THE THERMAL AND ELECTRICAL CONDUCTIVITY OF COPPER AT LOW TEMPERATURES

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Summary

Measurements have been made of the thermal conductivity from 2 to 160 °K and the electrical conductivity from $1 \cdot 4$ to 293 °K of copper in strained and annealed states.

From the results it is concluded that: (i) departures from the additive resistance hypothesis occur for both the thermal and the electrical resistance; (ii) whereas the values for "ideal" electrical resistivity, assumed due to scattering by lattice vibrations, are well represented by the theoretical relation $\rho_i = CT^5$ ($T < \Theta/10$), those for the ideal thermal resistivity require an expression $W_i = BT^{2 \cdot 4}$ ($T < \Theta/5$) rather than the theoretically derived expression $W_i = BT^2$; (iii) an anomalous increase in the product of the thermal resistance and temperature occurs at low temperatures ($T < 5$ °K), which is possibly related to the minimum in the residual electrical resistance.

I. INTRODUCTION

Theory and experiment have shown that, in most pure metals, electrons are almost solely responsible for the conduction of both heat and electricity. Wilson (1936, 1937) and Makinson (1938) have stated that the total resistivity in both cases is the sum of an impurity resistivity (W_0, ρ_0) and an "ideal" resistivity (W_i, ρ_i). Scattering by chemical and physical impurities and scattering by the lattice vibrations are the mechanisms responsible for the respective resistances.

For thermal conduction

$$1/K = W = W_0 + W_i, \qquad (1)$$

and for electrical conduction

$$1/\sigma = \rho = \rho_0 + \rho_i. \qquad (2)$$

From the experimental and theoretical aspects it is important to know the temperature dependence of these quantities and whether the additive resistance hypothesis is valid. Sondheimer (1950) has shown theoretically that departures from (1) and (2) should give a small increase in the total resistance at temperatures where the impurity and ideal resistances are of the same order of magnitude. As considerable evidence has been collected by previous workers on the failure of Matthiessen's rule for electrical resistance, the work reported here was done in order to compare the departure from additivity for the thermal

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resistance with that for the electrical resistance using materials in different states of purity.

Berman and MacDonald (1952) have examined carefully the electrical and thermal conductivities of an annealed specimen of copper of chemical purity similar to that used by the author. Their results confirmed earlier work (cf. Hulm 1950; Andrews, Webber, and Spohr 1951; Berman and MacDonald 1951) on relatively pure metals, which showed that the thermal conductivity at very low temperatures increases proportionately to temperature, reaches a maximum at $T\sim\Theta/15$, then falls approximately as T^{-2} up to $T\sim\Theta/5$, and finally approaches asymptotically a constant value; no trace of the minimum at $\Theta/4$ predicted by Makinson, Wilson, and Sondheimer is observed.

Reference should be made to the comprehensive investigation of Mendelssohn and Rosenberg (1952) on the thermal conductivity of many elements, from groups 1, 2, 3 and the transition group. Their work, however, was generally on one sample only of each element and did not extend above 40 °K, and so did not include a detailed examination of the variation of W or $W-W_0$ with temperature and purity.

In view of the results recently reported on the thermal conductivity of gold (White 1953*a*) and silver (White 1953*b*) in different states of purity, it was desirable to extend the measurements to copper and compare them with previous work. Firstly, although the impurity resistivity W_0 appears to vary inversely with temperature, the measurements on gold suggested a small increase in W_0T at very low temperatures, possibly related to the anomalous increase in ρ_0 that occurs in some metals (cf. de Haas and van den Berg 1936; Mendoza and Thomas 1951); Berman and MacDonald (1952) found a small thermal effect, much smaller than the electrical effect, in their specimen of copper. Secondly, it is well known that the Bloch-Gruneisen formula for the ideal resistivity of a pure metal in which the conduction electrons are quasi-free reduces to

$$\rho_i=CT^5, \quad \text{for } T\ll\Theta. \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (3)$$

Similarly, the transport theory predicts that

$$W_i=BT^n, \quad \text{where } n=2 \text{ for } T\ll\Theta. \quad \ldots\ldots\ldots\ldots \quad (4)$$

Measurements on gold by the author gave $n\simeq2\cdot0$, but those on silver indicated that $n\simeq2\cdot4$, hence the desirability of examining copper.

