated and the method cannot be applied to the ideally pure metal. Wilson (1937) has calculated the zero order approximation at low temperatures and gives an interpolation formula for intermediate temperatures. These formulae have been investigated in detail and evaluated by Makinson (1938).

2.2. *Makinson's Work*

Makinson quotes Wilson's result that the electronic heat resistance $1/K_e$ can be split into two parts (Matthiesen's rule) so that

$$1/K_e = 1/K_0 + 1/K_i \quad \ldots \ldots \quad (3)$$

where $1/K_0$ is the resistance due to impurity scattering, and $1/K_i$ is the resistance due to the scattering of the electrons by the lattice waves. K_0 is connected with the residual electrical resistance ρ_0 by the equation

$$K_0 = \frac{1}{3}\left(\frac{\pi k}{\epsilon}\right)^2 \frac{T}{\rho_0}. \quad \ldots \ldots \quad (4)$$

It will be noted that $\frac{1}{3}(\pi k/\epsilon)^2$ is the ordinary Lorenz number, L_0, valid for high temperatures where it is obtainable from fairly simple considerations. The ideal resistance $1/K_i$ is represented by the somewhat complicated expression:

$$\frac{1}{K_i} = \frac{27h}{8\pi^2 k^2 \zeta^2 \Lambda\theta}\left(\frac{T}{\theta}\right)^2 \left\{\mathcal{J}_5\left(\frac{\theta}{T}\right) + \frac{D}{\zeta}\left(\frac{T}{\theta}\right)^2 \left(\frac{2\pi^2}{3}\mathcal{J}_5\left(\frac{\theta}{T}\right) - \tfrac{1}{3}\mathcal{J}_7\left(\frac{\theta}{T}\right)\right)\right\}, \quad (5)$$

where ζ is the Fermi energy of the electrons,

$$D = \frac{(6\pi^2)^{2/3} h^2}{16\pi^2 m a^2}, \quad \ldots \ldots \quad (6)$$

$$\Lambda = \left(\frac{4\pi}{3}\right)^{1/3} \frac{4Mak\,\theta}{3\,h^2 C^2}, \quad \ldots \ldots \quad (7)$$

a is the lattice constant and k is Boltzmann's constant. This should not cause any confusion with the use of $\mathbf{k}$ as the wave vector.

C is a constant which gives the absolute amount of the interaction between the electrons and the lattice. M is the mass of an atom. The function $\mathcal{J}_n$ is given by:

$$\mathcal{J}_n(x) = \int_0^x \frac{z^n dz}{(e^z - 1)(1 - e^{-z})}. \quad \ldots \ldots \quad (8)$$

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For high and low values of the argument this reduces to

$$\mathcal{J}_n\left(\frac{\theta}{T}\right) \sim n\,!\sum_{r=1}^{\infty}\frac{1}{r^n} \qquad \text{for } \left(\frac{T}{\theta}\right)\to 0 \quad . \quad . \quad . \quad . \quad . \quad (9)$$

and

$$\mathcal{J}_n\left(\frac{\theta}{T}\right) \sim \frac{1}{n-1}\left(\frac{\theta}{T}\right)^{n-1} \qquad \text{for } \left(\frac{T}{\theta}\right)\to \infty, \quad . \quad . \quad . \quad . \quad (10)$$

thus $\mathcal{J}_5=124{\cdot}3$ at $T=0°\text{K}$ falling to 100 at about $\theta/T=8$. Intermediate values of $\mathcal{J}_n$ may be found tabulated by Sondheimer (1950).

It will be seen by inspection of (5) that at low temperatures (below about $\theta/10$) it reduces to $1/K_i=\alpha T^2$ and hence (3) becomes

$$1/K=\beta/T+\alpha T^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

where

$$\beta=\rho_0/L_0\,, \quad \alpha=\frac{95{\cdot}3\;N_a^{\;2/3}}{K_\infty\,\theta^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)$$

and K_∞ is the limiting thermal conductivity at very high temperatures. We may note that a simple calculation yields

$$D/\zeta=2^{-1/3}\,N_a^{\;-2/3} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (13)$$

where N_a is the number of free electrons per atom.

Makinson has examined the behaviour of eqn. (3) for the cases of copper and bismuth, for which he takes N_a to be 1 and $1{\cdot}8\times10^{-2}$ respectively. His curves for the variation of K in copper of various purities is shown in fig. 1. The relative amount of impurity is measured by the parameter $\rho_0/4A$ where

$$A=\frac{3\pi hD}{16\epsilon^2\,\zeta^3 A}\,. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (14)$$

The theoretical calculation of A depends upon our ability to calculate the interaction constant C. This calculation may, however, be avoided, since for $T/\theta>0{\cdot}6$ we have accurately

$$1/\sigma_i=AT/\theta \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (15)$$

where σ_i is effectively the electrical conductivity at high temperatures. There is a corresponding equation involving the thermal conductivity. A may thus be found by measurements at high temperatures on the electrical or thermal conductivity.

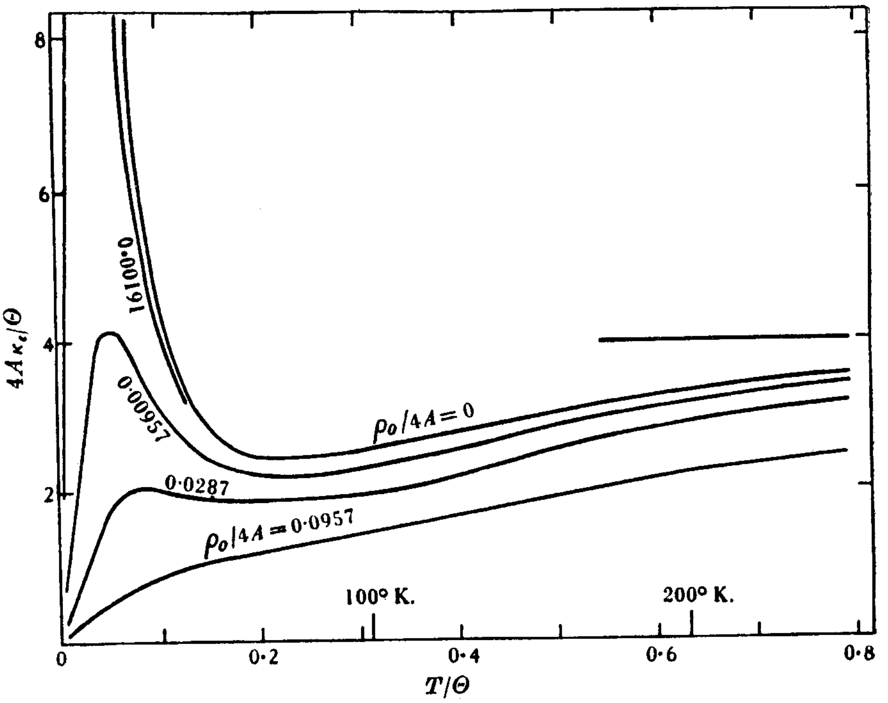
An examination of experimental data shows that for an extremely pure, unstrained specimen $\rho_0/4A$ might be of the order of 10^{-4} while in a specimen of lead containing $1/10\%$ of bismuth $\rho_0/4A$ would be about 5×10^{-2}.

It is seen in fig. 1 that for all the fairly pure specimens of copper, K_e first rises linearly, then less steeply to a maximum which is higher and occurs at a lower temperature the greater the purity. It then falls to a minimum at about $\theta/5$ and then finally rises slowly to a constant value at high temperatures.

2.3. *The Lorenz Number*

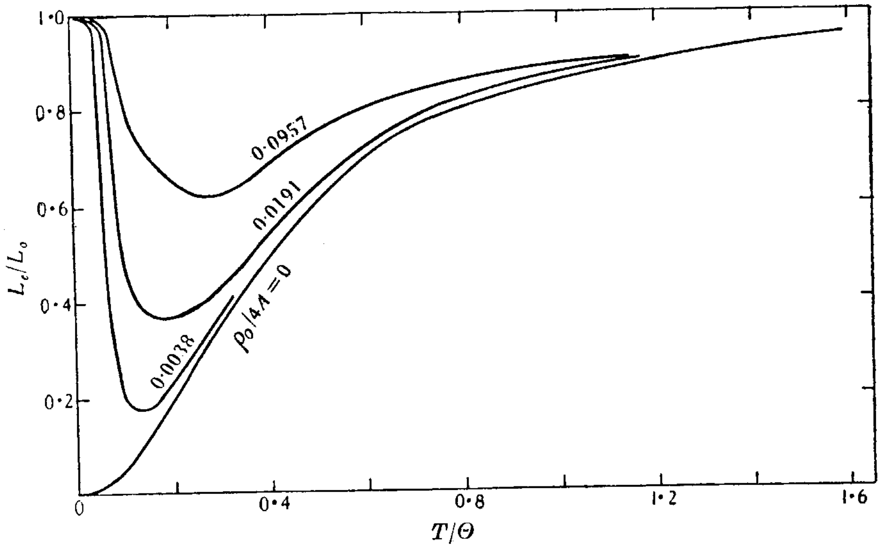
A series of curves is also given for the Lorenz number $L_e=K_e/\sigma T$. These are shown in fig. 2. At high and low temperatures these approach the value L_0, but in the case of a normal metal such as copper, there is a

Fig. 1



Theoretical electronic thermal conductivity for a monovalent metal showing the effect of impurity. The temperatures marked correspond to copper ($\theta=315°$ K). (Makinson 1938.)

Fig. 2



The ratio L_e/L_0 for monovalent metals showing its dependence on impurity and temperature. (Makinson 1938.)

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decrease at intermediate temperatures, this decrease being more the greater the purity. For an ideally pure metal L_e tends to zero as T tends to 0° K. For the bismuth model, with small N_a, there is a marked difference. As the temperature is lowered, L_e first increases to a maximum above L_0 and then goes to a minimum below L_0 as the temperature is lowered further, the variations from L_0 being again greater for higher purity.

2.4. *Sondheimer's Treatment*

A more accurate treatment of the problem valid for all temperatures has been given by Sondheimer (1950) who uses a method which is a synthesis of methods due to Kroll (1938) and Kohler (1949 d).

Sondheimer's result may be expressed in the form

$$K=K_{\mathrm{M}}+F \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (16)$$

where K_{M} is the conductivity as obtained from Makinson's treatment and F is a correction term which is always positive. F can be expressed in terms of infinite determinants and may be calculated to any degree of accuracy by terminating the determinants at the appropriate row and column. For a monovalent metal, however, only two or three rows and columns are necessary.

The minimum in K at about $\theta/5$ is also obtained by this method, but in general Makinson's results are found to be only qualitatively correct and his K is about 25% too small at low temperatures for an ideal metal.

A discrepancy which is more serious in principle arises from the fact that F depends upon both K_0 and K_i, and thus Matthiesen's rule breaks down. The departure from Matthiesen's rule is however only of the order of 1%.

The existence of the minimum has also been confirmed by Umeda and Yamamoto (1949) by an examination of Kroll's work (1933 a, b, 1938). There is thus no doubt that the minimum is inherent in the model used and is not a result of an inadequate degree of approximation in the solution of the equations.

2.5. *The Lattice Conductivity*

The lattice conductivity may, as will be seen in § 4.2, be taken to be very small in most metals due to the strong scattering of the lattice waves by the electrons. There is also some experimental evidence (§ 5) to support this theoretical conclusion, and in the discussion of the electronic thermal conductivity which follows we shall assume that K_g is either negligible or is known in some way.

