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Low-Temperature Anisotropy of Thermal Conductivity of Tin Single Crystals Doped with Zinc

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The thermal conductivity of tin single crystals with zinc admixtures has been measured in the temperature range 3.5–25 K for concentrations up to 0.1 wt%. The anisotropy of thermal conductivity for two orientations, [001] and [010], has been determined. It was found that the influence of zinc admixture on the thermal conductivity anisotropy is of a complex, temperature-dependent character.

KEY WORDS: anisotropy; low temperature; thermal conductivity; tin.

1. INTRODUCTION

The thermal conductivity of tin single crystals with a small concentration of admixtures has been the subject of several studies, and the experimental results have been collected in a review [1]. Usually the kind of admixtures was not specified, and in addition, the thermal conductivity was determined for the longitudinal axis only. During the last two decades few works appeared dealing with anisotropy of thermal conductivity in pure and doped tin. The thermal conductivity anisotropy of tin with different concentrations of admixtures was investigated in [2–4] and a maximum of the anisotropy was found.

The present work deals with thermal conductivity of pure tin and zinc-doped tin along the crystal lattice directions [001] and [010].

2. EXPERIMENTS

The single-crystal specimens (dimensions: $3 \times 3 \times 0.2\ \text{cm}^3$) of 99.999% (5N) pure tin and doped tin with Zn, concentrations of 0.004, 0.007, 0.04,

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and 0.1 wt% were made at the Institute of Nuclear Research in Świerk (near Warsaw). Prior to the measurements being made they were heated in helium atmosphere at 210°C (490 K) for some 3 h, then quenched to room temperature, at a rate of about $100\,\mathrm{K}\cdot\mathrm{s}^{-1}$. This heat treatment of the specimens has prevented the admixture from collecting along the dislocations. Thus the dopant atoms can be considered as isolated scattering centers. The influence of heat procedure on the electrical resistivity of metal specimens has been investigated in paper [5] as applied to aluminium. The square shape of specimens allows for convenient determination of the thermal conductivity anisotropy along the two longer dimensions of the same piece. Thus, it assured that the thermal conductivity directional differences are determined without changing the admixture concentration.

The measurements were conducted by the steady-state axial heat flow method [1, 6] in the temperature range 3.5–25 K. The temperature differences and the absolute temperature were determined with the aid of calibrated carbon resistors mounted on the specimen as depicted in Fig. 1. During the measurement cycle the calibration was checked by mutual comparison of temperatures indicated by different thermometers. Measurements carried out with two independent pairs of thermometers allowed for evaluation, by comparison of ΔT_1 and ΔT_2, of the quality of the thermal contact of the specimen to the heating copper block and the regulated-temperature heat sink.

The systematic error, associated with the specimen dimensions, is estimated to be 2% and the error of the temperature differences was between 1.5 and 4%. The overall error of the thermal conductivity coefficient measurement was estimated to be approximately 3.5% while at temperatures below 7 K and in the case of the three purest samples it approached about 6%.

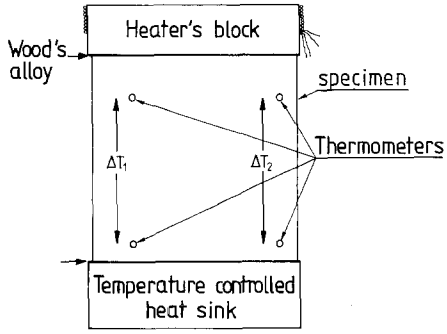

Fig. 1. Specimen mount in the measurement chamber.

3. RESULTS AND DISCUSSION

The dependence of the thermal conductivity coefficient λ on temperature for all the specimens undertaken in two mutually perpendicular crystal directions is shown in Fig. 2. The curves in Fig. 2 are drawn through the experimental points just as a guide. An attempt to fit these results to the standard relation developed for low-temperature thermal conductivity of metals [6, 7],[2]

$$\frac{1}{\lambda} \equiv W = AT^2 + CT^4 + \frac{B}{T} \tag{1}$$

was not successful over the whole range of temperature investigated. For the points from the low-temperature side of the maxima visible in Fig. 2,

[2] For definition of symbols refer to the Nomenclature.

