

LATTICE THERMAL CONDUCTIVITY OF SOME COPPER ALLOYS

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Summary

The thermal and electrical conductivities of three copper-zinc alloys annealed at high temperatures, and of two copper-gold alloys, were measured over a wide range of low temperatures, and their lattice component of thermal conductivity was deduced in the range 2–90 °K. It appears that the high lattice thermal resistance at liquid helium temperatures previously found in copper-zinc alloys is a function of solute content rather than of concentration of conduction electrons and that this resistance can be reduced by high-temperature annealing. This extra resistance is thus due to dislocations locked in stable arrays by the presence of solute atoms, and not due to changes in the electronic band structure on alloying.

The lattice thermal conductivity of copper-gold alloys at liquid oxygen temperatures is limited by the scattering of phonons at the gold atoms, which are much heavier than the copper atoms. The magnitude of the thermal resistance is consistent with the theory of isotope scattering in dielectric solids.

I. INTRODUCTION

It has previously been found that the thermal conductivity at liquid helium temperatures of a number of silver alloys (Kemp *et al.* 1954, 1956) and some copper alloys (White and Woods 1955 ; Kemp *et al.* 1957) can be expressed in the form

$$\kappa = AT + BT^2. \quad \dots \dots \dots (1)$$

This is in accord with theory (Klemens 1954, 1956). The first term describes the electronic thermal conductivity, limited at these temperatures because of the scattering of the conduction electrons by lattice imperfections (in these alloys mainly by solute atoms), and is related to the residual electrical resistivity ρ_0 by

$$A = L/\rho_0, \quad \dots \dots \dots (2)$$

where $L = 2.45 \times 10^{-8} \text{ W}\Omega/\text{deg}^2$ is the Sommerfeld value of the Lorenz number. The second term describes the lattice thermal conductivity, limited at these temperatures because of the scattering of phonons by the conduction electrons and by dislocations. These give rise to lattice thermal resistivities W_E and W_D respectively, both of which vary as T^{-2} , so that

$$W_g = W_E + W_D = 1/BT^2. \quad \dots \dots \dots (3)$$

Observations of the lattice thermal conductivity at lowest temperatures thus yield a measure of $W_E + W_D$. It is generally observed that W_g increases on plastic deformation (Estermann and Zimmerman 1952 ; Kemp *et al.* 1956 ;

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Kemp *et al.* 1957), and this increase can be ascribed to the introduction of dislocations on deformation. It does not follow, however, that W_D is negligible for annealed specimens.

In Figure 1 values of $1/B = (W_E + W_D)T^2$ are plotted as a function of solute concentration (and thus of the concentration of conduction electrons) for various silver and copper alloys. These alloys had been deformed and then annealed above the recrystallization temperature. Also shown are the theoretical values of W_E for pure silver and copper, as well as $1/B$ for a very dilute alloy of iron in copper (White and Woods 1955).

If one were to assume that these annealed specimens are appreciably free from dislocations, one would have to ascribe the variation in $1/B$ to a variation in W_E . One would expect W_E to vary with electron concentration (Klemens 1954), though this variation cannot be predicted, since reliable information about the electronic band structure is lacking. One would, however, not have

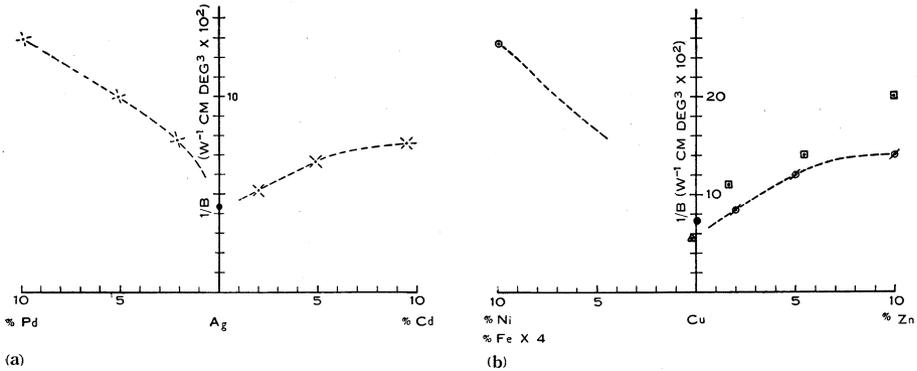


Fig. 1.—Values of $1/B$ for various annealed alloys: \times , Ag-Pd and Ag-Cd (Kemp *et al.* 1956); \odot , Cu-Ni (Estermann and Zimmerman 1952); \triangle , Cu-Fe (White and Woods 1955); \square , Cu-Zn (Kemp *et al.* 1957); ϕ , Cu-Zn (present work); \bullet , theoretical values for $W_E T^2$ (Klemens 1954).

expected to find such a strong variation with electron concentration, nor the cusp-like minimum at the electron concentration of the pure metal. It appears that $1/B$ does not depend on electron concentration, but rather on the number of impurity atoms, irrespective of their valency.