2.6. *Comparison of the Theory with Experimental Results*

At first sight the agreement between theory and experiment is quite good. The general shape of the conductivity curve is close to that shown in fig. 1. The conductivity increases linearly with temperature at the lowest temperatures, and as the temperature is raised a quadratic term appears in the resistance, so that the conductivity rises to a maximum and then falls above approximately $\theta/10$. At intermediate temperatures, however, no sign of a minimum in K_e is observed and the conductivity always decreases monotonically with increasing temperature once the maximum has been passed.

A less obvious, but much more serious objection to the theory is the fact that when N_a is calculated from the experimental value of α using expression (12), then N_a is seen to be of the order of 2×10^{-2} (Hulm 1950) for a large number of metals where the number of free electrons is generally thought to be of the order of one per atom. If this low value of N_a had any real significance we would also expect an appreciable lattice conductivity in monovalent metals and there is no evidence of this.

It should of course be remembered that the model used is only a very rough first approximation to the situation in a real metal. A rather simpler objection to the above calculation may be made on the grounds that the calculation of N_a has been made using the Debye θ rather than a θ, θ_L, specially associated with the longitudinal vibrations only, as would be expected from the Bloch theory (Blackman 1951). Blackman has calculated values of θ_L for a number of metals, and if these are used in the calculation of N_a much larger and more plausible values of N_a are obtained. If, however, θ_L were in fact the appropriate θ to use then it would be implied that only the longitudinal waves interacted with the electrons. In that case we should expect an appreciable lattice conductivity since to a first order the transverse waves would not be scattered by the electrons. This has not been observed experimentally.

2.7. *Modification of the Theory when N_a is small*

Very recently Sondheimer* (1952 a) has pointed out that the Wilson–Makinson theory is in any case invalid for metals in which N_a is small.

Allowance has to be made for the fact that electrons can only interact with lattice vibrations of wave number q such that

$$|q|\leqslant 2\,|\mathbf{k}|$$

where $\mathbf{k}$ is the wave vector of the electron. This does not affect the results when $2k_0 \geqslant q_0$ (where k_0 and q_0 are the wave numbers corresponding to the top of the Fermi zone and to the cut off frequency of the Debye spectrum respectively).

When, however, $2k_0 < q_0$ the usual expressions have to be modified. Since

$$D/\zeta = q_0^2/2k_0^2 = 2^{-1/3}\,N_a^{-2/3}$$

this condition is equivalent to $D/\zeta > 2$ or $N_a < \frac{1}{4}$. Thus when $N_a < \frac{1}{4}$ eqn. (5) has to be modified to

$$\frac{1}{K_i} = \frac{27h}{8\pi^3 k^2 \zeta^2 \Lambda\theta}\left(\frac{T}{\theta}\right)^2 \left\{\mathcal{J}_5\left(\frac{\theta'}{T}\right) + \frac{D}{\zeta}\left(\frac{\theta}{T}\right)^2 \left(\frac{2\pi^2}{3}\mathcal{J}_5\left(\frac{\theta'}{T}\right) - \tfrac{1}{3}\mathcal{J}_7\left(\frac{\theta'}{T}\right)\right)\right\}, \quad (17)$$

where $\theta' = \sqrt{(2\zeta/D)}\,\theta$.

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* We are very grateful to Dr. Sondheimer, who has shown us the manuscripts of his papers before publication.

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With this modified form for eqn. (5) Sondheimer (1952 b) finds for α in eqn. (12)

$$\alpha=6\zeta\,\mathcal{J}_5(\infty)/\pi^2 D\,K_\infty\,\theta^2 \qquad \text{for } D/\zeta\leqslant 2,$$

$$\alpha=3D\,\mathcal{J}_5(\infty)/2\pi^2\,\zeta\,K_\infty\,\theta^2 \qquad \text{for } D/\zeta>2 \quad . \; . \; . \; . \; . \; . \quad (18)$$

and this has a minimum value for $D/\zeta=2$, and it is found that *no* values of N_a will yield the experimentally observed α if the usual Grüneisen or Debye θ's are used in the formulae. As in § 2.6, however, an adjustment of θ allows a more acceptable value to be obtained.

It is always difficult to decide how much parameters of this sort may justifiably be adjusted. Sondheimer considers that the simplifying assumptions made in the model are so sweeping that it would even be reasonable to treat both θ and D/ζ as arbitrary parameters.

The suggestion that the value of D/ζ might not be exactly equal to that given by the simple theory, indicates that it is not surprising that the theoretical minimum in the conductivity, which should occur only if $D/\zeta<1{\cdot}7$ is not found in practice.

2.8. *Klemens' Work on the Form of the Distribution Function*

Klemens* (1952) has recently suggested that the disagreement between the theoretical and experimental values for α is due to a mathematical assumption in Sondheimer's and previous theories which may not be justified. Sondheimer assumes that the distribution function f of the electrons is of the usual form

$$f=f_0-k_1c(\eta)\frac{\partial f_0}{\partial E} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (19)$$

where $\eta=(E-\zeta)/kT$, f_0 is the Fermi function $1/(e^\eta+1)$, k_1, k_2, k_3 are components of the wave vector and $c(\eta)$ is an unknown function of η. He then assumes that $c(\eta)$ can be written as a series of positive powers of η. Klemens, however shows that in order to satisfy eqn. (5), $c(\eta)$ should vary between a function of the form $B\eta$, B being a constant and one proportional to η^{-2} and hence that Sondheimer's assumption as to the form of $c(\eta)$ is not justified.

Klemens has solved eqn. (5) very approximately using $c(\eta)$ in the form he suggests, and he then obtains a value of 16·1 for the numerical coefficient of α in (12) instead of 95·3 given by Wilson and by the zero approximation of Sondheimer. This new value of α does agree much better with the experimental results and lends weight to Klemens' suggestions although it must be stressed that these are at present determined in a very approximate manner. However, he hopes to give a more rigorous and exact derivation in the near future.

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* We are very grateful to Dr. Klemens for letting us see the manuscript of his paper before publication.

§3. EXPERIMENTAL WORK ON THE THERMAL CONDUCTIVITY IN THE NORMAL STATE

3.1. *General Form of the Results*

Experimental data for the thermal conductivity of pure non-superconducting metals and of superconductors above the superconducting transition temperature has been very meagre up till recently. For this reason it is only lately that it has been possible to compare theory and experiment in any detail. Qualitatively the results obtained agree with the curves of Makinson and therefore also with the later work of Sondheimer. For a fairly pure metal the conductivity does increase linearly from 0° K to a maximum at $T \sim \theta/10$° K, and then it decreases (sharply for pure metals with low θ). At higher temperatures this decrease is less steep. The value of the conductivity at the maximum is usually of the order of a few watt units except in the case of extremely pure metals or some single crystals when it may be 60 watt units or over.

Berman and MacDonald (1951, 1952) have measured the thermal and electrical conductivities of the monovalent metals sodium and copper in the range 4° K to 90° K and 2° K to 90° K respectively. Their curves for two samples of sodium are shown in fig. 3. Curve II is for the purer specimen and it can be seen that the maximum is much higher and occurs at a lower temperature than that for the less pure specimen shown by curve I. At the higher temperatures where the lattice scattering is dominant the two curves coincide. These workers made a careful search for the presence of the minimum in the thermal conductivity which should occur at 40–50° K for sodium and at about 80° K for copper, but there was no indication of any minimum at all. Work on copper has also been done by Allen and Mendoza (1948). Their determinations were in the range 1·8–4° K and hence they have only obtained part of the linear section of the curve.

For less pure metals, particularly those with a high Debye θ, the graph of thermal conductivity against temperature in the liquid hydrogen and helium region is approximately a straight line which sometimes curves slightly towards the temperature axis at higher temperatures. Such a curve is given by de Nobel (1951) for a 99·4% pure nickel in a report of some prewar work. Mendelssohn and Rosenberg (1952 b) have given similar results on an annealed nickel specimen of higher purity (99·997%). De Nobel also gives curves in the liquid hydrogen and liquid air region for a very pure iron (99·93%) and aluminium which each exhibit a broad maximum at about 50° K.

De Haas and de Nobel (1938) give measurements on a tungsten single crystal which exhibits a very high conductivity of about 75 watt units at its maximum in the region of about 15° K.

3.2. *Hulm's Work*

As can be seen from the above general outline, very little systematic research has been published on the thermal conductivity of metals in the normal state. Most workers have contented themselves with more or less isolated determinations for one or two specimens.

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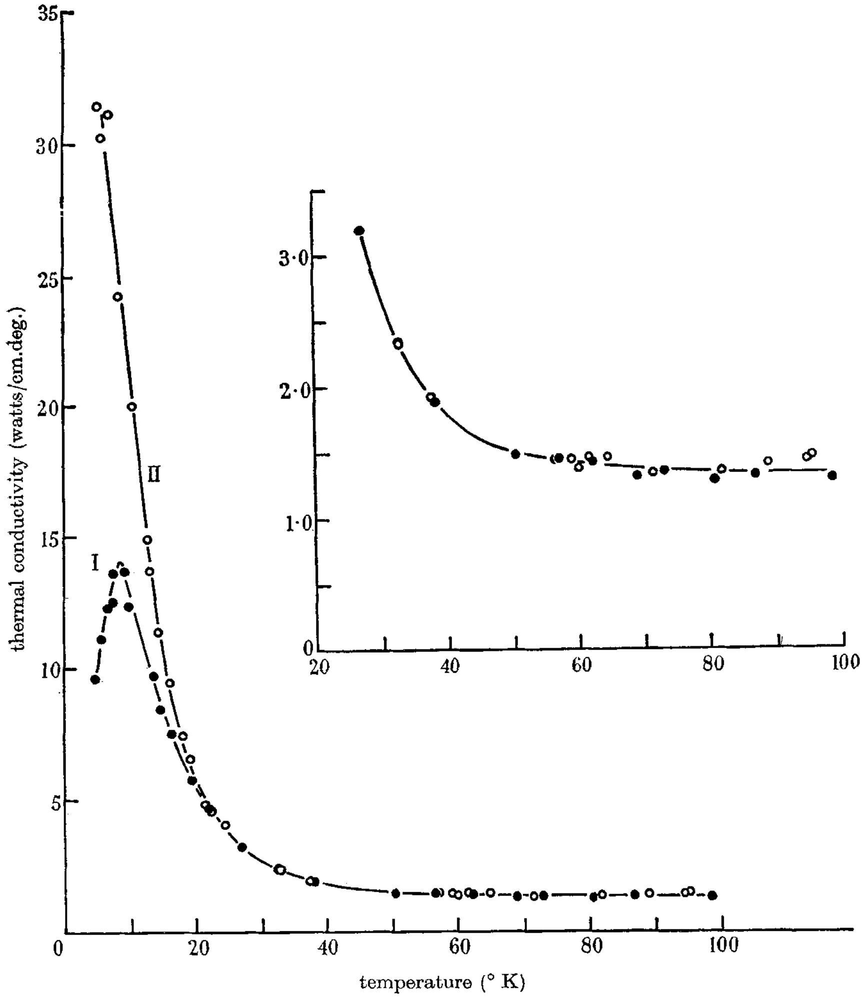
The first systematic set of experiments to be done and compared with theory is that of Hulm (1950). While his paper deals with superconducting metals, the part relating to their behaviour in the normal state is relevant to this section, and the superconducting aspect will be dealt with later.

Fig. 3



The thermal conductivity of two samples of sodium. Inset, the region between 30° and 100° K enlarged five times. (Berman and MacDonald 1951.)