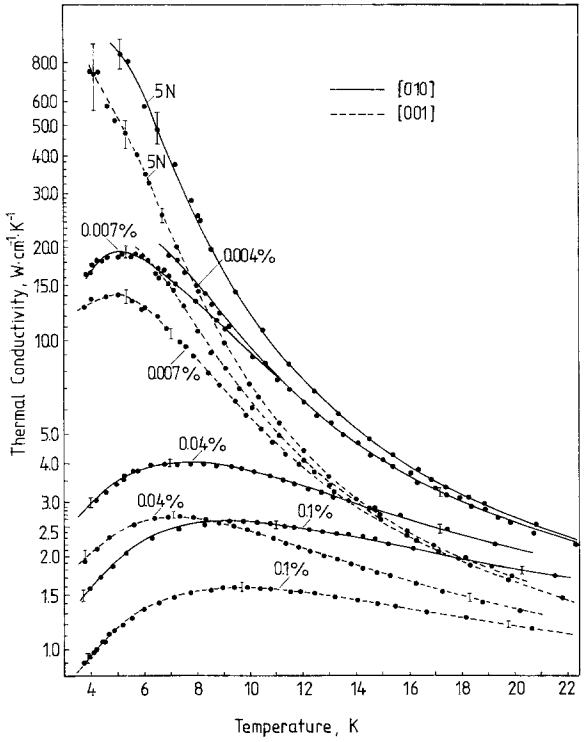

Fig. 2. Dependence of the thermal conductivity on temperature for the investigated Sn: Zn samples of [010] and [001] crystallographic directions.

the component B/T approximates well the real course of $1/\lambda$. It is the component introduced for the elastic scattering of electrons on admixtures and physical defects of the lattice [8], prominent in low temperatures. The term $(AT^2 + CT^4)$, being the result of Wilson's [7, 8] theory of the electron-phonon scattering, was treated here as a correction term by calculating B/T. Based on the values of B, determined for the particular concentrations of zinc and for both crystal orientations, the corresponding values of the residual resistivity ρ_0^{th} were calculated according to the Wiedemann–Franz law.

For zinc concentrations of 0.1 and 0.04 wt%, the values of ρ_0 were determined from the measurements of the electrical resistivity temperature dependence $\rho(T)$, applying extrapolation $\rho \to \rho_0$ for $T \to 0$. Measurements of $\rho(T)$ have been made for the two above-mentioned dopant concentrations, but for the purest speciens only estimated figures are available. In the cases of the 99.999% pure specimen and 0.004 wt% Zn specimen, it was not possible to determine also ρ_0^{th} because of a lack of experimental points on the low-temperature sides of the maxima (cf. Fig. 2). All of the values $\rho_0^{\text{th}} = BL_0$ and ρ_0 determined on the basis of measurements are collected in Table I. Table I shows a disagreement between the values ρ_0^{th} and ρ_0. This appears to be caused by the influence of inelastic scattering of electrons on impurities and physical defects of the lattice. Despite the fact that the B/T component in Eq. (1) was introduced for the purpose of taking into account the elastic scattering, in the present case it probably includes a considerable share of inelastic ones. As a result, the values of B are two- to threefold overestimated relative to those that might be obtained for the case of solely elastic scattering.

Based on the measurements of $\lambda(T)$, the temperature dependence of anisotropy coefficient α_{th} was determined:

$$\alpha_{\text{th}} \equiv \frac{\lambda_{010} - \lambda_{001}}{\lambda_{001}} \tag{2}$$

Table I. Comparison of Values of ρ_0 and ρ_0^{th}

Zn cont. (at%)	Cryst. dir.	ρ_0 ($10^{-8}\,\Omega \cdot$cm)	ρ_0^{th} ($10^{-8}\,\Omega \cdot$cm)
0.1	[001]	3.32	9.87
	[010]	2.67	5.90
0.04	[001]	2.12	4.46
	[010]	1.49	3.04
0.007	[001]	—	0.517
	[010]	—	0.424

for particular concentrations of Zn. For the maximum zinc content (0.04 and 0.1 wt%) the anisotropy α_{el} of electrical conductivity σ, defined in the same way as α_{th}, was also determined:

$$\alpha_{el} \equiv \frac{\sigma_{010} - \sigma_{001}}{\sigma_{001}} \tag{3}$$

The above-mentioned dependences, $\alpha_{th}(T)$ and $\alpha_{el}(T)$, are shown in Fig. 3. Also marked, near the y axis, are the values of α_{th} being the estiated limits of $\alpha_{th}(T)$ for $T \to 0$. From Eqs. (1) and (2) they should be described by the expression

$$\alpha_{th}(\to 0) = \frac{B_{010} - B_{001}}{B_{001}} \tag{4}$$

The factor B incorporates in considerable part the inelastic scattering contribution, and $\alpha_{th}(\to 0)$ is also influenced by it. However, α_{el} is determined mainly by the elastic scattering. The dashed lines in Fig. 3 depict hypothetical courses of the function $\alpha_{th}(T)$. The value of $\alpha_{th}(\to 0)$ in the case of the 5N-pure specimen was determined on the basis of literature data for a similar specien similarly prepared for measurements [1].

