

ROLE OF NORMAL PROCESSES IN PHONON THERMAL CONDUCTIVITY OF Bi

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The study of the effect of small but controllable amounts of Sn and Te on the thermal conductivity of Bi single crystals at low temperatures, when the scattering of phonons takes place only from impurities and by way of normal processes, allows one to make an estimate of the relaxation time  $\tau_N$  for these processes, which restore the equilibrium distribution of the phonons in the flow:  $\tau_N \approx 10^{-9}$  sec for 8°K and is an order of magnitude smaller when the temperature is increased to 20°K.

It is well known that normal processes of phonon scattering in a crystal (N-processes) which take place with conservation of the total quasimomentum, do not of themselves create thermal resistance. However, these processes can demonstrate an important effect on the lattice thermal conductivity of the crystal in that case in which they act together with resistive processes (R-processes), for which the total quasimomentum is not conserved, and therefore heat resistance is produced. By R-processes are meant the processes of umklapp (U-process) and scattering from defects and boundaries.

Callaway, introducing a number of simplifying assumptions, showed how one could take into account the effect of normal processes in the theoretical consideration of the problem of lattice thermal conductivity of the crystal  $\kappa$ . According to Callaway,<sup>[1]</sup>

$$\kappa = GT^3 \int_0^{\infty} \tau_c \left(1 + \frac{\bar{\tau}_R}{\tau_N}\right) \frac{x^4}{\text{sh}^2(x/2)} dx, \tag{1}$$

where

$$\bar{\tau}_R = \int_0^{\infty} \frac{\tau_c}{\tau_N} \frac{x^4}{\text{sh}^2(x/2)} dx \left( \int_0^{\infty} \frac{\tau_c}{\tau_N \tau_R} \frac{x^4 dx}{\text{sh}^2(x/2)} \right)^{-1}; \tag{2}$$

$\tau_R$  is the relaxation time of all resistive processes:  $\tau_R^{-1} = \sum_k \tau_k^{-1}$ ,  $\tau_N$  is the relaxation time of normal processes,

$\tau_C^{-1} = \tau_R^{-1} + \tau_N^{-1}$  is the combined relaxation time,  $x = \hbar\omega/k_0T$ ,  $x_0 = \hbar\omega_D/k_0T$ ,  $\omega$  is the phonon frequency,  $\omega_D$  is the Debye frequency,  $G = (k_0/8\pi^2v)(k_0/\hbar)^3$ , and  $v$  is the mean velocity of the phonons.

The relative role of the different phonon scattering processes changes with temperature. For the problem of the role of normal scattering processes, the greatest interest attaches to the case in which the relaxation of the phonon distribution function in the flow is due basically to N-processes, i.e., the relation  $\tau_N^{-1} \gg \tau_R^{-1}$  holds, and the only effective R-processes are those which can be controlled and their intensity variation is known. Such a process is scattering from point defects (i-processes), an example of which are foreign atoms or isotopes. The case of interest to us can be realized in the range of sufficiently low temperatures that U-processes do not play an important role, but, at the same time, not so low that scattering from the boundaries becomes significant. In the calculation of thermal

conductivity in this range of temperatures, the upper limit of integration in the expressions (1) and (2) can be extended to infinity. If the concentration of controlled point defects  $c$  is small, so that  $\tau_R^{-1} = \tau_i^{-1} = Acx^4T^4 \ll \tau_N^{-1}$ , and if we take  $\tau_N^{-1} = Bx^nT^m$ , then the calculation of  $\kappa$  after Callaway leads to the following results:

$$\kappa = G \frac{T^3}{v} \int_0^{\infty} (\tau_N + \bar{\tau}_i) \frac{x^4 dx}{\text{sh}^2(x/2)} = \kappa_N + \kappa_i = FT^{3-m} + \frac{P}{cT}. \tag{3}$$

The quantity  $\bar{\tau}_i$  computed according to (2) may not be of the same order of magnitude as  $\tau_i$ ; the order of magnitude of  $\tau_i$  is determined by the dependence of  $\tau_i$  on the phonon frequency. In the special case in which  $\tau_i$  does not depend on the frequency we have  $\bar{\tau}_i \equiv \tau_i$ . In our case of strong dependence of  $\tau_i$  on the frequency,  $\bar{\tau}_i$  can be of the same order of magnitude as  $\tau_N$ , and the quantity  $\kappa_i$  becomes of the same order as  $\kappa_N$ .