This suggests that the variation of $1/B$ is due not only to a variation of W_E , but mainly to an increase of W_D with increasing impurity content. This would imply that a number of dislocations are locked by the impurity atoms, and cannot be removed by normal annealing just above the recrystallization temperature. The number of dislocations thus locked in a stable configuration seem to depend mainly on the impurity content, with some dependence on the nature of the impurity.

This supposition was tested as follows:

(a) When the impurity is another monovalent metal, the concentration of conduction electrons is not affected by alloying, so that W_E should have the same value as for the pure metal. Any increase in the value of $1/B$ over that for an

alloy of similar electron concentration but smaller number of impurity atoms must thus be ascribed to locked dislocations. Two copper-gold alloys (7.5 and 16.5 per cent. Au per atom*) were measured, and their values of $1/B$ were indeed found to be comparable to those of copper-zinc alloys of similar solute content, rather than to alloys of similar electron concentration.

(b) An attempt was made to remove some of these locked dislocations by annealing as close as practicable to the melting point. Three copper-zinc alloys (2, 5, and 10 per cent. Zn) were annealed at 850 °C, some 150 °C below the melting point, with due precaution to prevent loss of zinc by evaporation. It was found that there was a change in B , so that this annealing treatment apparently did remove some dislocations. However, the new value of W_g still exceeds the theoretical value of W_E , as well as the value of W_g found by White and Woods for their very dilute alloy, so that it is concluded that this annealing treatment removed only a fraction of the dislocations.

II. COPPER-GOLD ALLOYS

Two specimens of copper-gold alloys (7.5 and 16.5 per cent. Au respectively) were prepared by Messrs. Garrett, Davidson, and Matthey in the form of rods, 8 cm long, 0.5 cm in diameter, annealed at 750 °C for 1 hr. Their thermal and electrical conductivities were measured and their lattice thermal conductivities were deduced from (1) and (2) in a manner previously described (Kemp *et al.* 1956; Kemp *et al.* 1957). The electrical resistivities and low

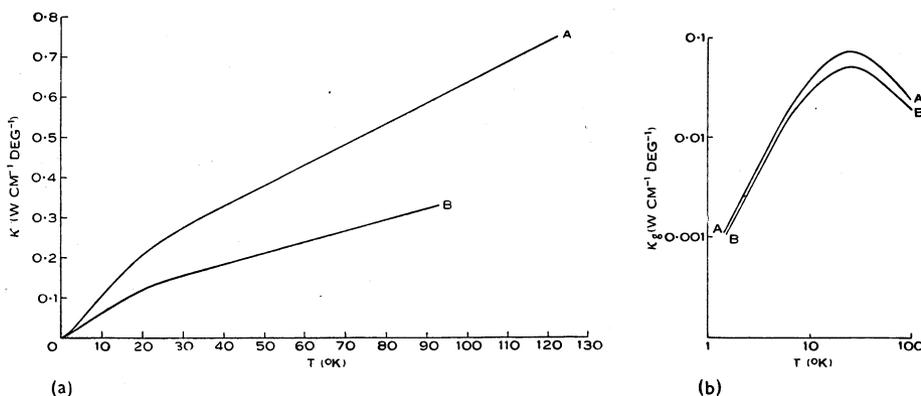


Fig. 2.—Thermal conductivity κ and lattice thermal conductivity κ_g as a function of temperature for Cu-7.5% Au (curve A) and Cu-16.5% Au (curve B).

temperature electronic thermal conductivities are given in Table 1, together with $A\rho_0$, the observed Lorenz number. The total thermal conductivities and lattice thermal conductivities are shown in Figure 2.

The electrical resistivities are in general accord with earlier measurements (e.g. Johansson and Linde 1936). At these low concentrations of gold, the alloy is a random solid solution; the higher concentration of gold (16.5 per cent.) was chosen so as just to avoid possible complications due to long-range ordering.