Hulm has measured the thermal conductivity of pure tin, indium, mercury and tantalum, and of tin and mercury with known small amounts of impurity. The measurements were made from 1·7–4·3° K.

The results have been compared with Makinson's theory and they agree qualitatively. Spectroscopically pure tin had a maximum at about 4° K, whilst a small amount of impurity decreased the conductivity and shifted the maximum to a higher temperature. Graphs of WT against T^3 are given for his specimens, where W is the thermal resistance, and as is to be expected from eqn. (11), these are in general straight lines for the samples of higher purity, indicating that the conductivity is nearly all electronic, the lattice conductivity being negligible. Different samples of the same metal gave $WT \sim T^3$ curves that were approximately parallel to each other, showing that the lattice scattering term in $1/T^2$ is the same for each, as the theory requires. The coefficient of T due to impurity scattering is shown to be roughly equal to ρ_0/L_0 where ρ_0 is the residual electrical resistance. This also follows from the theory.

Detailed examination of the $WT \sim T^3$ curves however, shows that they are not exactly linear (fig. 4), and this is dealt with in § 3.6.

Specimens which had an appreciable impurity did not give $WT \sim T^3$ curves which were at all consistent with the theory and Hulm assumes that in these cases there is an appreciable thermal conduction by the lattice as well as that by the electrons. In these cases he has examined the electronic conduction from the residual electrical resistance and has subtracted this from the measured conductivity hence giving the lattice conductivity K_g. In the case of impure tin K_g is approximately proportional to T^3, whilst for tantalum it varies as T^2. However, Hulm shows that in the case of tin which had large crystallites, the main resistance to lattice conduction is likely to be due to electron scattering, which should give a T^2 term as is shown in § 4.2, whereas for tantalum which had a very small grain size, the scattering at grain boundaries might also be important in determining the lattice conduction. This should be proportional to T^3 (§ 4.1).

3.3. *Hulm's Calculation of* N_a

An interesting feature of Hulm's paper is the section in which he has calculated, on the basis of Makinson's theory, the number of electrons per atom, N_a, both for his specimens and for some of earlier workers. He shows that the value of N_a comes out to be of the order of 0·03 whereas it is generally assumed that N_a is of the order of unity for the monovalent metals and should certainly be more than 0·03 even for those of higher valency.

3.4. *More Recent Work*

An investigation of the conductivity of several samples of one metal, aluminium, has been done by Andrews, Webber and Spohr (1951). They have measured the electrical and thermal conductivities of two single crystals and one polycrystalline specimen of high purity aluminium (99·995%) between 2 and 20° K. All the specimens had a very high conductivity, of the order of 50 watt units at their maxima, which occurred in the range 14–17° K. As is to be expected, the single crystals which were purer, and had fewer lattice defects had a higher conductivity than the polycrystalline specimen. They find that within the limits of experimental error, the lattice scattering term, α, is the same for each, confirming

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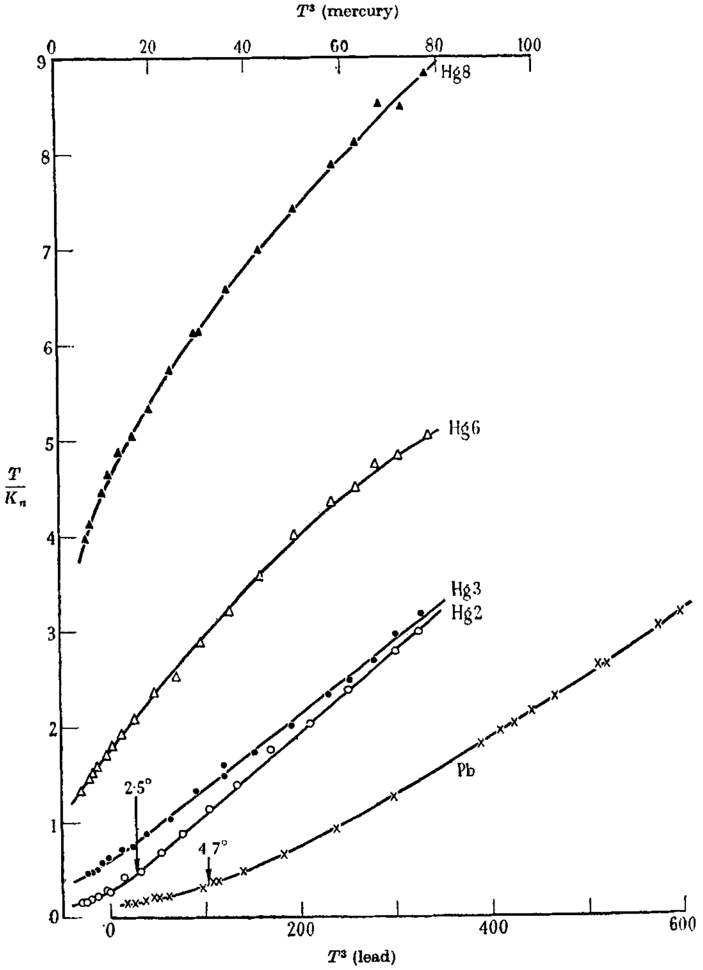
Hulm's results mentioned above. The curves are shown to agree with those to be expected from Makinson's and Sondheimer's theories, although in order to make them fit quantitatively N_a has to be assumed to be of the order of 0·05. They suggest that this small value of N_a might be resolved

Fig. 4



Variation of T/K_n with T^3 for mercury specimens and for the pure lead specimen of de Haas and Rademakers (1940). Hg 2, 3, 6, 8 have as impurity 0·002% Cd, 0·007% Cd, 0·10% In and 0·39% In respectively. (Hulm 1950.)

by modifying the transport theory of electrons to take into account the presence of filled and nearly filled zones in multivalent metals. Since however monovalent metals, which do not have nearly filled zones also give a small value of N_a by these theories it seems unlikely that this approach will solve the problem.

Johnston, Powers and Ziegler (1951) have measured the conductivities of pure iron, copper and aluminium and some aluminium alloys in the range 20° K to room temperature. One aluminium alloy did show a minimum in the conductivity but it is doubtful whether this really is strong evidence in favour of Makinson's theory since most alloys have an appreciable lattice conductivity and it is always possible to have suitable lattice and electronic components superimposed so that a minimum is obtained in the resultant conductivity.

A detailed series of experiments has been carried out by Mendelssohn and Rosenberg (1952 a, b) in which they have measured the thermal conductivities of as many metals as could be obtained in a very pure state. Over thirty elements have so far been investigated and the results give a general idea of thermal conductivity values and variation with temperature. All the metals of groups 1, 2, and 3 which were investigated had a fairly high conductivity of the order of 10 watt units or more in the neighbourhood of the maximum. In the 3d, 4d and 5d transition groups, the metals at the end of each group, i.e. the group 8 elements, have a much higher conductivity than the elements at the beginning of the group. Thus the conductivity of the iron specimen at 20° K was ~2 watt units, whereas the conductivity of manganese, the element before it in the 3d group, was about 0·02 watt units at the same temperature. It has been suggested by Mendelssohn and Rosenberg that this general effect is probably closely allied with the more complex crystal structure of these earlier elements and also to the fact that their general physical properties, e.g. hardness, ductility, etc. are very dependent on gaseous impurities which are very hard to remove.

3.5. *The Conductivity of Anisotropic Crystals*

One interesting set of curves that is presented is for two zinc single crystals from the same batch—one with the hexagonal axis at 80° to the rod axis and the other at 13° to the axis. The curves are identical at the high and low temperature ends but in the neighbourhood of the maximum the 13° crystal has a conductivity 10% greater than the 80° crystal. This is connected with the fact that the atomic spacing in zinc is different parallel and perpendicular to the hexagonal planes.

Later work of this type has been done on cadmium and gallium single crystals grown along different axes and this work may give an insight into the lattice–electron interaction.

3.6. *The Linearity of the $WT \sim T^3$ Curves*

Experimental results are frequently expressed in the form of curves of WT against T^3. They are seldom perfectly straight lines (fig. 4) and it seems of interest to calculate what deviation from linearity is to be expected from the theory.

At very low temperatures the function $\mathcal{J}_5$ in eqn. (5) is approximately constant and hence curves of WT against T^3 in this range will be linear.

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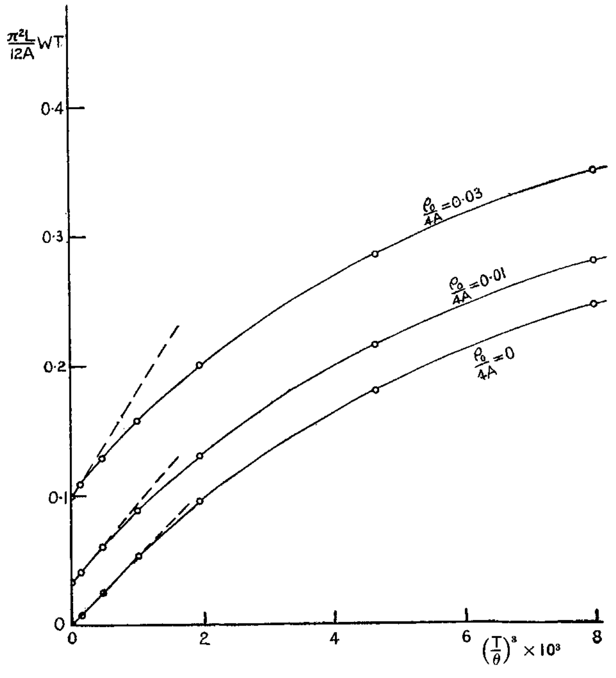
As the temperature is increased however, $\mathcal{J}_5$ starts to decrease fairly rapidly and so the curve in this region will bend over towards the T^3 axis. The second term in T^4 involving both $\mathcal{J}_5$ and $\mathcal{J}_7$ is very small in comparison and can be neglected. It is of interest to estimate up to what temperature the $WT \sim T^3$ curve can be expected to be linear.

This we have done using the more accurate computations in Sondheimer's (1950) paper. These show (fig. 5) that for an ideally pure metal ($\rho_0/4A=0$) the curve deviates from linearity by 10% (i.e. the slope is changed by 10%) at a temperature of approximately $0{\cdot}125\,\theta$, and by 15% at $0{\cdot}144\,\theta$. With increasing impurity this deviation starts at progressively lower temperatures. With $\rho_0/4A=0{\cdot}03$ there is a 25% deviation at $0{\cdot}1\,\theta$ and a 33% deviation at $0{\cdot}125\,\theta$. Incidentally this result that the impurity affects the deviation is an example of how Sondheimer's treatment shows that the ideal and impurity resistances cannot really be separated and that Matthiessen's rule is only a first approximation.

Fig. 5



Graphs of WT against $(T/\theta)^3$ as calculated from Sondheimer (1950), showing how the departure from linearity depends on impurity.

We should thus expect $WT \sim T^3$ curves to be linear up to about $0{\cdot}1\,\theta$ and above this temperature the curve should turn towards the T^3 axis. For most metals this does occur, confirming the theory, but in some cases the WT curve rises above the linear part. This is shown by Hulm (1950) for two mercury specimens Hg2 and Hg3 and also for a lead specimen of de Haas and Rademakers (fig. 4). It also occurs in Mendelssohn's and Rosenberg's results for platinum and iridium and in later work on gallium. It seems exceedingly unlikely that in these specimens this could be due to lattice conduction, particularly since any increasing lattice conduction would tend to decrease the resistance.

It should not be expected, however, that the theory, which is only for monovalent metals, although it gives a qualitative picture for polyvalent metals as well, should hold to the extent of the higher approximations of the $W \sim T$ relationship.