The parameters  $F$  and  $P$  can be determined from the experimental data obtained in those temperature and concentration ranges where (3) is satisfied.

Simons<sup>[2]</sup> provided a more rigorous theoretical basis of such a method of analysis of the lattice thermal conductivity and, using experimental data on the effect of the isotopic composition on the thermal conductivity, made clear the role of N-processes in LiF crystals, i.e., he determined the value and the temperature dependence of  $\tau_N$ . In research on the effect of the isotopic composition on the thermal conductivity of Te, an estimate of  $\tau_N$  could not be made because of the insufficient amount of experimental data.<sup>[3]</sup>

Investigation of Bi. In the present research, this method of analysis of the lattice thermal conductivity is applied to Bi, which is a single-isotope element and can be grown in the form of very pure single crystals. Therefore, by the introduction of small impurities of Sn and Te, one can change the intensity of impurity scattering in such crystals in a known fashion. A suitable temperature region for Bi is the range 8-20°K, in which, moreover, there is no electronic component of the thermal conductivity. The latter can be deduced from the insignificant effect of the magnetic field of intensity 15 kOe on the thermal conductivity.

Three series of single crystals of Bi were studied. In the crystals of the first series, the thermal flux was

directed along the principal threefold symmetry axis  $C_3$ , and Sn was introduced as the impurity with an atomic concentration  $c$ , which changed within the range from 0.015 to 0.1%. In the crystals of the other two series, the heat flux was directed along the bisector axis  $C_1$ , and either Sn with a concentration  $c$  from 0.01 to 0.1% was used as the impurity, or Te with a concentration  $c$  from 0.001 to 0.1%. Figures 1–3 represent the results of the measurement of thermal conductivity of these three series of samples with dimensions: diameter 2.5–2.7 mm and  $l = 50–60$  mm. In the same figures, graphs are shown of the dependence of the product  $c\kappa$  on  $c$  for different temperatures, making it possible to determine  $F$ ,  $m$  and  $P$  from the linear portions of these graphs, and consequently yielding  $\kappa_N$  and, ultimately  $\tau_N$ . As is seen, these graphs have linear portions only in a limited range of concentrations, where  $\tau_N^{-1} \gg \tau_i^{-1}$ , and where, moreover, one can neglect all the other scattering mechanisms, i.e., where formula (3) is satisfied.

If the concentration of the introduced impurities  $c \rightarrow 0$ , then the effect of other, comparatively weak mechanisms of scattering begin to appear in a real crystal, such as U-processes, scattering from all

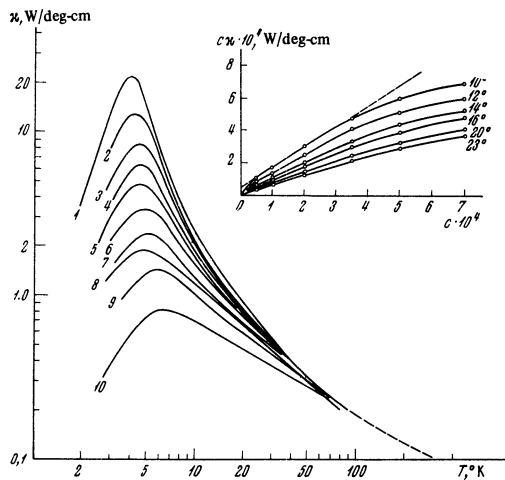


FIG. 1. Effect of Te impurity on the thermal conductivity of Bi;  $\nabla T \parallel C_1$ . Atomic percent of impurity: 1 – 0, 2 – 0.001, 3 – 0.0025, 4 – 0.005, 5 – 0.01, 6 – 0.02, 7 – 0.036, 8 – 0.05, 9 – 0.7, 10 – 0.1. The dashed lines indicate the results of [5].