II. Experimental Details

The electrical conductivity of copper has been measured, correct to $\pm2\times10^{-5}\,\Omega$, between $1\cdot4$ °K and room temperature in a cryostat (Fig. 1), using a Mueller pattern resistance bridge. The specimen wire S, wound loosely on a mica cross, rests in the inner copper enclosure B, containing a small pressure of helium gas to ensure that temperature equilibrium between the controlled enclosure and the specimen and the gas thermometer D is maintained. This adiabatic shield B is in an evacuated enclosure A, surrounded by liquid oxygen or liquid helium. The temperature of B is maintained by controlling the vapour pressure of liquid oxygen or liquid helium in C, or, in the temperature ranges

4·3–55 °K and above 90 °K, where vapour pressure control is unsuitable, by the electrical heater coil *H*. The current to this constantan coil is either varied manually or by an electronic controller (Wylie 1948) activated by the manganin resistance element *R*. *G* is a polished copper plate cooled by liquid nitrogen to reduce the heat inflow to the helium bath. Temperatures are determined from the vapour pressure of liquid in *C* or from a butyl phthalate filled manometer connected to the helium thermometer *D*.

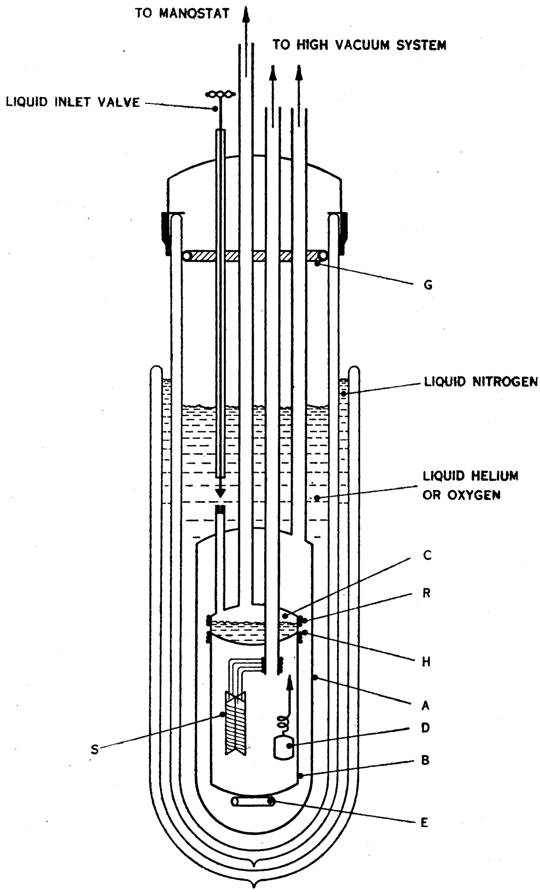

Fig. 1.—Cryostat for electrical resistance measurement.

The measurements of thermal conductivities have been made between 2 and 160 °K using the apparatus and method described elsewhere (White 1953*a*). At the higher temperatures a small correction for heat loss by radiation is applied; the probable experimental error in the results should not then exceed 1 per cent., except between 5 and 15 °K, where high values of conductivity and the necessity for small heat inputs and hence small temperature gradients increases the probable error to a maximum of about 4 per cent.

The measurements reported have been made on specimens prepared from 99·999 per cent. pure copper JM4272 for which Johnson, Matthey and Co. Ltd. quote the following impurities :

Silver $c.$ 0·0005%,
Nickel <0·0003%,
Lead $c.$ 0·0004%,

and barely visible spectral lines of gallium and iron.

The specimens for thermal conductivity were as follows :

Cu 1, 2-mm dia. rod drawn by Johnson, Matthey and Co. Ltd., measured in the " as drawn " condition ;

Cu 2, specimen Cu 1 after annealing *in vacuo* at 550 °C for 3 hr ;

Cu 3, 1-mm dia. rod drawn by Johnson, Matthey and Co. Ltd., measured in the " as drawn " condition.

