

THE THERMAL CONDUCTIVITY OF PURE METALS AT LOW TEMPERATURES ACCORDING TO THE FREE ELECTRON THEORY

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Summary

The paper discusses the validity of Sondheimer's (1950) variational method of solving the integral (Bloch) equation for the distribution of free electrons, interacting with lattice vibrations, in the case of thermal conduction at low temperatures. This equation is solved numerically, and it is found that the resulting thermal conductivity is about 11 per cent. larger than the value calculated by Sondheimer.

I. INTRODUCTION

It can easily be shown that the thermal conductivity of a pure metal, calculated on the assumption of energy transport by free electrons interacting with lattice vibrations but in the absence of scattering by static imperfections, should be inversely proportional to the square of the absolute temperature at sufficiently low temperatures. However, no analytical solution has been found to the Bloch integral equation which must be solved to obtain the multiplicative constant to that relationship.

The variational method of Kohler (1948, 1949), extended by Sondheimer (1950), overcomes the difficulty by adjusting the parameters of a linear trial function by a variational principle which leads to a stationary expression for the conductivity. The particular trial functions chosen are polynomials in the electron energy.

Clearly the results of such calculations must be sensitive, at least to some degree, to the particular form of the trial function used. Since it can be shown that the actual solution of the Bloch equation cannot be represented by a polynomial in electron energy, some doubt is thrown on the accuracy of Sondheimer's approximation. In order to clarify this point, the Bloch equation has been solved numerically for the region in which the T^{-2} law applies, where the error of the Sondheimer method is probably largest. The present result is estimated to be accurate to better than 0.5 per cent., and it is found that the theoretical conductivity exceeds Sondheimer's value by 11 per cent.

II. THE VARIATIONAL METHOD

Consider the equation

$$S \cdot c(E) = E^n, \dots\dots\dots (1)$$

where $c(E)$ is a function of E , later to be identified as the electron energy, and S is a linear operator, so that $S \cdot c(E)$ is also a function of E . Consider a real

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Hilbert space, whose elements are all self-adjoint and are the functions c . Scalar products are defined by the integrals

$$(c_1, c_2) = (c_2, c_1) = \int c_1(E) c_2(E) \frac{df^0}{dE} dE, \quad \dots\dots\dots (2)$$

$f^0(E)$ being the Fermi distribution function. Let S have the special property

$$(Sc_1, c_2) = (Sc_2, c_1), \quad \dots\dots\dots (3)$$

and

$$(Sc_1, c_1) \geq 0. \quad \dots\dots\dots (4)$$

It is then easily shown by considering the variation of c that the solution of (1) is such that

$$(Sc, c) \text{ is a maximum, } \dots\dots\dots (5)$$

subject to the normalization condition

$$(Sc, c) = (E^n, c). \quad \dots\dots\dots (6)$$

In the Kohler-Sondheimer method, S is the integral operator describing the rate of change of $c(E)$ —a measure of the deviation of the distribution function from equilibrium—due to the interaction of the free electrons with the lattice vibrations. It was shown by Kohler (1948), that (3) and (4) are indeed satisfied.

Let $c^{(3/2)}$ and $c^{(5/2)}$ be the solutions of (1) with $n=3/2$ and $n=5/2$. Defining coefficients

$$K_{m,n} = K_{n,m} = (c^{(n+\frac{1}{2})}, E^{n+\frac{1}{2}}) = (c^{(n+\frac{1}{2})}, E^{m+\frac{1}{2}}), \quad \dots\dots\dots (7)$$

then the electrical conductivity is proportional to $K_{1,1}$, while the thermal conductivity is proportional to

$$\frac{K_{2,2}K_{1,1} - (K_{1,1})^2}{K_{1,1}T}. \quad \dots\dots\dots (8)$$

It is obvious from (5) and (6) that the coefficients $K_{2,2}$ and $K_{1,1}$ are stationary; that is, given a trial function deviating from the true solution by δc , the error in these coefficients will be of order $(\delta c, \delta c)$. The coefficient $K_{1,2}$ is not stationary for general variations, but Makinson (personal communication) has shown that, with the trial function a polynomial in E and its variations thus restricted, the Sondheimer method also leads to a stationary expression for $K_{1,2}$. The expression (8) for the thermal conductivity is then stationary.

