

Isotope effect in the thermal conductivity of germanium single crystals

V. I. Ozhogin, A. V. Inyushkin, A. N. Taldenkov, A. V. Tikhomirov, and G. É. Popov

Institute of Molecular Physics, "Kurchatov Institute", Russian Science Center, 123182 Moscow, Russia

E. Haller and K. Itoh^{a)}

University of California at Berkeley and Lawrence Berkeley National Laboratory, Berkeley, California 94720

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The thermal conductivity of chemically, structurally, and isotopically highly pure germanium single crystals is investigated experimentally in the temperature range from 2 to 300 K. It is found that the thermal conductivity of germanium enriched to 99.99% ⁷⁰Ge is 8 times higher at the maximum than the thermal conductivity of germanium with the natural isotopic composition. © 1996 American Institute of Physics. [S0021-3640(96)01606-4]

Isotopic disorder greatly decreases the thermal conductivity $K(T)$ of dielectric single crystals if they are structurally perfect and sufficiently pure chemically. This effect was predicted by Pomeranchuk¹ in 1942. The effect of isotopes on the thermal conductivity of ordinary (nonquantum) crystals has been studied experimentally for Ge,² LiF,³ and recently for synthetic diamond.⁴ The thermal conductivity of diamond enriched to 99.9% ¹²C is 50% higher than the thermal conductivity of natural diamond, where the ¹²C content is equal to 98.9%, and at room temperature it is the highest of all known materials.

Geballe and Hull² found that the thermal conductivity of germanium enriched to 96% ⁷⁴Ge is approximately three times higher at the maximum than that of germanium with the natural isotopic composition. This increase in the thermal conductivity agrees qualitatively with the theory of Ref. 5, though it is much lower than the expected 15-fold increase calculated on the basis of the 15-fold decrease in the mean-squared deviation in the mass of the isotopes. In Ref. 2 it was suggested that the discrepancy between theory and experiment is due to the presence in Ge of a branch of acoustic phonons with strong dispersion, especially for the [001] and [111] directions. For this branch the energy of the phonon modes near the boundary of the Brillouin zone is low, and three-phonon scattering processes without conservation of the quasimomentum remain an important channel of thermal resistance down to temperatures below $\Theta_D/10$ ($\Theta_D=375$ K is the Debye temperature for Ge). Later, Callaway⁶ obtained good agreement between his model of the thermal conductivity and the experimental data of Ref. 2, except in the temperature range near the maximum of the thermal conductivity.

In connection with the substantial progress made in the centrifugal method of iso-

TABLE I. Parameters of the experimental samples.

Sample	^{70}Ge %	^{72}Ge %	^{73}Ge %	^{74}Ge %	^{76}Ge %	g	Dimensions, mm
natGe	20.5	27.4	7.8	36.5	7.8	$5.87 \cdot 10^{-4}$	$2.515 \times 2.525 \times 40$
$^{70}\text{Ge}96$	96.3	2.1	0.1	1.2	0.3	$7.57 \cdot 10^{-5}$	$2.50 \times 2.50 \times 40$
$^{70}\text{Ge}99$	≥ 99.99	≤ 0.01	—	—	—	$8.16 \cdot 10^{-8}$	$2.48 \times 2.47 \times 29$

tope separation, methods for growing high-quality germanium single crystals, and measuring techniques, we thought it would be interesting to perform accurate measurements of the temperature dependence of the thermal conductivity of the most perfect germanium crystals with different isotopic composition for the purpose of clarifying the role of the strong acoustic dispersion in phonon scattering processes. We note that in germanium the dispersion of the transverse acoustic phonons is strong.

Recently, the isotope ^{70}Ge enriched to 99.99% was obtained at the Institute of Molecular Physics at the ‘‘Kurchatov Institute’’ Russian Science Center by the centrifugal method of isotope separation. Fine chemical purification of polycrystalline ^{70}Ge was performed at the Lawrence Berkeley Laboratory by the method of repeated (33 times) zone melting. Chemically pure ^{70}Ge was employed as the initial material for growing by the Czochralski method single crystals with two orientations: with the [001] and [111] crystal axes along the axis of the rod. Hall conductivity measurements showed that the total concentration of electrically active chemical impurities does not exceed $2 \cdot 10^{12} \text{ cm}^{-3}$. According to the mass spectrometry data, the ^{70}Ge content in the grown single crystals was not less than 99.99%.

