LATTICE THERMAL CONDUCTIVITY COMPONENT OF BRASSES IN THE TEMPERATURE RANGE 4.2—30 K

By D. Włosewicz, K. Bartkowski, J. Rafałowicz

Institute of Low Temperature and Structure Research, Polish Academy of Sciences, Wrocław*

and E. Hegenbarth

Section of Physics, Technical University of Dresden, 8027 Dresden, Mommsen Strasse 13, German Democratic Republic

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An analysis of microscopic mechanisms of the lattice thermal conductivity component of the investigated brasses below the temperature maximum of thermal conductivity has been performed. The existence of three thermal conductivity mechanisms: phonon-elektron, phonon-dislocation and phonon-grain boundary interactions was shown. The dependence of these interactions on the residual electric resistivity of the investigated brass samples has been examined.

1. Introduction

The lattice thermal conductivity of brass of λ_1 was calculated as the difference between the total thermal conductivity coefficient λ and electronic thermal conductivity λ_e. The temperature dependences of the lattice thermal conductivity component of brasses are given in [1].

At low temperatures λ_1 grows with increasing temperature. Near 40 K λ_1 reaches a maximum and then diminishes. The temperature of the λ_1 maximum for the investigated samples lies in the region 35–45 K.

In [2] the dependence of the maximum value of λ_1 on the residual resistivity ϱ_0 was presented. This was assumed to be a measure of material purity.

The main aim of the present paper is to systematically analyse the microscopic mechanisms of heat flow dissipation in brasses in the temperature range 4.2–30 K. We hope to obtain a better understanding of the physics of heat conductivity in binary alloys.

* Address: Instytut Niskich Temperatur i Badań Strukturalnych PAN, Próchnika 95, 53-529 Wrocław, Poland.

The method of thermal conductivity measurements was realized under standard axial heat flow steady-state conditions. A detailed description of the investigated samples is given in [1].

2. *Microscopic phonon scattering mechanisms*

2.1. Phonon scattering on conductivity electrons

An analysis of the results of measurements shows that for temperatures above 4.2 K there is lack phonon scattering on sample boundary.

The two remaining scattering mechanisms, i.e. dislocations and free electrons, produce a thermal resistivity $W_e \sim T^{-2}$ ($\lambda_1 = AT^2$). In order to find the coefficient A for these

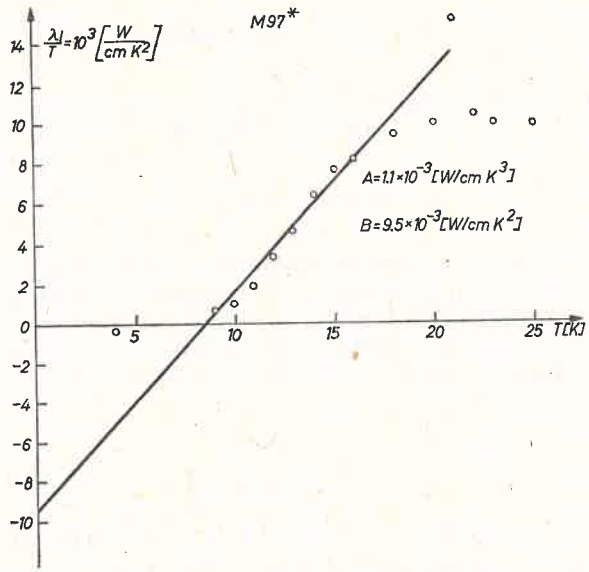

Fig. 1. The temperature dependence of the ratio of the lattice thermal conductivity λ_1/T for M 97* sample

two scattering types the graphs of λ_1/T versus T dependences have been drawn. The slope of the straight line designated by the least squares method is equal to A (figures 1 and 2). We have selected the most pure and impure brass samples. The equation of the straight line in coordinates λ_1/T and T has the form

$$\lambda_1 = AT^2 \pm BT. \tag{1}$$

Both scattering factors in the forms of dislocations and free electrons produce a thermal resistivity W_1. It is necessary then to use well annealed samples to obtain results concerning the value of the resistivity of phonon-electron W_E scattering.