§4. THE LATTICE CONDUCTIVITY

4.1. *General Remarks*

The lattice conductivity in a metal is influenced by all the factors which determine it in a non-conductor, and in addition the presence of free electrons play an important role in reducing its magnitude. The lattice conductivity of non-metals is described in another article in this volume, but it will be convenient also to give a brief summary of the theoretical results for non-metals here.

In such substances the lattice conductivity is limited by a number of scattering processes to which correspond resistances which may be treated as additive. One may consequently write

$$1/K_g = W = W_D + W_B + W_U. \qquad (20)$$

The terms are : W_D due to scattering of the lattice waves by defects in the crystal, these may be impurity atoms, unoccupied lattice points, or other dislocations ; W_B the term due to scattering of the lattice vibrations at the boundary of the specimen or at internal grain boundaries. W_U is the resistance due to interaction of the lattice vibrations amongst themselves. This is in the main due to umklapp processes.

The temperature dependence of these terms is given by

$$W_D \propto T,$$

$$W_B \propto T^{-3},$$

$$W_U \propto T^{\nu} \exp(-\theta/2T).$$

While eqn. (20) seems to be a satisfactory approximation, it is not completely reliable and in temperature regions where two of the terms are of the same order of magnitude, the total W becomes considerably larger than is to be expected from (20) (Klemens 1951). The total lattice conductivity in a pure specimen will have a maximum at about $\theta/20$ which may be of the order 20 watt units.

4.2. *The Effect of Electronic Scattering*

In the case of a metal the situation is complicated by the presence of electrons which scatter the lattice vibrations strongly. A further term has therefore to be added to the expression for W and we shall call this

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resistance due to the electrons W_E. Sommerfeld and Bethe (1934) and Wilson (1936) find that this term is given by

$$1/W_E = G\left(\frac{T}{\theta}\right)^2 \mathcal{J}_3 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (21)$$

where $$G = \frac{k^3 h\theta^2 M}{2\pi^2 m^2 a^3 C_j^2} \quad \text{(Makinson 1938)} \quad . \quad . \quad . \quad (22)$$

and the remaining symbols have the meanings used in the description of the theory of the electronic thermal conductivity in § 2.2.

Makinson assumes

$$C_j^2 = \tfrac{1}{3} C^2$$

where C is the interaction constant used in eqn. (7). This implies that the longitudinal and transverse waves interact equally with the electrons—which of course is contrary to the simple Bloch theory.

G may then be deduced from the electronic conductivity at high temperatures and it is found that

$$G = \frac{27}{4\pi^2 N_a^2} K_e \ (T > \theta) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (23)$$

or $L_0 \sigma T$ may be substituted for K_e to give G in terms of the electrical conductivity at high temperature.

Then $$G = \frac{27\, L_0 \sigma T}{4\pi^2 N_a^2} (T > \theta). \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (24)$$

4.3. *The Lattice Conductivity in a Metal*

In fig. 6 we show a general picture of the variation of a typical lattice conductivity with temperature. At very low temperatures scattering by the crystal boundaries will be important and the conductivity will vary as T^3. At slightly higher temperatures scattering by the electrons will become predominant and the conductivity will vary as T^2. Still higher temperatures will make the impurities and finally the umklapp processes of importance.

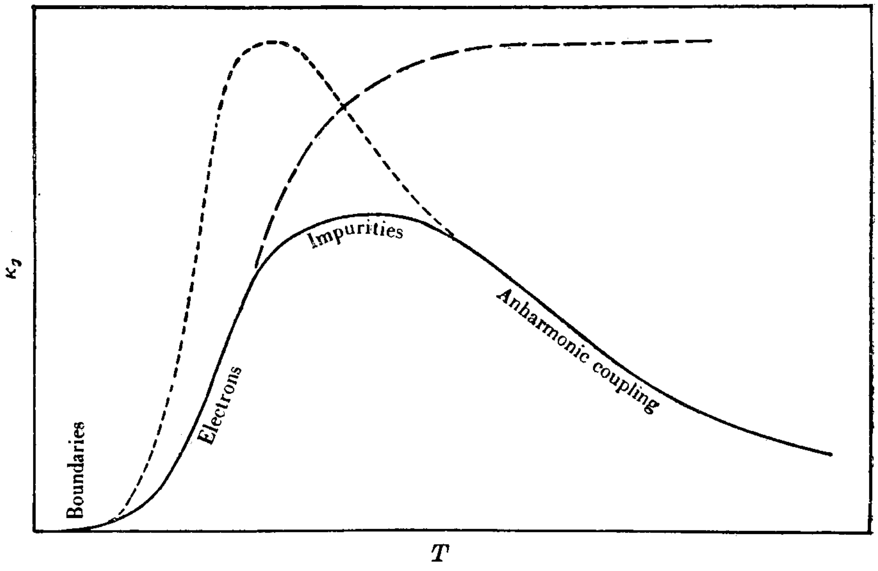
It is of interest to calculate the absolute value of the lattice thermal conductivity which may be expected in a metal in the region where the scattering is mainly due to the electrons. At 10° K this yields a conductivity of 2×10^{-2} watt units for lead, and 4×10^{-3} watt units for tantalum, while a metal like bismuth with very small effective number of electrons will be expected to have a conductivity of the order of 15 watt units. It is therefore obvious that the lattice conductivity of a metal can only be measured if some steps can be taken so to reduce the electronic thermal conductivity that K_g becomes a very much more important contribution to the total conductivity than the fractional percent to be expected in a pure metal with a large number of free electrons. This can be done in some cases in a high magnetic field, or by the addition of impurities. Descriptions of these methods are given in §§ 6 and 5 respectively.

§ 5. The Thermal Conductivity of Alloys

5.1. *The Effect of Impurities in a Metal*

As has been mentioned previously, the electronic thermal conductivity K_e is considerably reduced when a small amount of impurity is present. The impurity scattering becomes the dominant cause of thermal resistance over quite a wide temperature range, instead of being effective only at the lowest temperatures. It overshadows the resistive effect of the lattice vibrations and the curve of K_e against T shows no maximum but is linear up to quite a high temperature.

Fig. 6



The theoretical general form of K_g. The dotted line shows the form for an insulator and the dashed line the form for a metal if only electrons scattered the lattice waves. (Makinson 1938.)

In an alloy (which will usually contain several percent of effective impurity atoms) the electronic thermal resistance is very much increased and K_e is very often reduced until it is of the same order of magnitude as K_g, the lattice conductivity, which is not affected so much. Hence the curves of total K against T for an alloy differ from those to be expected from a pure metal, not only by the orders of magnitude involved, but also by the fact that whereas in a pure metal K_g is negligible, in an alloy its contribution is a considerable proportion of K.

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5.2. *Experimental Results*

Where the thermal resistance is dictated by impurity scattering the Wiedemann–Franz law holds and the value of K_e can be found from electrical measurements of the residual resistance ρ_0. Then we have

$$K_g = K - L_0 T/\rho_0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (25)$$

This type of calculation has been made by Hulm (1951) and Berman (1951 b). Hulm's results on a Cu80 Ni20 specimen show that the lattice conductivity is proportional to T^2 between 2 and 20° K. This indicates that in this range the lattice waves are scattered by electrons.

This is borne out by the work of Berman (1951 b) on German silver, stainless steel and constantan in the range 2–90° K. He also finds the lattice conductivity is of the same order as the electronic conductivity and is proportional to T^2 up to 20° K. Above this temperature, however, the increase is more gradual and in all cases K_g reaches a maximum in the range 50–90° K. Berman has further analysed the lattice conductivity of his German silver specimen and has estimated the effects of the various scattering mechanisms (fig. 7). He suggests that whilst the low temperature scattering is due to the electrons, scattering due to small scale lattice defects and impurities becomes increasingly important at higher temperatures. This resistance W_D begins by being proportional to T but at higher temperatures becomes less temperature dependent. He also shows that the resistive effect due to scattering at grain boundaries W_B is only about $\frac{1}{2}\%$ of the total resistance at 2° K and it decreases rapidly at higher temperatures, hence it can be ignored.

Earlier work by Karweil and Schaeffer (1939) on German silver, silver bronze, contracid and steel also shows an abnormally high Lorenz number and hence an appreciable lattice conductivity.

5.3. *Alloys for Cryogenic Apparatus*

Cold working, which introduces dislocations into the lattice, usually decreases the conductivity (e.g. Cu90 Ni10 Estermann and Zimmerman 1951, 1952). It is difficult, however, to judge the effects of these treatments since no really systematic work on these lines has been done.

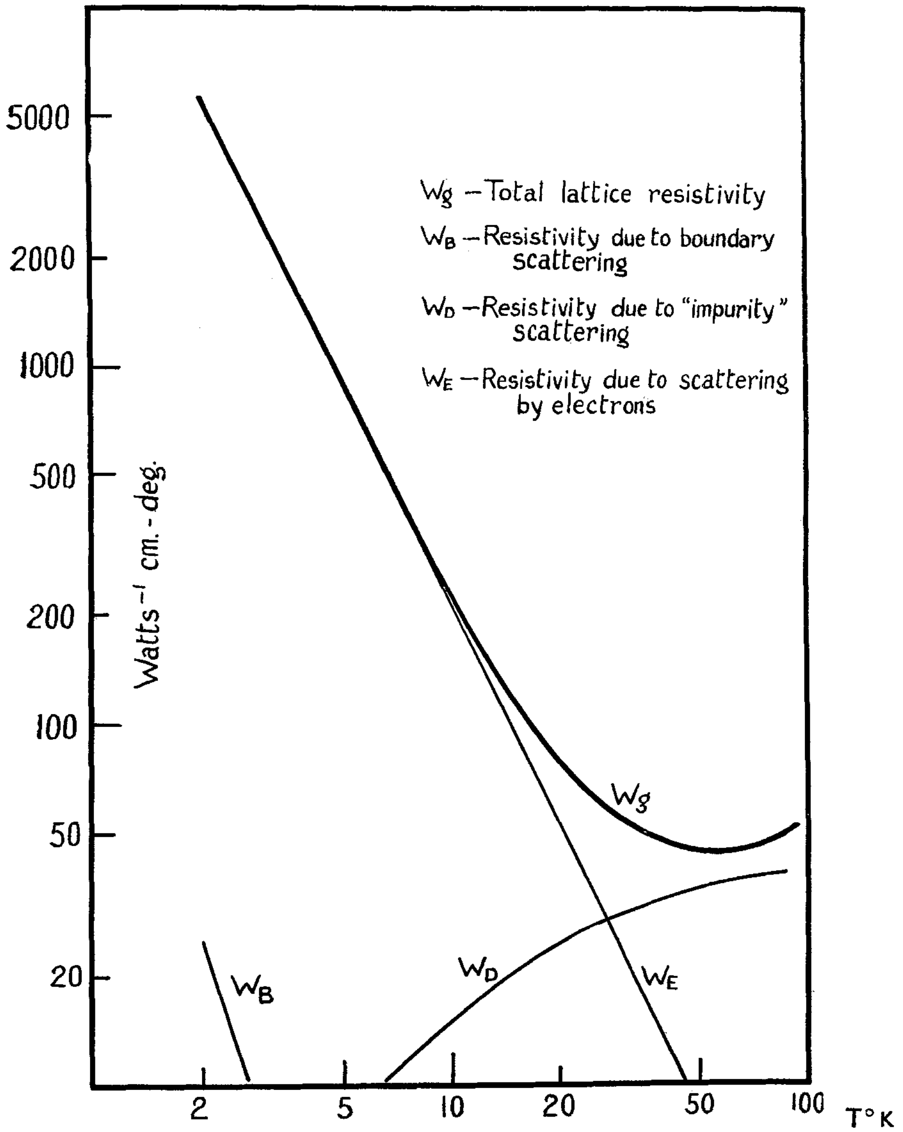
In general the conductivity of the various iron and copper alloys in the range 2–20° K is of the order of 10^{-2} or 10^{-3} watt unit. German silver and stainless steel are particularly bad conductors and for this reason are very much used in the construction of low temperature apparatus where the heat input must be cut down as much as possible. For the same reason constantan is particularly useful for the electrical leads into a cryostat or liquefier.