* All compositions are stated in atomic percentages.

The lattice conductivities are shown in Figure 2 (b). Two resistance mechanisms are clearly discernible. At low temperatures $\kappa_g \propto T^2$, and the resistance is thus due to electrons and dislocations. This resistance will be discussed in Section IV. At high temperatures $\kappa_g \propto T^{-1}$, indicating that the lattice waves are scattered by point imperfections.

TABLE 1
ELECTRONIC CONDUCTION DATA

Alloy	ρ_0	$\rho_{90} - \rho_0$ ($\mu \Omega \text{ cm}$)	$\rho_{293} - \rho_0$	A ($\text{W cm}^{-1} \text{ deg}^{-2}$)	$A\rho_0$ ($\text{W } \Omega \text{ deg}^{-2}$)
Theoretical ..	—	—	—	—	2.45×10^{-8}
Pure copper ..	—	0.28	1.67	—	—
Cu- 7.5% Au ..	3.53	0.38	1.84	6.81×10^{-3}	2.40×10^{-8}
Cu-16.5% Au ..	7.04	0.34	1.85	3.58×10^{-3}	2.52×10^{-8}
Cu- 2% Zn ..	0.56 _s	0.31	1.71	4.25×10^{-2}	2.39×10^{-8}
Cu- 5% Zn ..	1.20	0.33	1.80	1.98×10^{-2}	2.37×10^{-8}
Cu-10% Zn ..	1.94	0.37	1.95	1.24×10^{-2}	2.42×10^{-8}

The most numerous point imperfections are the gold atoms. These are much heavier than the copper atoms. There is also a difference in ionic radii, but it can be shown from the theoretical expressions for the phonon scattering cross section (Klemens 1955) that in this case the mass difference is the major source of scattering.

The thermal resistance due to foreign atoms, differing from the atoms of the parent material only with respect to their mass, is given by

$$W = \frac{\pi^2 a^3}{0.9 h v^2} \left(\frac{\Delta M}{M} \right)^2 n T, \dots\dots\dots (4)$$

where a^3 is the atomic volume, v the phonon velocity, h Planck's constant, n the impurity concentration, M the mass of a parent atom, and $M + \Delta M$ the mass of an impurity atom. If the concentration of impurity atoms becomes

TABLE 2
IMPURITY LATTICE RESISTANCE IN COPPER-GOLD ALLOYS

Alloy	ϵ	(W/T) _{calc.} ($\text{W}^{-1} \text{ cm}$)	(W/T) _{obs.} ($\text{W}^{-1} \text{ cm}$)
Cu- 7.5% Au ..	0.200	0.68	0.4
Cu-16.5% Au ..	0.331	1.12	0.5

larger, so that the average atomic mass is appreciably affected by them, the quantity $n(\Delta M/M)^2$ in (4) should be replaced by $\epsilon = \sum_a n_a (M_a - \bar{M})^2 / \bar{M}^2$, where $\bar{M} = \sum_a n_a M_a$, the summation being over all atomic species.

Values of W/T calculated from the above theory are compared in Table 2 with values of the point imperfection resistance derived from that section of

the curve of κ_g versus T where $\kappa_g \propto T^{-1}$, that is, from the values of κ_g at liquid oxygen temperatures. The observed values of W/T are smaller than the calculated ones by a factor which increases with increasing gold content.

This discrepancy is to be expected if it is remembered that the perturbation treatment must fail when the perturbation becomes too strong. The quantity ε is a convenient parameter describing the strength of the perturbation. The present theory was derived on the assumption $\varepsilon \ll 1$, which is not so in the present case. The next order of perturbation would lead to a term in the resistance proportional to ε^2 . One may still expect the perturbation treatment to converge, since $\varepsilon < 1$. The term in ε^2 would have a different temperature dependence from that in ε (W would vary between T and T^2).

The present experiments are not of sufficient accuracy to test such deviations from linear temperature dependence of W . If one thus puts empirically

$$W/T = a\varepsilon - b\varepsilon^2, \dots\dots\dots (5)$$

and determines a and b from the data of Table 2, then the coefficient a should agree with the predictions of equation (4).

From the present data, one obtains $a=3$, $b=5$, while from equation (4) $a=0.68/0.200=3.4$. Thus, considering the inaccuracy of the deduced values of κ_g at these higher temperatures, and the nature of the extrapolation of W/T to small values of ε , the agreement between theory and observation is quite satisfactory.