The experimentally obtained W_1 dependence ought to be handled as a sum

$$W_1 = W_E + W_D, \tag{2}$$

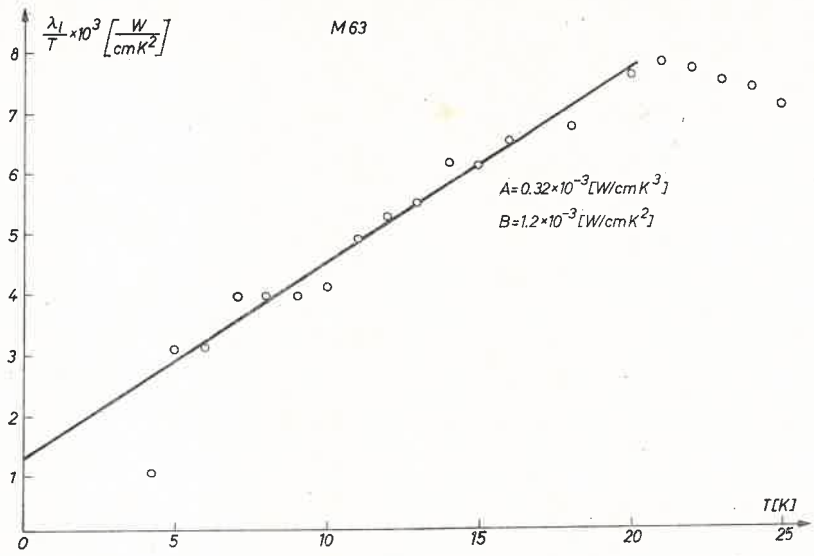

Fig. 2. The temperature dependence of the ratio of lattice thermal conductivity λ_l/T for M 63 sample

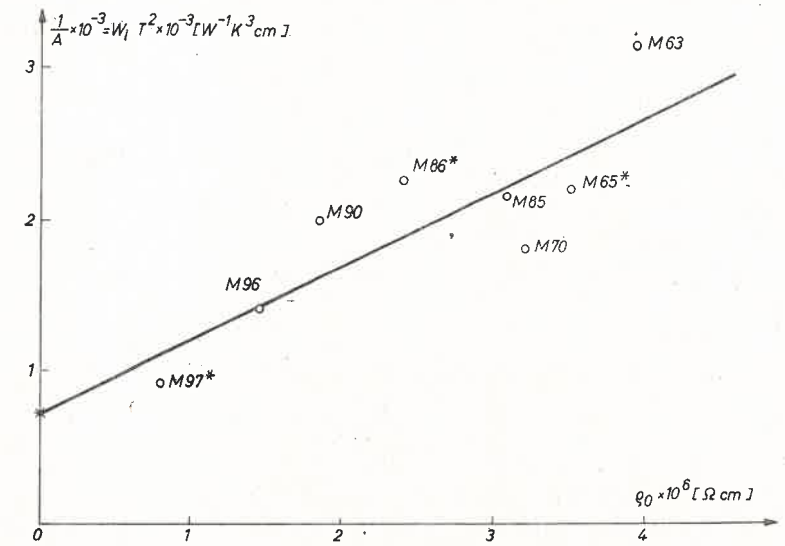

Fig. 3. The thermal resistivity dependence caused by phonon scattering on electrons and dislocations as a function of electric residual resistivity of brass samples

where W_D is the resistivity of phonon-dislocation scattering. However, the results of many investigators [3–5] show that even the best annealing reduces only part of the dislocations.

In Fig. 3 the $W_1T^2 = A^{-1}$ dependence is presented for the residual resistivity ϱ_0 of the investigated samples. By using the least squares method the values of the W_1T^2 function have been averaged by the linear equation. The obtained straight line crosses

the ordinate axis at the point strictly corresponding to the theoretical $W_E T^2 = 7.1 \times 10^2 \mathrm{W}^{-1}$ cm deg^3 value given by Klemens for pure copper [6]. The deviation of the $W_1 T^2$ values from a straight line may testify differently for different samples about the contributions of phonon-dislocation scattering effects. In order to determine W_E for pure one-valence metals one should investigate the thermal resistivity of the alloys of these metals as a dependence on ϱ_0. The electron concentrations in these alloys are both below and above the electron concentration in a one-valence metal (e.g. CuZn, and CuNi). W_E is obtained by interpolation [7]. In general the metal alloying changes the electron concentration in alloy and for that reason can change W_E value.

For brass alloys one may assume after Klemens [7] and Olsen [8], that $W_E T^2$ as a function of ϱ_0 changes a little for good annealed samples with admixture amounts of 4–30%. W_E for the examined alloys is near W_E for pure copper.