Berman (1951 b) has given a useful table which shows the heat flow down stainless steel, constantan and German silver when the ends of the specimen are at temperatures in the range 0–80° K. This is particularly useful when cryogenic apparatus is being designed.

5.4. *List of Alloys that have been Measured*

There would be no point in giving a full description of all the alloys that have been measured and the values obtained since this would add little to a general description of the subject. For reference, however, we give as complete a list as possible of papers which describe such experiments and the alloys that they deal with.

Fig. 7



Estimated contributions to the lattice thermal resistivity, W_g, in German silver from scattering of the lattice waves by electrons, grain boundaries and ' impurities ' (i.e. lattice defects etc.). (Berman 1951 b.)

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Karweil and Schaeffer (1939) German silver, silver bronze (Cu46 Zn41 Ni13), contracid B7M (Ni60 Cr15 Fe16 Mo7), steel.

Allen and Mendoza (1948) German silver.

Wilkinson and Wilks (1949) Nickel silver (Cu63 Zn17 Ni20), stainless steel, Cupro-nickel (Cu70 Ni30).

De Nobel (1951) monel, dural and various steels.

Estermann and Zimmerman (1951, 1952) monel, inconel, Cu90 Ni10, stainless steel.

Schmeissner and Meissner (1950) Croman B2Mo.

Hulm (1951) Cu80 Ni20.

Berman (1951 b) German silver, stainless steel, constantan.

Superconducting alloys.

de Haas and Bremmer (1936 a).

Mendelssohn and Pontius (1937) Pb90 Bi10.

de Haas and Rademakers (1940).

Hulm (1950) Tin/mercury, mercury/cadmium, mercury/indium.

Mendelssohn and Olsen (1950 a, b, c) and Olsen (1952). Lead/bismuth.

§ 6. EFFECT OF A MAGNETIC FIELD ON THE THERMAL CONDUCTIVITY

6.1. *Early Work on Bismuth*

Just as the application of a magnetic field on a metal usually increases the electrical resistance, so in many cases it also increases the thermal resistance, although the thermal effect is not always so great as the corresponding electrical effect.

Some of the earliest work was done by de Haas, Gerritsen and Capel (1936) on bismuth single crystals. They found that whilst the thermal resistance increased with increasing field it tended to a saturation value in a field of 5·3 kgauss at liquid nitrogen temperatures and in a field of only 400 gauss at liquid hydrogen temperatures. This effect was interpreted by assuming that the lattice heat conductivity K_g was unaffected by the magnetic field and that the saturation value obtained by extrapolating to infinite field was in fact the value of the lattice conductivity. In this way they calculated K_g and K_e.

Experiments on bismuth at liquid air temperatures have also been carried out by Grüneisen, Rausch and Weiss (1950) who show that the effects of saturation in their specimens become evident in a transverse field of 10 kgauss. They calculate that $K_g = 0{\cdot}145$ watt units and $K_e = 0{\cdot}0493$ watt units at 85·7° K. These values are of the same order as those given by de Haas and his co-workers.

This is in agreement with theory which suggests that due to its small number of free electrons, bismuth should have an appreciable lattice conductivity. As the temperature is decreased the electronic contribution is reduced until nearly all the conductivity is due to the lattice.

Measurements by Shalyt (1944) at lower temperatures bear this out. In the range 2–4° K the conductivity curve seems to be due to the lattice, K varying as $T^{2\cdot 5}$ approximately and the magnetic field of 4·2 kgauss has no effect. At 20° K this field increases the thermal resistance by 4% and at 65–80° K by 15 to 20%. This shows that the electronic contribution has reached a negligible amount in the lowest temperature region.

6.2. *Work on Antimony*

Similar work on antimony single crystals of various orientations has been done by Rausch (1947) in the liquid air region. In this case no saturation was found in a field of 10 kgauss and K_g and K_e were separated by a method (indicated below) involving the measurement of the electrical resistance in the magnetic field. Depending on the orientation of the crystal axis to the axis of the specimen the lattice conductivity varied between one-third and two-thirds of the total conductivity.

Measurements of conductivity were also taken in a constant transverse field which was rotated about the axis of the specimen. A periodicity was observed, the conductivity decreasing to a minimum and then increasing to a maximum in a rotation of 180°.

6.3. *Experiments on Tungsten*

Whilst these experiments are of interest, they do not give a good idea of the general results to be expected because neither bismuth nor antimony are good representative metals—both have a small number of free electrons and an appreciable lattice conductivity whereas in most metals the lattice conductivity is very small.

Early experiments on more normal metals were made by Grüneisen and Adenstedt (1938) who measured the effect of a field up to 12 kgauss on the thermal and electrical resistances of copper, tungsten and beryllium single crystals and of platinum and silver polycrystals at the temperature of liquid hydrogen. They found that only in the case of the single crystals was there an appreciable change in the thermal conductivity. The largest effect that they measured was for a beryllium sample whose thermal resistance increased about 60 times in a 12 kgauss field.

Experiments have also been made on a tungsten single crystal by de Haas and de Nobel (1938). Their work was in the range 14–20° K and in fields up to 26·3 kgauss. Later experiments by de Nobel (1949) extended the range of measurements up to a field of 36·4 kgauss. Both thermal and electrical conductivities were measured as a function of temperature and of field. At 15° K they found that the thermal resistance was increased 222 times in a field of 36·4 kgauss, several orders of magnitude greater than the bismuth results quoted above. Another difference they found was that the effect of the magnetic field increased at lower temperatures, whereas for antimony and bismuth the opposite occurred.

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6.4. *Calculation of the Lattice Conductivity from Magnetic Effects*

The value of the lattice conductivity can be found as follows:— Since $K=K_e+K_g$ and K_e is related to the electrical conductivity, σ, by $K_e=L_e\sigma T$ where L_e is the Lorenz number, then

$$K=L_e\sigma T+K_g. \qquad (26)$$

Hence assuming that L_e does not alter in a magnetic field, a plot of K against σT as H is varied should be linear and the intercept on the K axis (i.e. at $H=\infty$) should give K_g.

This is the basis of the method for deriving K_g for antimony used by Rausch. For tungsten, however, de Nobel found that although at lower fields K was proportional to σ at constant temperature, at higher fields the slope of the curve was increased and he found it impossible to separate out the lattice and electronic components.

6.5. *Experiments on Beryllium*

Experiments on beryllium single crystals at 20° K have been done by Grüneisen and Adenstedt (1938) and Grüneisen and Erfling (1940). They measured the conductivity as a transverse field was rotated about the specimens and they found strong anisotropy, the conductivity being dependent on the angle between the field direction and the direction of the z axis of the crystal. By taking electrical measurements as well they were able to estimate the value of the lattice conductivity and confirm that at 20° K it is very small, while at 90° K it is a considerable proportion of the total conductivity. They also give rotation diagrams for copper and tungsten single crystals.

6.6. *Experiments in the Liquid Helium Region*

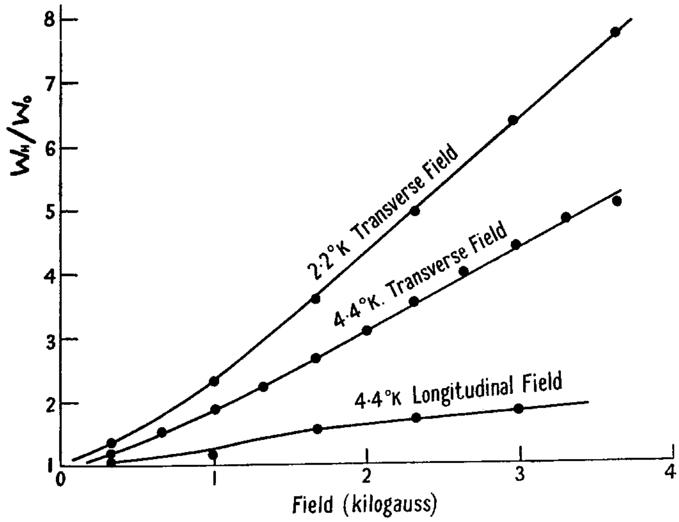
Up till recently very little work has been done in the liquid helium region. Hulm (1950) has determined the change in thermal resistance for pure tin at 4·29° K in a longitudinal field. He finds that the resistance is nearly doubled in a field of 1 500 gauss and that up to 400 gauss the relative change in conductivity $(K_0-K_H)/K_H$ is of the form $\lambda H/(1+\mu H^2)$ where K_0 and K_H are the conductivities in zero field and field H respectively and λ and μ are adjustable parameters. For small impurities in the tin no magnetic effect was observed.

Mendelssohn and Rosenberg (1951) have published measurements on a polycrystalline specimen of cadmium whose thermal resistance increases in a transverse field of 3·8 kgauss by a factor five at 4·4° K and by over seven times at 2·2° K (fig. 8). In a longitudinal field the effect was very much smaller. They have continued this work with other elements (1952 c) and in general they find that a field of 3·8 kgauss produces a measureable effect only in metals that have a relatively low melting point and are mechanically rather soft. So far measurements have been taken on polycrystalline indium and thallium and on single crystals of zinc, cadmium, tin, lead and gallium. In general the graphs of thermal resistance against field are linear except for small fields up to 300 gauss. A given field usually has an appreciably larger effect at lower temperatures and the effect of a transverse field is usually much greater than that of a longitudinal field. They also find that the effect is greatly reduced in polycrystalline specimens and also by the presence of impurities.

6.7. *The Theory of Sondheimer and Wilson*

The simple quasi-free electron model of a metal is of no use for giving us an insight into the magnetic effects as it gives us zero change of resistance in a magnetic field. A more complicated model must be used which, however, must still be simple enough for us to be able to derive a result that is capable of being evaluated. The simplest model assumes that the conduction electrons occupy two overlapping bands, the s and d bands and there is no interaction between the electrons in one band and those in the other. The heat flow is calculated separately for each band and the total flow is obtained by simple addition.

Fig. 8



The increase in the thermal resistance of cadmium in a magnetic field. (Mendelssohn and Rosenberg 1951.)

This is the model used by Sondheimer and Wilson (1947) who calculate the conductivity due to each band under the influence of a transverse magnetic field using as a basis the theory given by Wilson (1936) and developed by Makinson (1938). This model is not sufficiently general to give a non-zero result for longitudinal fields. They find simplified formulae for high and low temperatures and for a large magnetic field and a general formula is given which reduces to these in the three limiting cases,

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If n_s is the number of electrons in the s band, n_d is the number of holes in the d band then

$$\frac{K_0-K}{K}=\frac{CH^2}{1+FH^2}, \text{ for } n_s\neq n_d, \quad . \; . \; . \; . \; . \quad (27)$$

$$\frac{K_0-K}{K}=EH^2, \quad \text{for } n_s=n_d \quad . \; . \; . \; . \; . \quad (28)$$

where C, E and F are functions of K_0, T, n_s and n_d. Hence for $n_s\neq n_d$ we get saturation at large fields and for $n_s=n_d$ we get infinite resistance in infinite field. They also show that the application of a magnetic field does not affect the lattice thermal conductivity. The corresponding electrical effects have also been calculated and the dependence of the Lorenz number, L, on the field is given.