possible unavoidable defects, and finally, if this scattering is not sufficiently effective, boundary scattering sets in, i.e., as  $c \rightarrow 0$ , the thermal conductivity of a real crystal remains a finite quantity and consequently, the product  $c\kappa$  must tend to zero as  $c \rightarrow 0$ . Thus, in the region of very small concentrations, a deviation from linearity ought to be observed, which is noted in experiment—see the graphs  $c\kappa = f(c)$  (Figs. 1–3). On the other hand, when  $\tau_i^{-1}$  becomes comparable with or larger than  $\tau_N^{-1}$  with increase in the concentration, the relaxation of the phonon distribution function begins to take place not only by N-processes but also by resistive i-processes, the thermal conductivity begins to fall off with increase in concentration more rapidly than in the linear portion, and the increase in

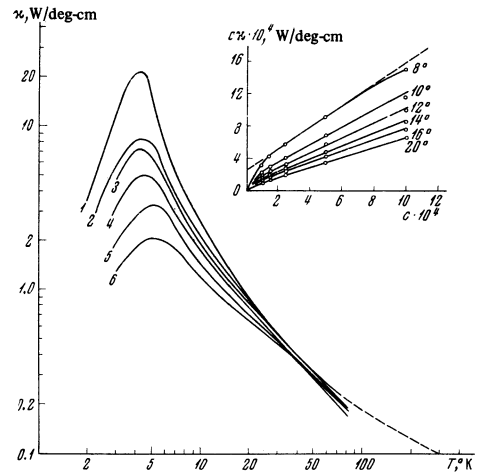


FIG. 2. Effect of Sn impurity on the thermal conductivity of Bi;  $\nabla T \parallel C_1$ . Atomic percent of impurity: 1 – 0, 2 – 0.01, 3 – 0.015, 4 – 0.025, 5 – 0.05, 6 – 0.1. Dashed curve is according to [5].

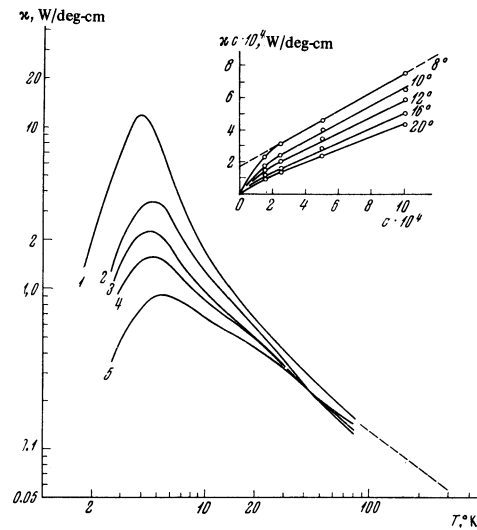


FIG. 3. Effect of Sn impurity on the thermal conductivity of Bi;  $\nabla T \parallel C_3$ . Atomic percent of impurity: 1 – 0, 2 – 0.015, 3 – 0.025, 4 – 0.05, 5 – 0.1. Dashed curve is according to [5].

$c\kappa$  with increase in  $c$  is slowed, which is also observed in practice.

Figure 4 shows the temperature dependence of  $\tau_N$  for the two fundamental directions in the Bi crystal— $C_1$  and  $C_3$  (correspondingly,  $\kappa_N^{(1)}$  and  $\kappa_N^{(3)}$ ), obtained by means of graphs of Figs. 1–3 on the basis of Eq. (2). It is seen from Fig. 4 that although the Te impurity lowers the thermal conductivity of Bi more strongly (by a factor of 1.5–2) than the Sn impurity, the value of  $\kappa_N^{(1)}$  in Fig. 4 is found to be the same as before, as was to be expected if the employed method of analysis serves its purpose.