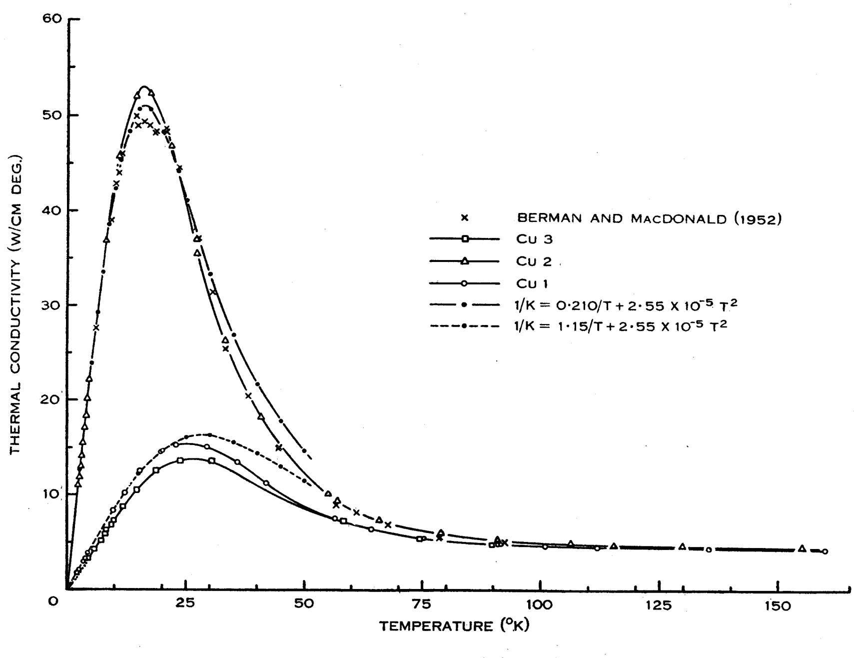

Fig. 2.—Thermal conductivity of copper.

The specimens for electrical conductivity were :

Cu I, 40 S.W.G. wire drawn by Garrett, Davidson, and Matthey Pty. Ltd., measured in the " as drawn " condition ;

Cu II, specimen Cu I after annealing *in vacuo* at 550 °C for 3 hr ;

Cu III, similar to Cu I.

The rods were about 5 cm long and the wires 300 cm. The wires had a room temperature resistance of about 4 Ω ; since the resistance of the annealed Cu II fell to about 0·05 Ω at liquid helium temperatures, the maximum error in the determination of resistivity is 0·05 per cent.

III. Results

(a) *Thermal Conductivity*

Figure 2 shows that the thermal conductivity follows the general form discussed above ; as the physical purity is increased the magnitude and temperature of the maximum varies from 13·8 W/cm deg. at 26 °K to 53 W/cm deg. at 16 °K. Disregarding for the moment the small departures of W_0T from