6.8. *The Theory of Kohler*

Similar results have been derived by Kohler (1949 a, b, c). His first paper (1949 a) gives the general equation

$$\frac{\Delta W}{W_0}=G\left(\frac{H}{W_0TL}\right) \quad . \; . \; . \; . \; . \; . \; . \; . \quad (29)$$

where ΔW is the change in the thermal resistance in a field H, W_0 is the thermal resistance in zero field and L is the theoretical value of the Lorenz number. This is the type of relation we should expect on the basis of Kohler's rule for the change of electrical resistance in a magnetic field, if we assume L to be independent of T. This he applies to the results of de Haas and de Nobel for their tungsten single crystal.

He shows that a plot of $\Delta W/W_0$ against H/W_0TL gives a single curve for all the experimental points and G is a monotonically increasing function. The second paper (1949 b) deals with the special case of a metal with $n_s=n_d$ in a strong magnetic field and he derives the relation, which can be obtained from (28), that at constant temperature K_e is proportional to $1/H^2$. This he uses to give the following method for separating K_e from K_g without necessitating any electrical measurements. We have $K_H=K_g+K_e=K_g+E/H^2$. Thus a plot of K_H against $1/H^2$ should give a straight line with an intercept of K_g. This he applies to the measurements on beryllium crystals of Grüneisen and his co-workers.

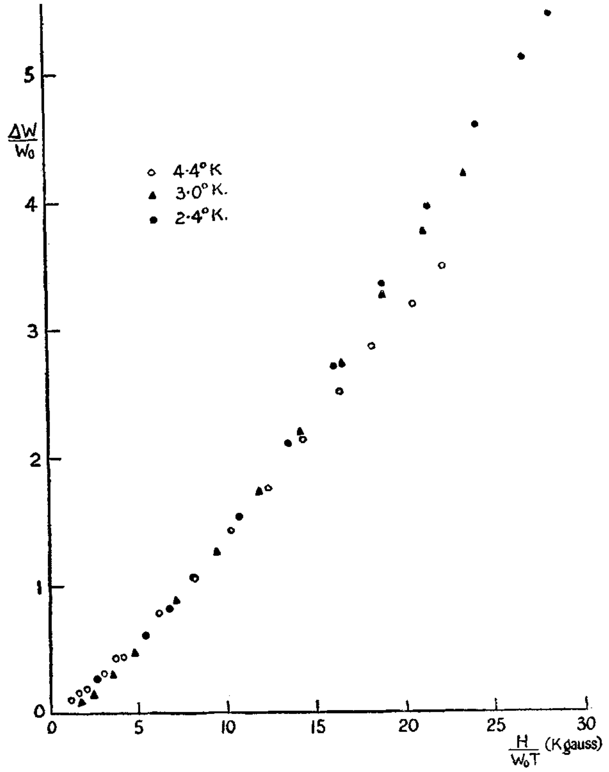
The third paper (1949 c) gives the theoretical derivation of the formulae in which he obtains the same results as Sondheimer and Wilson. This he generalizes to the equation containing the function G quoted above.

6.9. *Comparison of Theory with Experiment*

Recent work seems to confirm eqn. (29) given by Kohler although the function G does not appear to be in the actual form that he or Sondheimer suggests. This is not surprising since the models used are really too simple to enable quantitative results to be obtained although they do give a qualitative picture. From the results of Mendelssohn and

Rosenberg (1952 c) in the range 2–5° K, graphs of $\Delta W/W_0$ against H/W_0T show that all the experimental points for one metal at different temperatures do lie on a single curve. Since these results cover a change in temperature of 100% this is a much more stringent test than that applied by Kohler himself from the results of de Haas and de Nobel on tungsten, since this work was in the liquid hydrogen region and the maximum temperature change was only 25%. Graphs for the effect of a magnetic field on the thermal conductivity of tin are shown in fig. 9. It can be seen that whilst $\Delta W/W_0$ varies as approximately $(H/W_0T)^2$ for small values of H/W_0T, for larger values the ratio tends to become proportional to H/W_0T.

Fig. 9



$\Delta W/W_0$ against (H/W_0T) for tin in a transverse magnetic field, showing how the points for three different temperatures fall approximately on one curve. (Mendelssohn and Rosenberg 1952 c.)

The points corresponding to high fields at the lowest temperatures, however, do tend to fall above the main line of the curve, but it should be noted that the maximum field of 4 kgauss at 2° K corresponds to 40 kgauss

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at 20° K. It is possible that the variation of L with field may be appreciable in this region and this has not been taken into account. In general no sign of saturation has been observed in the normal metals.

Similar graphs for the effects due to a longitudinal field show that Kohler's equation holds in this case as well, although the curves are not linear and tend to bend over slightly towards the H/LW_0T axis.

We should note that the assumption of two bands having additive conductivities each limited by resistances obeying Matthiessen's rule cuts out any possibility of the total conductivity obeying this rule.

§ 7. THE THERMAL CONDUCTIVITY OF SUPERCONDUCTORS

7.1. *Theory*

The theory of the thermal conductivity of a metal in the superconducting state is by no means in the advanced stage which the theory of the normal state has reached. However, a fairly simple consideration of the factors involved allows one to draw conclusions of some interest.

A superconductor below the transition point which has had its superconductivity destroyed by the application of a magnetic field will presumably (except for the effects of magneto resistance) behave in the way we have described in the preceding paragraphs for normal metals. We may then write eqn. (1) in the form

$$K_n = K_{en} + K_{gn}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (30)$$

Here we have added the suffix n to indicate that it is the behaviour in the normal state that we are discussing. The values for K_{en} andK_{gn} will be governed by the same factors that were found to govern the values of K_e and K_g.

In the absence of a magnetic field, however, when the substance is superconducting, the distribution of the electrons in phase space will be altered, and it may be expected that the electronic thermal conductivity in the superconducting state K_{es}, will be different from K_{en}. Since K_{gn}, the lattice conductivity in the superconducting state, is also to a large extent dependent upon the amount of scattering by the electrons, we may expect that the new electronic distribution will also cause a change in the lattice thermal conductivity from its normal value.

It was pointed out be de Haas and Rademakers (1940) that the 'superelectrons' which carry the resistanceless current in a superconductor cannot be expected to take part in carrying the thermal current and that therefore K_{es} would be expected to be smaller than K_{en}. Hulm (1950) has pointed out that since the 'superelectrons' move without friction against the lattice, they presumably do not contribute to the scattering of the lattice waves and that therefore K_{gs} might be expected to be greater than K_{gn}.

We thus have for the superconducting state

$$K_s = K_{es} + K_{gs}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (31)$$

where $K_{es} < K_{en}$, and where $K_{gs} > K_{gn}$. Since in pure substances K_{en} is much greater than K_{gn} we may expect that, unless the change in K_g is very large, the total K_s will be smaller than the total K_n.

Whilst the above general remarks give a qualitative idea of the behaviour, some more detailed prediction of the actual values of the ratios K_{es}/K_{en} and K_{gs}/K_{gn} is of course desirable. Such a calculation has been made by Heisenberg (1948) on the basis of his theory of superconductivity and the calculations of Koppe (1947).

Heisenberg considers the general formula for the thermal conductivity

$$K = \tfrac{1}{3} l v C, \qquad (32)$$

where l is the mean free path, v the velocity of the particles carrying the thermal current and C their specific heat.

As a rough approximation he assumes that the mean free path of the 'normal' heat transporting electrons in the superconducting state is longer than that of the electrons in the normal metal by a factor $1/(1-w/2)$ where w is the fraction of superelectrons. v is of course very nearly the same in the two states and

$$C_s = C_n k(w), \qquad (33)$$

where $k(w)$ is a function which at the highest temperatures is very nearly equal to the value to be expected on the Casimir-Gorter (1934) theory of superconductivity. For $T/T_c > 0{\cdot}3$ this gives to a fair approximation

$$K_{es}/K_{en} = 2t^2/(1+t^4), \qquad (34)$$

where $t = T/T_c$. At lower temperatures this is no longer correct and the ratio of the two conductivities falls exponentially with temperature (Goodman 1951). It is pointed out by Heisenberg that the approximation chosen for the mean free path of the 'normal' electrons can only be relied upon for the case where the main scattering of the electrons is by impurities and that this calculation also contains other approximations which may be expected to break down in the vicinity of the transition temperature.

The success of the theory of Fröhlich (1950) in explaining the isotope effect on the critical field and transition temperatures of superconductors seems to indicate that the Heisenberg theory and calculations of the type described above should not be taken too literally. On the other hand it would appear that the Heisenberg theory has been so adjusted that one may expect it to give a reasonably correct estimate of the behaviour of the superconducting thermal conductivity.

7.2. *The Circulation Hypothesis*

Before continuing to a description of the experimental side of the subject it is appropriate to mention an interesting idea first suggested by Mendelssohn (1946) and later used by Mendelssohn and Olsen (1950 a, b, c) in an attempt to explain certain of their results. It was suggested that there might exist in superconductors an analogue of the fountain effect in liquid helium II. This would consist of a stream of 'superconducting'

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electrons flowing from the cold to the hot end of a specimen, being converted to 'normal' electrons there and flowing back as 'normal' electrons with a finite heat content, which is given up at the cold end of the specimen again. Thus a circulation process is set up. This circulation might be expected to vanish at the transition temperature and at the absolute zero and to have a maximum at some intermediate temperature. Its absolute magnitude would be difficult to calculate a priori.

7.3. *Experimental Work*

While experiments were made as early as 1914 by Kammerlingh-Onnes and Holst to investigate whether the thermal conductivity showed as startling a discontinuity as the electrical conductivity, no further research was carried out in this field until the thirties (de Haas and Bremmer 1931, 1936 b, Mendelssohn and Pontius 1937, and de Haas and Rademakers 1940). The results of these investigations were that for pure substances K_n was greater than K_s, while for alloys this was not always so. The ratio K_s/K_n even for the pure metals showed two distinct types of behaviour. In the case of tin this was very like that to be expected as the result of Heisenberg's calculation, but in lead K_s/K_n did not approach unity asymptotically as predicted by eqn. (34) but the superconducting curve approached the normal one at a finite angle (fig. 10). A similar effect was also observed in mercury by Hulm (1950). He carefully investigated the behaviour of the ratio K_s/K_n in a series of tin and mercury specimens containing small known amounts of impurity. He showed that for the ideal case of a metal where the main mechanism limiting the mean free path of the electron is scattering by impurities, the ratio K_s/K_n is given by a characteristic function $f(t)$ very closely resembling that suggested by Heisenberg. For the ideal case of lattice scattering alone (pure lead and pure mercury) the ratio K_s/K_n is given by some other function which he denotes by $g(t)$. Hulm suggests that $g(t)$ is very well represented by t^5. At low temperatures even in the purest samples the impurity scattering will become predominant, and there K_s/K_n will tend to the impurity scattering type of function, $f(t)$.