Simons [2] showed that the quantity  $\kappa_N$  can be represented in the form

$$\kappa_N = \frac{1}{3} \alpha c v v^2 \tau_N, \tag{4}$$

where  $c v$  is the heat capacity of the crystal,  $v$  the speed of sound, and  $\alpha$  is a nondimensional, theoretically

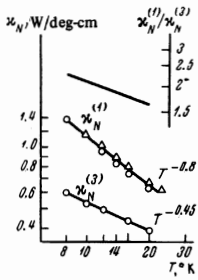


FIG. 4

FIG. 4. Temperature dependence of  $\kappa_N$  for two principal directions in the Bi crystal:  $C_3$  (the line  $\kappa_N^{(3)}$ ) and  $C_1$  (the line  $\kappa_N^{(1)}$ );  $\circ$  — Sn impurity,  $\Delta$  — Te impurity.

FIG. 5. Temperature dependence of the quantity  $\kappa_N/c_V$ , which is proportional to the relaxation time  $\tau_N$ , for two principal directions in the Bi crystal:  $C_1$  — curve 1 and  $C_3$  — curve 3.

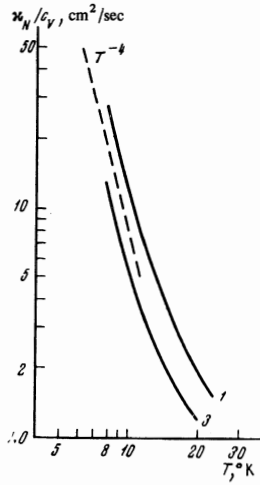


FIG. 5

to the anisotropies of  $v$  and the anisotropy of the relaxation time of the N-processes  $\tau_N$  in Bi is not large. Such a conclusion can be drawn also with respect to the anisotropy of the total thermal conductivity of pure Bi, which does not exceed 1.5 in the range 8–20°K.

The temperature dependence of the relaxation time of the N-processes  $\tau_N$  is determined by the ratio  $\tau_N/c_V$ , shown in Fig. 5. The experimental data for the heat capacity  $c_V$  are taken from<sup>[4]</sup>. In the theory of Herring,  $\tau_N \propto T^{-5}$ . It is seen from Fig. 5 that in the experiment on the very steep portion this dependence only achieves  $T^{-4}$ . Such a difference can be explained by the fact that in the investigation of the thermal conductivity of Bi we have to deal with thermal phonons, while the Herring theory deals with subthermal long-wave phonons.

An estimate of the quantity  $\tau_N$ , which can be made with the help of (3), leads to the following result:  $\tau_N \approx 10^{-9}$  sec for  $T = 8^\circ\text{K}$  and decreases by a factor of 10 when the temperature is increased to 20°K.

derivable quantity which changes within the limits 1-2, depending on how the various relaxation times entering into the theory of thermal conductivity depend on the wave number. Therefore, when the value of  $\kappa_N$  is known from experiment,  $\tau_N$  can be determined on the basis of Eq. (4) with accuracy not exceeding  $\pm 50\%$ . The anisotropy of  $\kappa_N$  is shown in Fig. 4. If we take it into account that the anisotropy of the speed of sound  $v$  in Bi amounts to  $\approx 1.3$  and  $\kappa_N \propto v^2$ , then we can conclude that the significant part of the anisotropy of  $\kappa_N$  is due

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<sup>4</sup>W. H. Keesom, Y. N. van den Ende, Proc. Kön. Nederl. Akad. Wetensch. **34**, 210 (1931); P. Fransozini and K. Clusius, Z. Naturforsch. **19a**, 1430 (1964).

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