The same result would be obtained if the Bloch equation for the case of thermal conduction were written in the form given by Bethe (see Sommerfeld and Bethe 1933), who showed that the thermal conductivity, correct to the first significant order in KT/ζ , is given by

$$\kappa \propto (c, \varepsilon), \quad \dots\dots\dots (9)$$

where $c(\varepsilon)$ is the solution of

$$S \cdot c(\varepsilon) = \varepsilon, \quad \dots\dots\dots (10)$$

and $\varepsilon = (E - \zeta)/KT$. The variational method can again be applied to (10). The expression (9) is of similar form to $K_{1,1}$ or $K_{2,2}$, and it is easily seen to be

stationary and a maximum. This formulation of the problem is more easily discussed than Kohler's. The function $c(\varepsilon)$ is, except for terms of higher order in KT/ζ , a linear combination of $c^{(3/2)}$ and $c^{(5/2)}$.

In the Kohler-Sondheimer method, the trial functions $c(E)$ are expressed in a series of ascending powers of E , whose coefficients are evaluated and substituted into the stationary expression for the transfer coefficients. This is equivalent to expressing $c(\varepsilon)$ as a power series in ε , and substituting the coefficients into (9). In practice only terms up to the cubic are retained. Now the function $c^{(3/2)}$ can be expressed very well by the first few terms of a power series; but the function $c^{(5/2)}$ cannot be thus represented at low temperatures for a pure metal, because the solution $c(\varepsilon)$ of (10)—given explicitly in (11) below—approaches a constant value asymptotically, as is easily seen by inspection. Thus the variational method, while giving good results for electrical conduction, and for thermal conduction when the Wiedemann-Franz law is obeyed, cannot give the correct solution $c(\varepsilon)$ for thermal conduction in a pure metal at low temperatures.

It does not necessarily follow that the variational method gives a value of the thermal conductivity seriously in error, for, if $c_p(\varepsilon)$ is the polynomial trial function, the approximation (c_p, ε) to (9) differs from the true value only by a term of second order in $\delta c = c_p - c$. However, this term is not necessarily small. In the real Hilbert space introduced above, all functions $c_p(\varepsilon)$ which are cubic polynomials form a subspace P . The true solution $c(\varepsilon)$ evidently lies outside this subspace, since it cannot be represented by a cubic. Thus the length $(\delta c, \delta c)^{1/2}$ cannot be less than that of the component of $c(\varepsilon)$ orthogonal to P , and this sets a lower limit to the second order error in (c, ε) . It may be that $(\delta c, \delta c)$ is not negligible compared with (c, c) .

It does not seem possible to give more than this qualitative discussion of the error, which from the above considerations must of course be negative. Equation (10) has therefore been solved numerically for a pure metal at very low temperatures, and the conductivity, varying as T^{-2} , has been evaluated from (9).

III. NUMERICAL SOLUTION OF THE BLOCH EQUATION

Disregarding multiplicative constants, the explicit form of (10) at low temperatures ($T \ll \theta$) in the absence of scattering by static imperfections is

$$\int_0^\infty \frac{x^2 dx}{e^x - 1} \left\{ [c(\varepsilon + x) - c(\varepsilon)] \frac{e^\varepsilon + 1}{e^\varepsilon + e^{-x}} + [c(\varepsilon - x) - c(\varepsilon)] \frac{e^{-\varepsilon} + 1}{e^{-\varepsilon} + e^{-x}} \right\} = \varepsilon. \quad \dots (11)$$

The symmetry of (11) requires that $c(\varepsilon)$ shall be an odd function of ε , and it is seen easily that $c(\varepsilon) \propto \varepsilon$ for small ε , and that $c'(\varepsilon) \propto \varepsilon^{-2}$ for large ε .