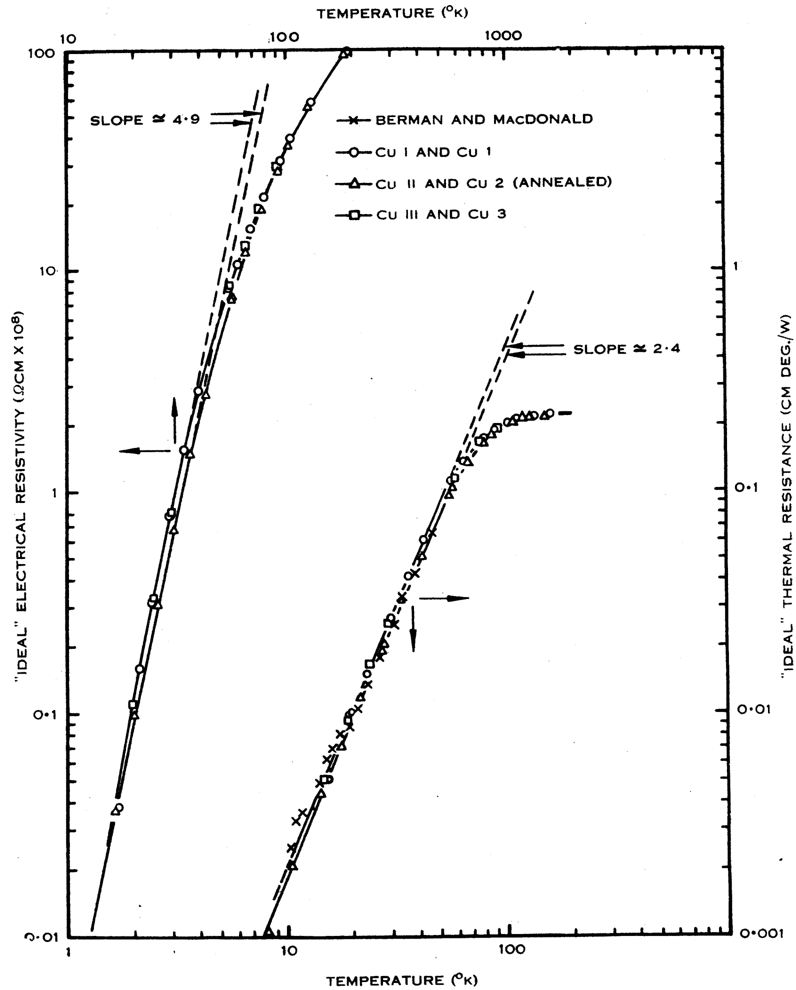

Fig. 3.—" Ideal " electrical and thermal resistance of copper.

constancy, the ideal thermal resistivity W_i will be calculated assuming equation (1) to be valid. The values of W_0T taken from Figure 4, which are used in calculating W_i for the three specimens Cu 1, Cu 2, and Cu 3, are 1·15, 0·210, and 1·32 cm deg.^{2}/W respectively.

The logarithmic plot (Fig. 3) shows that $W_i = BT^n$ up to a temperature of nearly 55 °K, with $n \simeq 2 \cdot 4$ and with the following values for B :

$$7 \cdot 9_5 \times 10^{-6} \text{ for Cu 1, Cu 3 ;}$$
$$7 \cdot 0_6 \times 10^{-6} \text{ for Cu 2.}$$

Figure 4 (*a*) illustrates the departure of the conductivity from proportionality with temperature in the region where impurity scattering is dominant. The ideal resistivity extrapolated from Figure 3 is so small below 5 °K that W_iT may be neglected in comparison with W_0T, and small corrections have been applied to the values of W_0T for $T > 5$ °K.

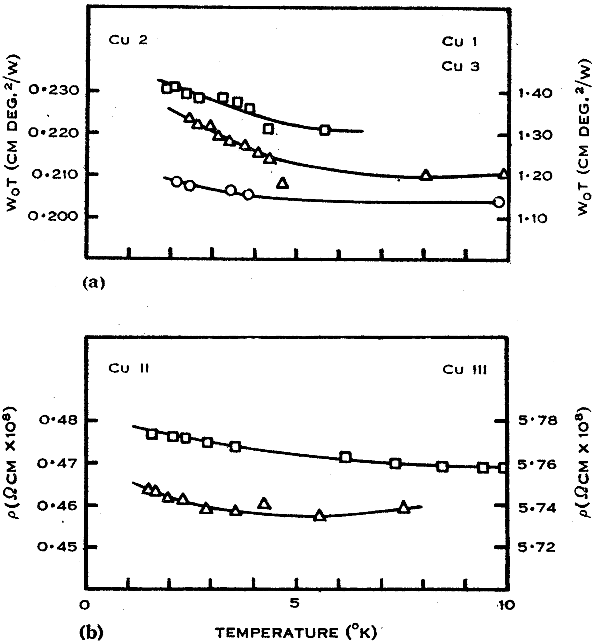

Fig. 4.—Residual resistance of copper below 10 °K. (*a*) The product of the residual thermal resistance and temperature, (*b*) the electrical resistance.
—○— Cu 1.
—△— Cu II and Cu 2 (annealed).
—□— Cu III and Cu 3.