For other copper alloys [9] and for alloys of Sn and In [10] a considerable increase of $W_E T^2$ with an increase of admixture amount was observed.

2.2. Phonon scattering by dislocations

Assuming $W_E T^2 = 7.1 \times 10^2$ W^{-1} cm deg^2 one may calculate the W_D values for the investigated samples: $W_D = W_1 - W_E$.

On the other hand, the thermal resistivity arising as a result of phonon dissipation on dislocations may be calculated from the theoretical equation given by Klemens [11]

$$W_D T^2 = 1.1 \times 10^{-2} \frac{vh^2}{k^3} b^2 N, \tag{3}$$

where h, k are Planck and Boltzmann constants, respectively, v — sound velocity, b — vector Burgers value, N — dislocations density. For Cu: $v = 2.4 \times 10^5$ cm/s, $b^2 = 6.6 \times 10^{-16}$ cm^2. Dividing the right side of Eq. (3) by 16, which is the result of a correction introduced by Klemens [12] for the active scattering area for this kind of collision, we obtain for Cu

$$W_D T^2 = 5 \times 10^{-9} N. \tag{4}$$

If W_D is known we can calculate from (4) the dislocation density

$$N = \frac{W_D T^2}{5 \times 10^{-9}}. \tag{5}$$

Using Eq. (5) the dislocation density for the investigated samples has been calculated. The results of these calculations are collected in Table I. From Table I it is seen that the estimated dislocation densities are about two orders larger than expected ones. For annealed alloys one assumes the dislocation density to be about 10^9 cm^{-2} [13, 5]. Such a large dislocation density can manifest that despite the fact of sample annealing (according to recommendation of other authors [3, 14]) it was not possible to suppress dislocations in our brass alloys.

The authors [3] have shown that for the same sample (Cu+10% Zn) annealed at temperatures 500°C and 850°C during the same period of time $W_D T^2$ has attained values of 13×10^2 and 7×10^2 W^{-1} cm deg^3, respectively.

TABLE I

The values of physical magnitudes W_1T^2, W_ET^2, W_DT^2, $\frac{W_D}{W_E+W_D}\times 100\%$ and B constants and dislocations density N for examined brass sample

Investigated samples	$W_1T^2 = 1/A = (W_E+W_D)T^2$ $\left[\frac{\text{cm K}^3}{\text{W}}\right]$	W_ET^2 $\left[\frac{\text{cm K}^3}{\text{W}}\right]$	W_DT^2 $\left[\frac{\text{cm K}^3}{\text{W}}\right]$	$N\times 10^{-11}$ [cm^{-2}]	$\frac{W_D}{W_E+W_D}$ [%]	$B\times 10^3$ $\left[\frac{\text{cm K}^2}{\text{W}}\right]^{-1}$
M 97*	0.91×10^3	7×10^2	2.1×10^2	0.42	23.0	−9.5
M 96	1.41×10^3	7×10^2	7.1×10^2	1.42	50.0	−2.6
M 90	2.00×10^3	7×10^2	13.0×10^2	2.6	65.0	−4.2
M 86*	2.27×10^3	7×10^2	15.7×10^2	3.14	69.0	−1.25
M 85	2.17×10^3	7×10^2	14.7×10^2	2.95	67.8	−1.00
M 70	1.81×10^3	7×10^2	11.1×10^2	2.23	61.5	−0.1
M 65*	2.22×10^3	7×10^2	15.2×10^2	3.04	68.5	0.4
M 63	3.12×10^3	7×10^2	24.2×10^2	4.85	77.6	1.2

The dislocation densities for the samples investigated in this work increases in general with increasing admixture concentration (Fig. 4). For the samples M 97*, M 96, M 90, M 86* this rise is considerable, for samples M 85, M 86*, M 65* one can observe nearly a constant $N = N(\varrho_0)$ value and for M 63 the N value grows again.