This may be contrasted with the disagreement between theory and observations in respect to values of W/T due to the scattering of phonons by atoms of different isotopic mass. Slack (1957) has used (4) to calculate W/T due to isotopic scattering for a number of dielectric solids, and compared them with measured values of the point imperfection resistance. The measured resistances exceeded the calculated values in all cases; in one case (germanium) by a factor 3, in other cases by even larger factors. In many cases there are, undoubtedly, other point imperfections which are important as phonon scatterers, but Slack concluded from his collected data that (4) probably underestimates the isotopic scattering by a factor of order 3. Since the present results, without extrapolation, yield a discrepancy in the opposite sense, and after extrapolating according to (5) give fairly good agreement with theory, it is unlikely that the theory should underestimate the isotope scattering by such a large factor. It seems more likely that the isotopic variation is not the principal source of point scattering of phonons in any of the materials studied so far. This, of course, raises the question of what type of point defect could be present in germanium to account for the thermal resistance but which does not influence the electrical conduction properties.

III. COPPER-ZINC ALLOYS

Three specimens of copper-zinc alloys (containing 2, 5, and 10 per cent. Zn respectively) were prepared by Messrs. Garrett, Davidson, and Matthey in the form of rods, 8 cm long, 0.5 cm in diameter. After drawing, the specimens were annealed at 850 °C for 4 hr. In order to prevent loss of zinc by evaporation

during annealing, the specimens were enclosed in closely fitting sheaths of the same material.

As in the case of the copper-gold alloys, the thermal and electrical conductivities were measured and the lattice thermal conductivities deduced. Electrical resistivities, low temperature electronic thermal conductivities, and Lorenz numbers are given in Table 1. The thermal conductivities and lattice thermal conductivities are displayed in Figure 3.

The lattice conductivities of these three alloys are higher, both in the low temperature ($\kappa_g \propto T^2$) and the high temperature ($\kappa_g \propto T^{-1}$) regions, than those of similar alloys annealed at 500 °C and measured by Kemp *et al.* (1957). It is not possible to compare directly the high temperature (point imperfection) resistances, as there was some difference in zinc content, and a corresponding

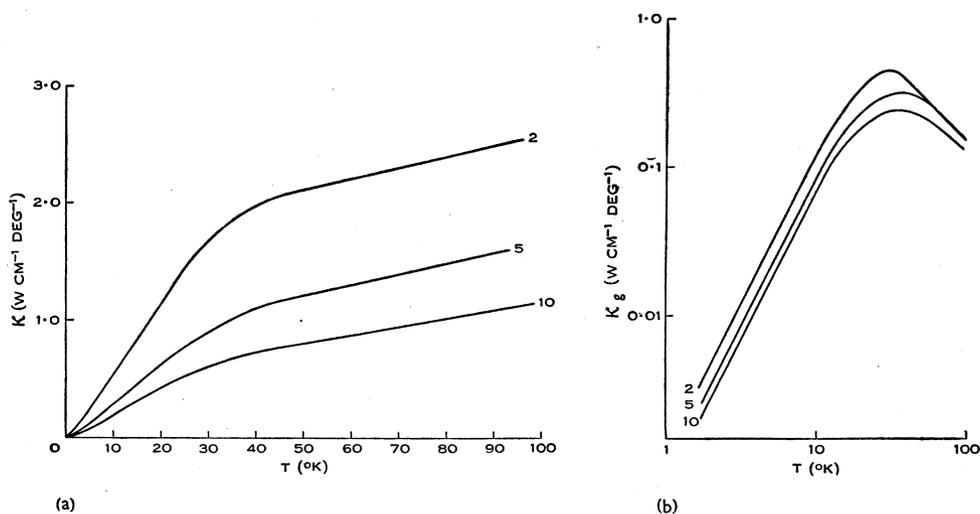


Fig. 3.—Thermal conductivity κ and lattice thermal conductivity κ_g as functions of temperature for Cu-Zn alloys annealed at 850 °C; numbers denote percentage zinc content.

difference in ρ_0 . However, in the case of the 5 and 10 per cent. alloys it is possible to compare the ratios $W_p/\rho_0 T$, where $W_p \propto T$ is the lattice thermal resistance due to point imperfections. If W_p and ρ_0 are due only to the scattering of phonons and electrons by zinc atoms, this ratio should be constant. In fact, it had been noted in the case of the previous specimens that $W_p/\rho_0 T$ decreased with increasing zinc content. It is now observed that $W_p/\rho_0 T$ is significantly lower in the highly annealed specimens than in the old specimens. Whether this is due to the removal by high temperature annealing of point imperfections with a higher value of $W_p/\rho_0 T$ than the value for zinc atoms, or due to some rearrangement of the zinc atoms themselves, cannot be decided at present.