(*b*) *Electrical Conductivity*

The values of electrical conductivity or resistance are not presented over the full temperature range, as superficially they show no unusual features. The resistance is almost constant below 10 °K and, at relatively high temperatures, increases proportionately to the temperature. For the range from 10 to 35 °K, the resistivity in ohm cm is well represented by

$$\rho = 0 \cdot 0510 \times 10^{-6} + 3 \cdot 7 \times 10^{-16} T^5 \text{ for Cu I,}$$
$$\rho = 0 \cdot 0576 \times 10^{-6} + 3 \cdot 7 \times 10^{-16} T^5 \text{ for Cu III,}$$
$$\rho = 0 \cdot 00458 \times 10^{-6} + 2 \cdot 7_5 \times 10^{-16} T^5 \text{ for Cu II.}$$

The value for C of $2 \cdot 7_5 \times 10^{-16}$ lies reasonably close to the figure of $2 \cdot 64 \times 10^{-16}$ obtained by Berman and MacDonald (1952) for a specimen of similar purity. Figure 3 shows the ideal resistivity ρ_i, calculated from the experimental values of ρ assuming Matthiessen's rule, that is, $\rho_i = \rho - \rho_0$, to be valid.

The small variation in residual resistivity with temperature is illustrated in Figure 4 (*b*) in which the observed values ρ have been plotted.

IV. Discussion

(*a*) *Additivity and Ideal Resistance*

In both the electrical and the thermal measurements, the specimens of higher physical purity have a lower apparent ideal resistance, an effect previously noted by the author in the thermal conductivity of gold and silver. This may be accounted for by a departure from the additive hypothesis of equations (**1**) and (**2**). The direction of the departure and the fact that, for the electrical resistance at least, the departure appears greatest in the range 30–40 °K, where the ideal and impurity resistances are comparable, are as predicted by Sondheimer (1950) although the effect appears to be of greater magnitude than the theory predicts. The variation of the ideal resistivity with purity is illustrated by calculation at various temperatures of the Lorenz number $L_i = \rho_i / W_i T$ from the smoothed values of ideal resistivity (Fig. 3) for the annealed and strained specimens. The former yield values in fairly close agreement with those of Berman and MacDonald (1952); the latter give values up to 25 per cent. greater at intermediate temperatures ($T \sim 35$ °K) but comparable below 20 °K and above 45 °K.

A feature more difficult to explain is the departure of the temperature dependence of W_i from a T^2 law. It is interesting to note that the results of Berman and MacDonald* on pure annealed copper yield values of W_i (Fig. 3) which appear to vary as T^2 below 20 °K but as $T^{2 \cdot 4}$, in agreement with those of the author, between 20 and 50 °K. Since for copper $\Theta \simeq 330$ °K, it is only below $\Theta/10 \simeq 33$ °K that the theoretical temperature dependence for W_i might be expected to be well obeyed. In Figure 2 are also shown two curves calculated assuming the relation $W = A/T + BT^2$ to be true, substituting two suitable values of A from these measurements and a value of B reported by Berman and MacDonald (1952).

(*b*) *Impurity Resistance*

The evidence (see Fig. 4) for an effect in the thermal conductivity related to the changing residual electrical resistance is not conclusive but merits presentation. The electrical resistance of Cu I was not determined with sufficient accuracy to show any obvious minimum, so that an additional series of observations were made on a similar specimen Cu III. The minima observed in both strained and annealed wires were much less marked than that of Berman and MacDonald (1952). However, this is perhaps not surprising, despite the apparent

* The author is indebted to Dr. Berman for supplying numerical results of their observations, and for helpful discussion.

similarity of the samples, in view of the experiments of Gerritsen (1951) and MacDonald (1952) which showed that very small traces of particular elements might produce a strong minimum in the parent metal.

V. Conclusions

The measurements on the thermal conductivity of copper support the theory of non-additivity of the impurity and ideal resistances, as did those on gold and silver reported earlier. The electrical resistance of copper in different states of physical purity indicates a similar departure from Matthiessen's rule in the direction suggested by Sondheimer (1950).

Whereas the ideal electrical resistance varies as T^5 at temperatures below $\Theta/10$, the ideal thermal resistance varies as $T^{2.4}$ up to nearly $\Theta/5$.

At temperatures in the liquid helium region, there is a slight increase in residual electrical resistance, accompanied by a rather similar variation in the thermal parameter W_0T.

VI. Acknowledgments

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