In fig. 11 we show values of K_s/K_n for lead, tin and mercury specimens of various purities. This information has been drawn from papers by de Haas and Rademakers (1940), Rademakers (1949), Hulm (1950) and Olsen (1952). It seems reasonable to suppose that the shape of the K_s/K_n curve might be a function of the proportion of the impurity scattering present and we have therefore marked all the curves with a parameter X which gives this relationship. We have defined

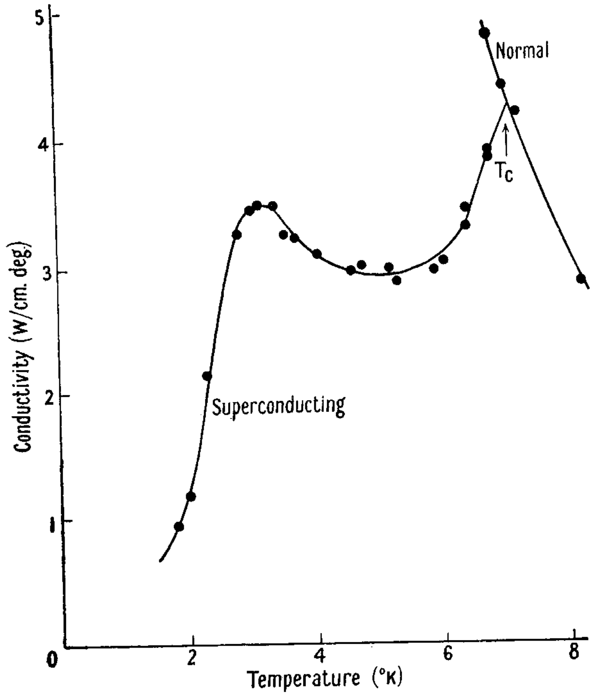
$$X=\alpha T^3/\beta, \qquad (35)$$

where α and β are the constants occurring in eqn. (11). Thus the larger the value of X the smaller the relative amount of impurity scattering. It will be seen that although K_s/K_n may to a moderate accuracy be described as a function of T/T_c and X only, this can at best be a first approximation.

Interpolation formulae have been given by Hulm (1950) and by Olsen (1952) to describe the behaviour of the thermal conductivity for specimens with finite values of X.

Neither of these formulae can be considered to be very satisfactory. That given by Hulm is based upon a method of calculation which would appear to imply that the reduced value of the thermal conductivity in the superconducting state is a consequence of a decreased mean free path of the electrons when the substance becomes superconducting, rather than being due to a fall in the effective number of electrons. The formula given by Olsen although empirical would also appear to imply a rather unrealistic solution to the problem of combining the mean free paths.

Fig. 10



The thermal conductivity of lead in the superconducting state, showing the sharp breakaway from the normal curve at the transition temperature. (Mendelssohn and Rosenberg 1952 b.)

7.4. *The Lattice Conductivity in the Superconducting State.*

In some cases the thermal conductivity lies considerably above the value to be expected from the Heisenberg theory. We have seen in fig. 11 that the K_s/K_n ratio became larger in the tin and mercury alloys as

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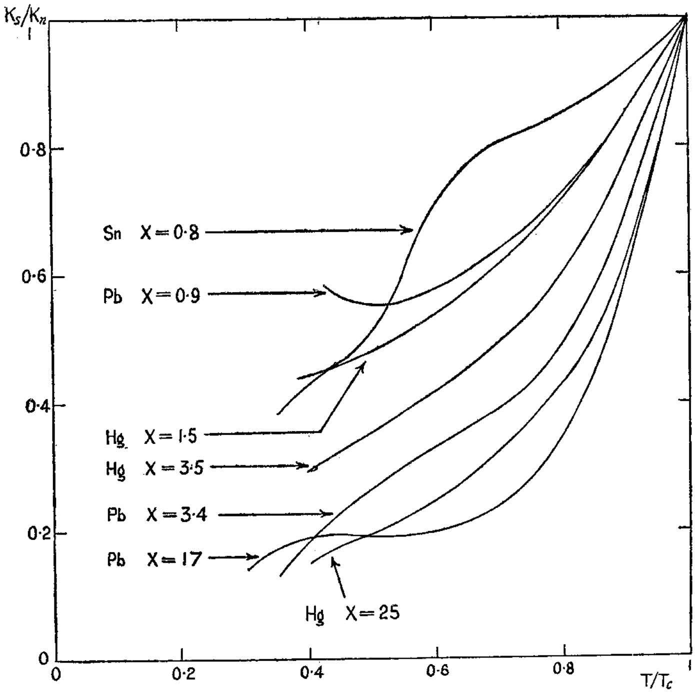
the impurity increased and the absolute value of the thermal conductivity decreased. Abnormally high values were found in the prewar results on alloys containing large percentages of indium and bismuth (de Haas and Bremmer 1936, Mendelssohn and Pontius 1937). Mendelssohn and Olsen (1950 a) were able to show that for lead–bismuth alloys the K_s/K_n function could be made to vary, as bismuth impurity was increased, from a function like that found by de Haas and Rademakers, to one where the K_s/K_n increased from unity to ten as the temperature was lowered from the critical to one third the critical temperature. They suggested that this might best be explained by some additional flow of heat such as that described in § 7.2.

Fig. 11



Graphs of K_s/K_n against T/T_c for tin, lead and mercury showing their dependence on X, the relative amount of impurity scattering. From various sources, see § 7.3.

An examination of the consequences of the alternative assumption (suggested by Hulm 1950), that these high values for K_s are due only to an increase in the lattice conductivity in the superconducting state, has been made by Olsen (1952). Assuming also the validity of his interpolation formula for K_{es}/K_{en} he calculated K_{gs}/K_{gn}. This could be described with very moderate accuracy by t^6. This does not seem to be far from what might be expected if one remembers that when the electronic thermal conductivity of superconductors is limited mainly by the lattice scattering of the electrons then K_s/K_n varies as t^5. On the other hand, the only case for which Hulm has made an evaluation of the amount of the lattice conductivity indicates that the superconducting lattice conductivity increases only as the second power of the temperature. However, in the tantalum specimen for which these calculations were made the amount of impurity scattering of the lattice waves was very considerable.

In order to disentangle the problems sketched above it would appear to be extremely desirable for some more accurate work to be carried out to clarify the behaviour of the K_s/K_n ratio and hence that of the lattice conductivity. Only a series of measurements on different substances and with varying impurity contents would allow sufficiently confident estimates of K_{es}/K_{en} to be made to establish the temperature dependence of the lattice conductivity in the superconducting state.

7.5. *Thermal Conductivity in the Intermediate State*

The experiments of Mendelssohn and Pontius (1937) and of de Haas and Rademakers (1940) showed that when the superconductivity of a cylinder of pure lead was destroyed by a transverse magnetic field the heat resistance changed almost linearly from its superconducting to its normal value as the field was increased from $\frac{1}{2}H_c$ to its critical value H_c. A specimen of lead containing 10% bismuth showed a more extended transition, as might also be expected from a knowledge of the electrical behaviour of superconducting alloys. This linearity of the change of thermal resistance is in good agreement with that obtained if calculations are carried out on the assumption that the cylinder in the intermediate state is made up of a series of laminae normal to the axis, each with either the normal or the superconducting conductivity.

Measurements of the transition in a longitudinal field have been made by Hulm (1950) on tin, and Mendelssohn and Olsen on lead, and it is found that these transitions are sharp within the limits set by the demagnetization factors of the specimens. In the case of lead at 2·7° K it is even found (Olsen 1952) that the transition in the thermal conductivity is sharper than the electrical transition observed by MacDonald and Mendelssohn (1949) in very pure specimens of small demagnetizing factor.

Transverse transitions observed by Mendelssohn and Olsen (1950 c) in lead with a small (0·02%) impurity of bismuth at 5·3° K were found to be similar to those found by earlier workers. At a lower temperature (2·9° K) however, an entirely new and unexpected type of transition (fig. 12) occurred. Instead of increasing monotonically from the superconducting to the normal value as the magnetic field increased, the thermal conductivity fell very sharply when field first penetrated the metal, and then after reaching a minimum the conductivity increased to the normal value. This has since been found in pure lead by Webber and Spohr (1951), Olsen and Renton (1952) and Mendelssohn and

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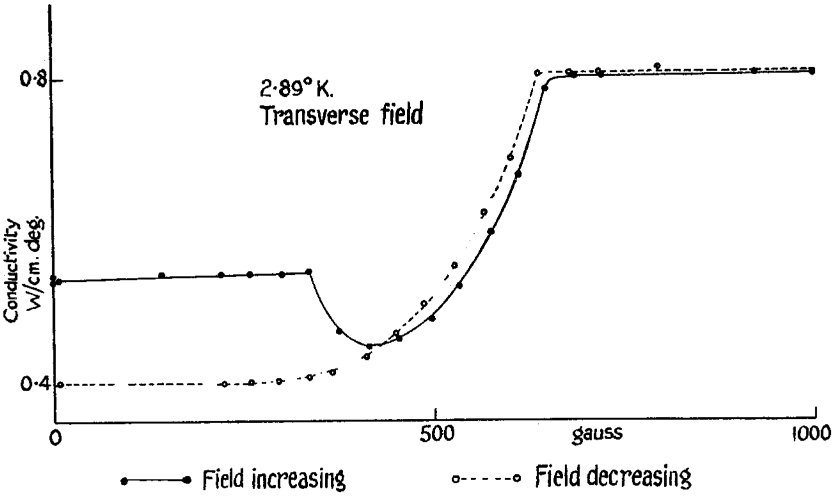
Rosenberg (1952 c). Detwiler and Fairbank (1952) have also observed similar transitions in very pure tin and indium at about 2·2° K. This behaviour is of course inconsistent with any combination of regions having either the normal conductivity K_n, or the superconducting conductivity K_s, and this has been pointed out by Mendelssohn and Olsen (1950 c).

A solution can however be found in terms of either of three explanations. That first suggested by Mendelssohn and Olsen was one based on the hypothesis of a heat circulation in the superconducting state. A second explanation is based on a suggestion by Landau (1943) that there might be an extra scattering of the electrons at the boundaries of the laminae constituting the intermediate state. The transitions observed may however also be explained on the basis of Hulm's suggestion of an increased superconductive lattice conductivity (Olsen 1951, Webber and Spohr 1951, Olsen 1952) if the mean free path of the electrons and/or lattice waves is comparable in length with the thickness of the regions forming the intermediate state. The appearance of a very small percentage of normal material can then remove the high lattice conductivity.

Fig. 12



The change in the thermal conductivity of a lead–bismuth alloy during the transition from the superconducting to the normal state showing the initial decrease in the conductivity in increasing field. (Mendelssohn and Olsen 1951 c.)

7.6. *Work below* 1° K

The first work on the thermal conductivity of superconductors below 1° K was carried out by Heer and Daunt (1949 a). They were able to measure K_s/K_n for tin and tantalum between 0·2 and 1° K and their measurements indicated that K_s/K_n varied as $(T/T_c)^2$. For tin at 0·65° K it was found that $K_s/K_n = 1/40$, and for tantalum at 0·55° K that $K_s/K_n = 1/60$.

Goodman (1951) has measured the thermal conductivity of tin specimens of various purities down to 0·2° K. He was able to eliminate the effect of the lattice conductivity and he gives a curve for the ratio K_{es}/K_{en}. This is found to be in close agreement with the ratio obtained from Heisenberg's theory.

Olsen and Renton (1952) have made measurements on a lead single crystal down to 0·3° K. They find that the superconducting thermal conductivity follows a T^3 law below about 0·9° K. Above that temperature the conductivity rises somewhat more steeply.