In [3] also an increase of W_DT^2 with increasing zinc concentration in the alloy was

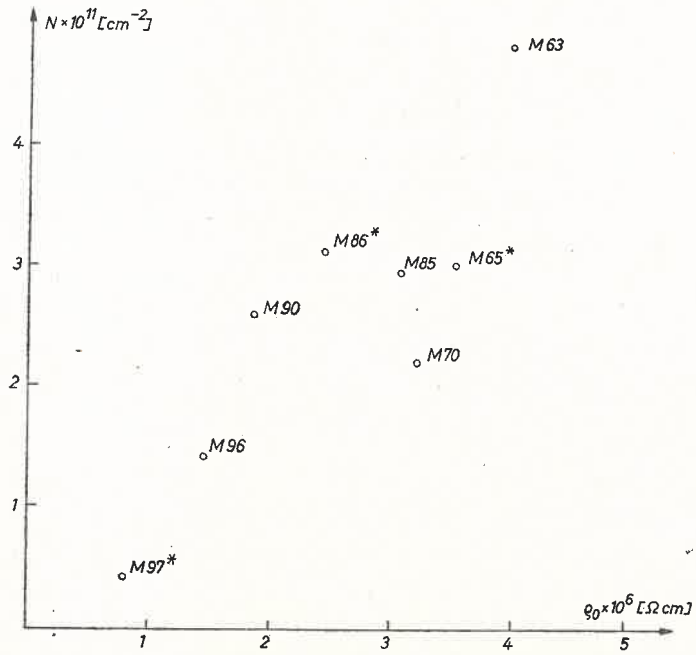

Fig. 4. Dislocation density dependence on electric residual resistivity of brass samples

also observed. This was explained by the concentration of dislocations around admixture atoms. It is a well known fact in metallurgy that along the dislocation the admixture atoms are concentrated and vice versa [15]. This kind of dislocations is a specially stable configuration and cannot be removed by usual annealing in the region of the recrystallization temperature.

Although thermal resistivity is a good measure of dislocation density the absolute calibration of Eq. (3) has not been yet conducted because of the difficulties of precisely determine the dislocation density by other methods. Eq. (3) gives in general N values one order higher than those obtained from X-ray measurements or estimated from the energy value accumulated in deformations [7]. Klemens suggests [7] that dislocations of the same sign have the tendency to agglomerate in groups (so-called superdislocations) and reach the value of phonon wave length. The superdislocations are for phonons the centres of strong dissipations. The superdislocation walls can play the role of the boundary grains. They arise during sample annealing.

For the brass samples investigated by us the large amount of dislocations is the result of non-satisfactory annealing and accumulation of dislocations of the same sign.

2.3. Phonon scattering on grain boundaries

Below the temperature of maximum lattice thermal conductivity a linear part $\pm BT$ (Eq. (1)) also occurs. Such a linear term in the $\lambda_l(T)$ dependence was observed first by Zimmerman [16] in a CuNi alloy at liquid helium temperature. The existence of the linear part has also been reported for CuAl, CuZn, AgSb alloys [17, 5, 18–21]. In each case the quadratic term dominates over the linear one ($AT^2 \gg BT$). The values of linear and quadratic terms in Eq. (1) depend on degree of deformation i.e. the number of dislocations produced [16, 17, 19].

The authors in [18] observed a smaller contribution of the linear term for monocrystalline samples than for identically prepared polycrystalline ones and also for polycrystalline samples with larger grain dimensions.

The presented facts lead to the assumption that the linear dependences of thermal resistance on temperature are the result of phonon scattering on dislocations and grain boundaries. One may demonstrate this [20] if one assumes that mechanisms determining the lattice thermal resistivity W_E, W_D and W_G are phonon-electron scattering, phonon-dislocation and phonon-grain boundaries respectively and that $W_G \ll W_E + W_D$. W_1 were obtained by a simple mathematical transformation and represented the linear part of thermal resistivity caused by phonon scattering on grain boundaries, electrons and dislocations, respectively. For the investigated brass sample the dependence $AT^2 \geqslant BT$ was stated while for other alloys $AT^2 \gg BT$ was obtained. This may be caused by the larger contribution of phonon scattering on grain boundaries for CuZn samples. This is the result of dislocation groups appearing as walls at which the phonons are scattered just as at grain boundaries independently of proper scattering on grain boundaries.

The phonon scattering on grain boundaries appear for such alloys for which $g \geqslant l_{ef}$ [20] (g — grain dimension, l_{ef} — phonon free path length colliding with conductivity electrons).