Two methods were used to solve (11) numerically, both of which gave substantially the same results. The lengthy computations involved were done on an automatic desk calculator.

In the first method the integral equation was replaced by a set of 10 simultaneous linear equations, with the values of $c(\varepsilon)$ at 10 equally spaced points as unknowns. The coefficients of the equations were the values of the kernel at these discrete points. Use was made of the property $c(-\varepsilon) = -c(\varepsilon)$, $c(0) = 0$.

It was assumed that $c(\epsilon)=0$ for all values beyond the 10th point. The set of 10 equations was solved by a method of successive elimination adapted for desk machines, as described for example by Milne (1949). Two such calculations were made, using spacings of 0.5 and 1.0 respectively, and the two sets of solutions are marked in Figure 1. The assumption $c(\epsilon)=0$ for large ϵ was seen to be inconsistent with the results, but, since the two sets of results did not differ greatly in spite of the different cut-off, it seems that the effect of this cut-off is not critical.

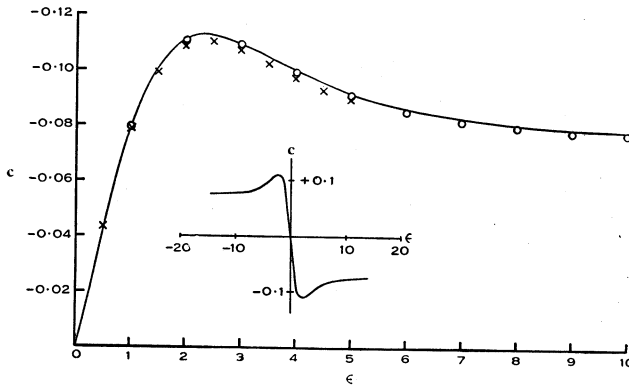


Fig. 1.—Solution of equation (10), replacing the integral equation by a discrete and finite set of linear equations. Crosses for $\epsilon=0.5, 1, \dots, 5$; circles for $\epsilon=1, 2, \dots, 10$. Full curve: result of the iterative method. Inset shows the form of $c(\epsilon)$.

It would have been desirable to shorten the intervals without decreasing the range of unknown values. Unfortunately the methods of computation available did not permit a significant increase in the number of unknowns. However, it was noticed that in each equation the diagonal term was dominant, which suggested the following iterative procedure:

Let $c(\epsilon)=c_0(\epsilon)+c_1(\epsilon)+c_2(\epsilon)+\dots$, where $c_0(\epsilon)$ is given by

$$\int_0^\infty \frac{x^2 dx}{e^x - 1} \left[\frac{e^\epsilon + 1}{e^\epsilon + e^{-x}} + \frac{e^{-\epsilon} + 1}{e^{-\epsilon} + e^{-x}} \right] c_0(\epsilon) = -\epsilon, \quad \dots \dots \dots (12)$$

and

$$\int_0^\infty \frac{x^2 dx}{e^x - 1} \left\{ [c_{n-1}(\epsilon+x) - c_n(\epsilon)] \frac{e^\epsilon + 1}{e^\epsilon + e^{-x}} + [c_{n-1}(\epsilon-x) - c_n(\epsilon)] \frac{e^{-\epsilon} + 1}{e^{-\epsilon} + e^{-x}} \right\} = 0. \quad \dots \dots \dots (13)$$

Evaluating $c_0(\epsilon)$, $c_1(\epsilon)$, $c_2(\epsilon)$, etc. in turn from these definite integrals, successive approximations were obtained. The integrations were done numerically and $c_{n-1}(\epsilon)$ was obtained for a few values of ϵ . The intermediate values were obtained by interpolation and used for the next iteration. The iteration was broken off after c_3 . The smallness of $c_n(\epsilon)$ indicates whether $c(\epsilon)=c_0(\epsilon)+c_1(\epsilon)+\dots+c_{n-1}(\epsilon)$ is a good approximation. While the convergence of this method was not examined, the actual results, plotted in Figure 2, indicate that it is satisfactory.