Heisenberg's theory and Goodman's experimental work indicate that the electronic thermal conductivity will be very small below 1° K. It is therefore reasonable to suppose that the conductivity is entirely due to the lattice. The actual observed conductivity would correspond to the case of pure boundary scattering with free path 5 times less than the diameter of the single crystal rod. It is not clear whether this discrepancy is to be ascribed to an unreliability in the simple theory of boundary scattering or whether it is simply due to filaments of normal metal remaining frozen in after demagnetization. Such filaments might also be expected to give a $1/T^3$ term in the thermal resistance. The closeness with which the conductivity follows a T^3 law would appear to confirm that the amount of electronic scattering of the lattice waves is very small.

Olsen and Renton have also measured the variation with magnetic field of the thermal conductivity at 0·43 and 0·7° K. Their curves show the minimum observed at higher temperatures, but in a less pronounced form. The possibility of some field remaining frozen in after the demagnetization makes it difficult to draw reliable conclusions from these measurements, but the shallowness of the minimum might well be taken as evidence that K_{es} and K_{gs} are more nearly equal than is assumed above.

§8. EXPERIMENTAL TECHNIQUES

8.1. *General Arrangement*

The basic set-up for all the experimental work is essentially the same. The specimen is in rod form, a few centimetres long and perhaps up to five millimetres in diameter. It is usually mounted vertically by one end in an evacuated container so that no heat can be transmitted by conduction or convection to the walls. This end is in good thermal contact with a liquid helium bath for the lowest temperature measurements and with liquid hydrogen or air for readings at higher temperatures. Radiation losses are small at these temperatures, but in some cases a radiation shield is fitted to surround the specimen and the thermometers. A small electric heater is fitted to the free end of the specimen. Potential as well as current leads are fitted to the latter so that the power supplied can be measured. This is usually of the order of a few milli-watts.

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8.2. *Measurement of the Temperature Difference*

The measurement of the temperature difference along the rod due to a given heat flow from the free end, was in the earlier experiments made with one thermometer (e.g. de Nobel 1951). This was attached near the heater and the fixed end of the rod was assumed to be at the temperature of the helium bath, which could be found with a knowledge of its vapour pressure. Whilst this assumption is sometimes quite justified, it requires an almost perfect thermal contact at the cold end and this is in many cases extremely difficult to make. A more satisfactory method of measuring the temperature gradient is to use two thermometers fixed a few centimetres apart along the rod. This is done in most of the recent work. The thermometers are either helium gas thermometers or electrical resistance thermometers and the measuring device either records the absolute temperature of each thermometer, or a differential arrangement is used which gives the temperature difference directly.

8.3. *Resistance Thermometers*

Electrical resistance thermometers have been used by de Nobel (1949, 1951) and by Allen and Mendoza (1948). De Nobel (1949) used lead resistance wire for measurements in the liquid hydrogen range. These were calibrated against a platinum resistance thermometer. For experiments in a magnetic field they were calibrated in that field against the vapour pressure of hydrogen. Allen and Mendoza, in the liquid helium range have used phosphor-bronze wire wound on copper formers. At each temperature where a reading was required the thermometers were calibrated at four or more points about 0·01° apart, against the helium vapour pressure. Temperature differences of 0·01 degrees were used. They state that two or three temperatures could be measured to 2% in a three to four hour run. For experiments below 1° K carbon resistance thermometers have been used (Olsen and Renton 1952).

8.4. *Gas Thermometers*

The advantage of electrical resistance thermometers is that the external equipment required is readily available—a potentiometer or a bridge—and that they are probably simpler to make and to fit than are gas thermometers. Nevertheless gas thermometers are widely used. The most important reason for this is that the calibration is unaffected by a magnetic field and hence they are particularly useful in the investigations of superconductors and magneto-resistive effects. Another advantage is that the number of calibration points required is very small because the gas can be assumed to obey the ideal gas laws so long as the pressure is not too high. Hence a calibration at the boiling point of liquid hydrogen is usually sufficient for readings between 10° and 40° K, and one at the boiling point of liquid helium for readings between 2° and 10° K, although these can be supplemented by extra calibrations against vapour pressure of the bath at various temperatures. A correction must be applied to take into account the 'dead' or external volume of the gas thermometer system and for this reason the connecting capillary and the dead space at the top of the manometer used to measure the gas pressure should be made as small as possible. In this way the corrections can be greatly reduced. To measure temperature differences directly, it is simple to connect the two thermometers to opposite sides of a differential manometer, a U-tube containing butyl phthalate usually being used. The difference in levels then gives a direct indication of the temperature difference. Such an arrangement also cancels out certain small correction factors.

When used in this way it is important that both thermometers and their tubing have exactly the same dimensions. This is usually achieved sufficiently by careful machining and measurement although Andrews, Webber and Spohr (1951) have gone farther and have etched the copper thermometer bulbs and have then adjusted a moveable piston in a cylinder in one thermometer circuit until no difference in pressure was observed between the two thermometers when the temperature was varied from nitrogen to room temperature. It is of course important, particularly if the external volume is unavoidably large, to protect it from sudden changes of temperature. The absolute pressure in each thermometer can be measured by joining a third arm, which is kept continuously pumped, to the centre of the differential manometer. Systems on these lines are used by Hulm, Andrews, Webber and Spohr, Berman and MacDonald, Estermann and Zimmerman, Mendelssohn and Olsen, and Mendelssohn and Rosenberg. The difference in levels is measured on a scale either directly or through a telescope. Hulm (1951) illuminated the meniscuses from behind and measured the position of each on a travelling microscope and could measure temperature differences of the order of 0·01 degree to about 1%. Estermann and Zimmerman (1951) had an interesting arrangement in which a calibrated adjustable bellows in one limb of the manometer was adjusted until the difference in levels in the manometer was zero. From the amount of movement required the temperature difference could be calculated. This method had the advantage that no external volume correction was necessary. They were not able, however, to measure the absolute temperature of the thermometers and they had to estimate the temperature of the specimen from the temperature of the helium bath. This necessitates having a very good thermal contact between the bath and the specimen.

8.5. *Thermal Contact with the Specimen*

The attachment of the specimen to the thermometers occasionally causes difficulty, especially if the metal will not take hard or soft solder. In this case it is sometimes possible to copper plate the specimen and to soft solder on to this plating. This has been done for the aluminium specimens of Webber, Andrews and Spohr (1951). Another technique is to spot weld a small platinum ring to the specimen and to solder a copper contact to this ring. The copper is then soldered with Wood's

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metal to the thermometer. Mendelssohn and Olsen have used this method for tantalum and niobium. Small clamps can be used if soldering techniques are not possible and in this case thermal contact can be improved by coating the clamp and specimen with glycerol or celluloid cement before tightening it up.

8.6. *Method of Mounting for Magnetic Measurements*

Most workers have mounted their specimens vertically in the apparatus. If magnetic measurements are being taken, however, it is often convenient to mount it horizontally, because readings can then be taken in both a transverse and in a longitudinal field with the same type of magnet. If the specimen is vertical two different magnets will be required—a solenoid for the longitudinal field and an ordinary magnet for the transverse field.

8.7. *Attainment of Steady Temperatures in the Full Range up to* 90° K

In order to obtain results over the full temperature range it is necessary to obtain steady temperatures not only in the helium, hydrogen and oxygen regions, but also in the ranges 4–10° K and 20–60° K. Temperatures in the 4–10° K region are obtained fairly easily if a Simon expansion liquefier is used. The gas is not expanded fully to atmospheric pressure but is allowed to expand slowly. By controlling this expansion with a needle valve any temperature between 4 and 10° K can be maintained (MacDonald and Mendelssohn 1950). For temperatures above 20° K a small heater is fitted either to the fixed end of the specimen or around the high pressure pot of the liquefier and this is used to raise the temperature of the specimen by any desired amount above 20° K. This method may also be used for temperatures between 4° and 10° K.

Further details covering the experimental technique of gas thermometry are given by Hulm (1950) and Berman (1951 a).

8.8. *Method of Wilkinson and Wilks*

A useful method of determining the mean conductivity of a specimen has been given by Wilkinson and Wilks (1948). One end of the specimen is in contact with liquid helium but the other one is kept at the temperature of liquid hydrogen. The heat input is found by measuring the amount of liquid helium which is evaporated. No heater or thermometers are required. This is a particularly useful technique when information is needed regarding materials to be used in the construction of low temperature apparatus.

8.9. *Technique below* 1° K

Measurements in the adiabatic demagnetization region present new problems both because of the limited range of thermometers available, and because of the need for very small heat input.

Heer and Daunt (1949 a) used the specimen as a connecting link between a large and a small pill of paramagnetic salt. These were demagnetized to slightly different temperatures, and the heating up rate of the smaller pill was observed with the specimen in the normal and in the superconducting state. Goodman (1951) also used a two-pill technique, but with pills of equal size. The rate at which temperature equilibrium was established between the two pills was observed. He was able to allow for the effects of contact resistance between salt and specimen by making measurements on several specimens with a wide range of conductivities.

Olsen and Renton (1952) had only a single pill and used a technique similar to that normally used at higher temperatures. Carbon thermometers painted directly on the specimen measured the temperature gradient established by a small electric heater at one end of the specimen. It was of course necessary to work with very small heat inputs to avoid heating the paramagnetic salt too rapidly. One advantage of this technique is that it allows measurement of approximately isothermal magnetic hysteresis cycles.

8.10. *Superconducting Heat Switch*

One of the problems of very low temperature work is the need for a method of making and breaking thermal connection between different parts of an apparatus. The normal method using an exchange gas ceases to work at temperatures below about 0·7° K when even helium has too low a vapour pressure to conduct heat effectively. The use as a heat switch of a superconductor where K_n and K_s are widely different has been suggested independently by Gorter (1948), Heer and Daunt (1949 a, b) and by Mendelssohn and Olsen (1950 a).

Darby, Hatton, Rollin, Seymour and Silsbee (1951) have successfully used this type of heat connection in experiments on two stage demagnetization. The aim in designing a heat switch will be to have as high an on/off ratio of conductances as possible. This ratio will be very nearly equal to the ratio at the temperature, T, of the hot end. K_s/K_n will vary at least as $(T/T_c)^2$ at the lower temperatures, and it is thus clearly desirable to have as low a value of T as possible.

Darby *et al.* used lead as the connecting link between a pill of paramagnetic salt at 0·25° K and the pill it was desired to demagnetize to a low temperature. They were able to obtain a temperature of approximately 3×10^{-3} ° K by demagnetizing from a magnetic field of only 4300 gauss, and 10^{-3} ° K from a field of 9000 gauss. A heating up rate of only 1 erg/min was obtained and it was possible to keep the temperature below 10^{-2} ° K for 40 minutes. It is of interest to note, as the original paper shows, that this heating up rate may be considered a confirmation that K_{es}/K_{en} drops more rapidly that T^2 at the lowest temperatures.

§9. CONCLUSION

In concluding this paper we should like to list some of the programmes of experimental work on thermal conductivity which we regard as the most immediately desirable.

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(*a*) An extension of the work on the thermal conductivity of the elements in the highest state of purity, preferably in the form of single crystals. This is particularly important for elements with simple atomic and crystalline structures where the theoretical predictions can be more easily evaluated.

(*b*) An investigation of the effect of known amounts of impurity and an examination of how this alters the lattice and electronic conductivities.

(*c*) An investigation into the effects of mechanical and heat treatments and the correlation between the change in the thermal conductivity and the mechanical properties of the metal. This is of course connected with the need for similar research on the electrical conductivity.

(*d*) Further measurements on anisotropic single crystals.

(*e*) Further data concerning the change of thermal and electrical conductivities, and of the Lorenz number, in a magnetic field.

(*f*) Further experiments on superconductors and superconducting alloys which will give more data on the K_s/K_n relationships.

Experiments on these lines will yield valuable information on electron and phonon scattering mechanisms.

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