The main result of the work shown in Fig. 3 is rather unexpected. It is found that doping of tin with zinc, in the concentration range below

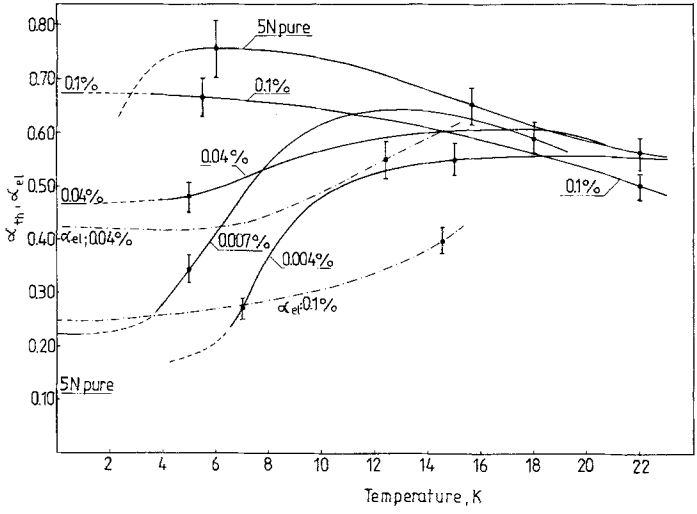

Fig. 3. The anisotropy of thermal conductivity α_{th} (solid lines) and of electrical conductivity α_{el} (dashed lines) as function of temperature for various Zn contents.

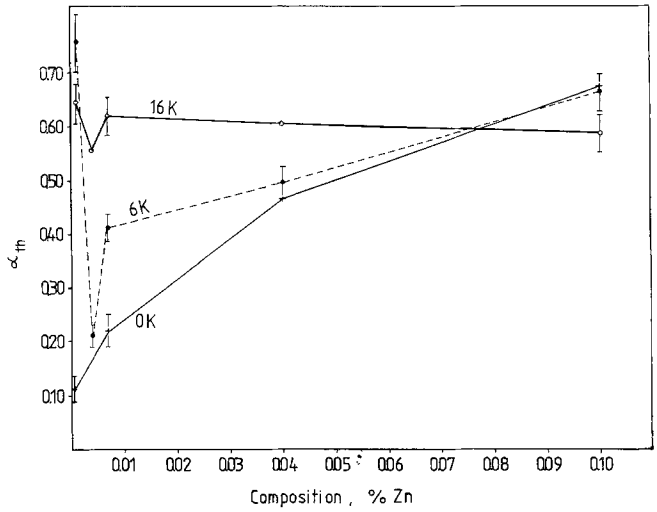

Fig. 4. Changes of the anisotropy coefficient α_{th} with changes of Zn concentration for three chosen values of temperature.

0.1 wt%, has a different influence on the anisotropy in different ranges of temperature. It had been expected that there would be a diminishing of the anisotropy with the increase in admixture concentration, and this tendency, marginally above error limits, can be noted at temperatures above 16 K. At lower temperatures the situation is different, as shown more distinctly in Fig. 4. This shows that α_{th} changes with c changes for three chosen values of temperature (the line here is drawn only as a guide). For $T \to 0$ α_{th} increases with c increase, at least in the range of $c \leqslant 0.1$ wt% Zn. For $T = 6$ K an intermediate course of $\alpha_{th}(c)$ appears, with the minimum for low values of c.

4. CONCLUSIONS

The above description leads to the conclusion that the introduction of small amounts of Zn to single-crystalline specimens of tin is not the sole introduction of isotropic scattering centers for electrons. It appears that some complex processes of correlative scattering on admixtures and dislocations at higher temperatures are taking place also on phonons. Combination of these factors causes a complicated dependence of anisotropy on doping concentration and nonlinear effects with respect to this concentration. The results (cf. the last column in Table I) confirm this nonlinear behavior. Also, the dependence of ρ_0 on c, if one considers estimated data for the purest specimen, is nonlinear for small values of c.

Qualitatively, similar effects of the correlative effect of electron-impurity and electron-dislocation scattering have been investigated for the case of electrical resistivity [9, 10]. However, from Fig. 3 it is found that the influence of the change of Zn doping concentration on the anisotropy factor as in the case of thermal conductivity is essentially different from the analogical influence on electrical conductivity. Also, the differences between the values of ρ_0 and ρ_0^{th} corroborate the conclusion that thermal conductivity is the right method for investigation of types of electron scattering other than the electrical conductivity one. It is obvious that mostly inelastic processes, and, to a lesser degree, elastic ones, are involved in the former method, while in the case of the latter method the opposite is true.

NOMENCLATURE

ΔT_1 ΔT_2	Temperature differences in the specimen
λ	Thermal conductivity coefficient
W	Thermal resistivity
A, B, C	Constants in Eq. (1)
T	Temperature
ρ^{th}	Residual electrical resistivity calculated from W–F law
ρ_0	Residual electrical resistivity from measurements
L_0	Lorenz constant
α_{th}	Anisotropy coefficient of thermal conductivity
α_{el}	Anisotropy coefficient of electrical conductivity
c	Admixture concentration

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