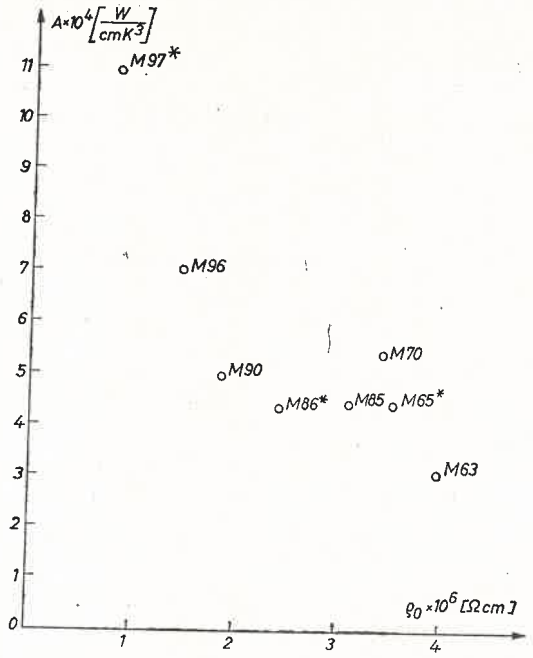

Fig. 5. The dependence of the constant A connected with the interaction of phonon-electron and phonon--dislocation on electric residual resistivity of brass samples

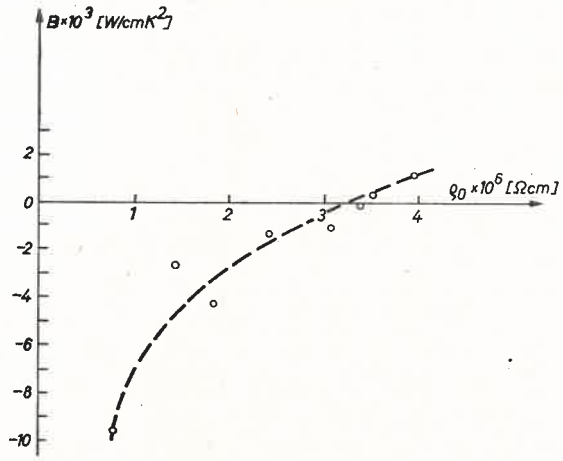

Fig. 6. The dependence of the constant B connected with the interaction of phonon-grain boundaries on electric residual resistivity of brass samples

Using Pippard's equation [22, 23] for ultrasonic absorption in solids for the investigated CuZn samples one may obtain l_{ef}. l_{ef} is of the order of 10^{-3}–10^{-4} cm for dominating phonon waves (the order of a few hundreds Å) in the discussed temperature range (5–20 K).

From estimations given by the Institute of Nuclear Research for the samples M 97*,

M 86*, M 65* the grain dimensions were of the order of 10^{-2}–10^{-3} cm. From the results obtained for the remaining samples one may conclude that grain dimensions were approximate similar.

In Table I the values of the parameter B in Eq. (1) are given. For M 65*, M 63 samples B is positive and for the remaining samples it is negative. The authors [18] have tried to investigate the change in sign of the parameter B. They describe the minus sign for the case of partly screened ion admixtures.

Figs 5 and 6 show the plot of the parameter A and B vs sample purity ϱ_0. With increasing ϱ_0 the parameter B increases and a change in sign can be observed. The parameter A decreases with increasing ϱ_0 and A is smaller than in Eq. (1).

Fig. 6 has dependences similar to those observed for CuAl alloys in [24] and for CuZn alloys in [25]. The value of this ratio grows with admixture concentrations. It means that in connection with admixture concentration the phonon scattering on grain boundaries grows more than phonon scattering at boundaries of accumulated dislocations.

3. *Conclusions*

It was shown that besides phonon scattering on conductivity electrons and dislocations described by the dependence $\lambda_1 = AT^2$ the linear term exists in the dependence $\lambda_1 = AT^2 \pm BT$ (figures 1 and 2).

It was stated that the linear increase exists of the thermal resistivity component caused by phonon scattering on electrons and dislocations with the increase of residual resistivity ϱ_0 of brass samples (Fig. 3). Phonon-dislocation scattering grows in a dominating manner with ϱ_0 increasing and the phonon-electron scattering weakly depends on ϱ_0.

The increase of dislocation densities has been reported for the investigated brass samples for increasing residual resistivity or increasing admixture contamination (Fig. 4).

It was shown that on the basis of literature data analysis the linear term BT is caused by phonon scattering on grain boundaries.

The increase of the constant B (describing the interaction of phonon-grain boundaries) with increasing residual electric resistivity of samples is shown in Fig. 6.

The decrease of the constant A (describing the interaction of phonon-electron and phonon-dislocation) with increasing ϱ_0 (Fig. 5) was mentioned.

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