No investigation was made of the accumulation of errors, and therefore the solution had to be tested by substitution into (11). The conductivity can then be obtained from (9). These two steps were combined and a further correction to the conductivity was obtained by multiplying the solution by an arbitrary constant and renormalizing it using the relation

$$(Sc, c) = (\varepsilon, c). \quad (14)$$

As before, with c thus normalized, the expression (ε, c) is stationary. The renormalization correction was only 0.4 per cent.; hence the conductivity thus calculated is accurate to at least the same limit.

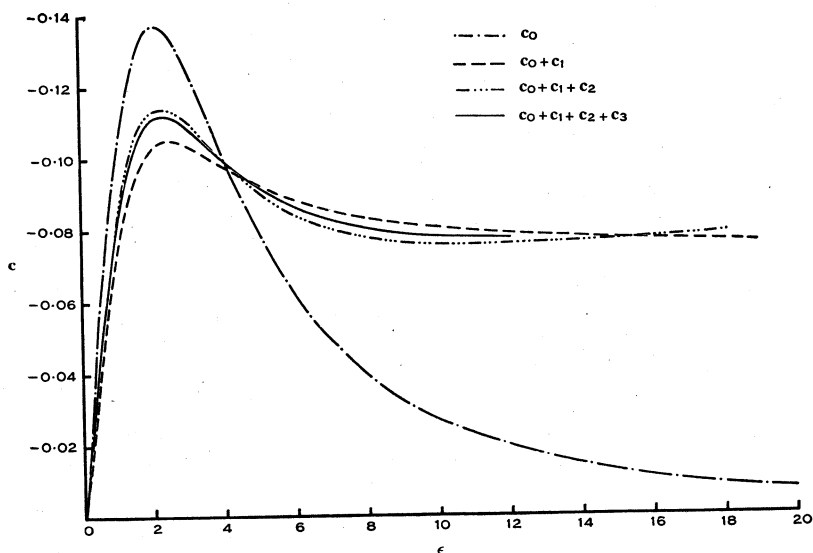


Fig. 2.—Solution of equation (9) by iteration.

IV. CONCLUSION

Including the multiplicative factors in the Bloch equation and the expression for the thermal conductivity, which have not been stated here, but are given by Bethe (see Sommerfeld and Bethe 1933, Section 39), the thermal conductivity in the T^{-2} region has been obtained from the numerical solution of (11). Expressing this in terms of a hypothetical thermal conductivity at high temperatures, assuming a Debye spectrum of limiting frequency $2\pi K\theta/h$, a spherical Fermi surface due to N free electrons per atom, and absence of any processes other than those considered in the Bloch theory for a pure metal (in particular no Umklapp-processes), one obtains

$$\kappa(T) = \kappa(\infty)(\theta/T)^2(64 \cdot 0 N^{2/3})^{-1}. \quad (15)$$

The result of Sondheimer's (1950) third approximation, when similarly expressed, has a numerical constant of 71.6 in place of 64.0, while the first approximation, obtained by Wilson (1937), leads to 95.3. Sondheimer's value differs from the present solution by only 11 per cent. As is to be expected, the present method gives a larger value for the conductivity than Sondheimer's.

In addition to the conductivity, these calculations also give the functional dependence of $c(\epsilon)$. The variational method, using a polynomial trial function, does not even approximate the true solution, though it gives reasonable values for the conductivity. While the function $c(\epsilon)$ is only of secondary interest, knowledge of it may be useful in other work.

There are well-known discrepancies between the Bloch theory and the thermal conductivity observed at low temperatures (Hulm 1950, 1952; Andrews, Webber, and Spohr 1951; Berman and MacDonald 1951, 1952; White 1953), which are hardly reduced by the result of the present calculations. It thus appears that the simple free electron model is inadequate. The required modifications of the model will be discussed subsequently.

V. ACKNOWLEDGMENTS

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