IV. LOW TEMPERATURE LATTICE THERMAL RESISTANCE

Values of $1/B = (W_E + W_D)T^2$ measured for the copper-gold alloys and the three highly annealed copper-zinc alloys are given in Table 3, together with the values of the other copper alloys previously measured (see also Fig. 1 (b)).

It can be seen from these results that the addition of monovalent gold to copper, though it should not alter the concentration of conduction electrons, does in fact increase the resistance to a value comparable to that for alloys containing from 10 to 30 per cent. zinc. The extra resistance is thus probably due to dislocations, the dislocation density being governed by the number of impurity atoms, irrespective of their valency.

It is also seen that a high-temperature anneal can remove some of these dislocations. Thus in a 2 per cent. Zn alloy, W_D is reduced from a value of $4\text{--}6 \times 10^2$ to $1\cdot3\text{--}2\cdot8 \times 10^2$ (depending on whether one chooses for W_E the theoretical value 7×10^2 , or White and Woods' observed value of $5\cdot5 \times 10^2$). Similar reductions are obtained in the alloys of higher zinc content: from 7×10^2 to 5×10^2 for 5 per cent. Zn and from 13×10^2 to 7×10^2 for 10 per cent. Zn.

TABLE 3
LATTICE THERMAL RESISTANCE AT LOW TEMPERATURES

Alloy	Annealed at	$(W_E + W_D)T^2$ (W cm deg ³)
Cu- 1·63% Zn	500 °C	11 × 10 ²
Cu- 2% Zn	850 °C	8·3 × 10 ²
Cu- 5·4% Zn	500 °C	14 × 10 ²
Cu- 5% Zn	850 °C	12 × 10 ²
Cu-10% Zn	500 °C	20 × 10 ²
Cu-10% Zn	850 °C	14 × 10 ²
Cu-20% Zn	500 °C	20 × 10 ²
Cu-30% Zn	500 °C	20 × 10 ²
Cu- 7·5% Au	750 °C	18 × 10 ²
Cu-16·5% Au	750 °C	22 × 10 ²
Cu- 0·06% Fe	530 °C	5·5 × 10 ²
Cu-theoretical value for W_E	—	7 × 10 ²

An estimate of the number of dislocations removed by high-temperature annealing and remaining after annealing can be made from their lattice resistivity, using theoretical values (Klemens 1955) for the scattering of phonons by dislocations. For copper

$$W_D T^2 = 3\cdot2 \times 10^{-10} N W^{-1} \text{ cm deg}^3, \dots\dots\dots (6)$$

where N is the number of dislocation lines per cm². Thus, for example, a 2 per cent. alloy, having a lattice resistance of $W_D T^2 \sim 2 \times 10^2$ remaining after annealing, has a residual dislocation density of $N \sim 5 \times 10^{11} \text{ cm}^{-2}$.

However, there is considerable uncertainty in the absolute values of dislocation densities thus deduced. Estimates of the densities of additional dislocations in cold-worked materials (e.g. Kemp *et al.* 1957) seem excessively high compared with what is known about these densities from other sources, such as stored energy and X-ray line shape, though other methods of determining dislocation densities are also not very reliable. Relative values of dislocation densities obtained from their thermal resistance should be more reliable. It thus appears

that many alloys, except the most dilute, always contain a large number of dislocations, even after annealing. For example, in a cold-worked specimen of Cu-1.6 per cent. Zn, $W_D T^2$ is decreased by $9 \times 10^2 \text{ W}^{-1} \text{ cm deg}^3$ on annealing at 500 °C. A further reduction of 3×10^2 is effected by annealing at 850 °C, but there probably still remains a resistance of similar magnitude. Thus, the number of dislocations is reduced only by a factor 3 on annealing at 500 °C, and by a further factor from 2 to 3 on annealing at 900 °C, leaving perhaps 15 per cent. of the original number of dislocations still in the material. It thus appears that the behaviour of alloys on plastic deformation must be substantially different from that of pure metals.

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