The thermal conductivity of the germanium single crystals was measured by the method of stationary axial heat flow using two thermometers and one heater. One thermometer was a TSU-2 carbon resistance thermometer and the other was a thin-film semiconductor thermometer. The thin-film thermometer was calibrated against the TCU-2 during each experiment. The TCU-2 thermometer was calibrated in the MTS-90 scale relative to the standard iron–rhodium thermometer from the All-Russia Scientific-Research Institute of Physicotechnical and Radiotechnical Measurements. The absolute accuracy of the measurements of the thermal conductivity was better than 2% in the temperature range from 2 to 300 K.

Samples in the form of parallelepipeds were cut from the germanium single crystals. The long edge of the sample and the heat flux were oriented along the [100] direction, and the lateral faces were parallel to the {100} planes. The samples were polished with the aid of diamond powder (the average particle size was equal to approximately $30 \mu\text{m}$) in order to ensure that phonons are scattered diffusely at the surface of the samples. The isotopic composition of the samples, their dimensions, and the parameter g of isotopic disorder (see Eq. (2) below) are presented in Table I.

The temperature dependences of the thermal conductivity of the three germanium samples (with the natural isotopic composition and enriched to 96.3% and 99.99% ^{70}Ge) are displayed in Fig. 1. The thermal conductivity of isotopically pure germanium ^{70}Ge (99.99%) at the maximum at a temperature of 15 K is equal to approximately 110

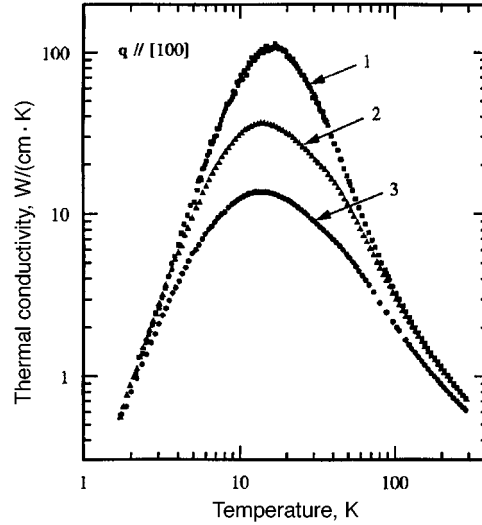


FIG. 1. Temperature dependence of the thermal conductivity along the [100] direction of germanium single crystals with different isotopic composition: 1 — 99.99% ^{70}Ge ; 2 — 96.3% ^{70}Ge ; 3 — natural Ge.

$\text{W}/\text{cm}\cdot\text{K}$, which is approximately 8.1 times higher than the thermal conductivity of germanium with the natural isotopic composition. Hence it follows that in the natural germanium at temperatures close to the maximum of the thermal conductivity the thermal resistance is determined practically completely (by 85%) by the scattering of phonons on isotopes.

At low temperatures (below 4 K) the thermal conductivity of isotopically pure ^{70}Ge (99.99%) closely follows the T^3 law characteristic for heat transfer under diffuse boundary scattering conditions. This indicates that the mean free path of the thermal phonons is comparable to the transverse dimensions of the sample. In isotopically disordered samples the temperature dependence $K(T)$ is weaker than T^3 . This is due to the large contribution of isotopic scattering right down to the lowest temperatures.

At temperatures above the maximum the role of isotopic scattering decreases against the background of increasing three-phonon relaxation processes which give a temperature dependence of the form $K(T) \propto T^{-1}$ as the temperature approaches Θ_D . At room temperature the thermal conductivity of 99.99% ^{70}Ge is 20% higher than that of natural germanium and equal within the experimental error to that of 96.3% ^{70}Ge .

The rate of scattering of phonons by isotopes in an isotopically disordered crystal is given by the expression (see, for example, Ref. 7)

$$\tau_{\text{iso}}^{-1}(\omega) = \frac{\pi}{6} V_0 g \omega^2 D(\omega), \quad (1)$$

where V_0 is the atomic volume and $D(\omega)$ is the phonon density of states per unit volume. The parameter g characterizes the isotopic disorder in the crystal:

$$g \equiv \sum_i f_i \left(\frac{\Delta M_i}{\bar{M}} \right)^2, \quad (2)$$

where f_i is the concentration of the i th isotope, whose mass differs from the average mass \bar{M} by ΔM_i . The isotopic scattering rate in ^{70}Ge samples enriched to 96.3% and 99.99% is lower by a factor of 7.75 and 7200, respectively, than in germanium with the natural isotopic composition. In spite of the large decrease in τ_{iso}^{-1} , however, the temperature dependence of the thermal conductivity of isotopically pure ^{70}Ge does not exhibit the exponential character expected in the Debye model of the lattice dynamics under the conditions of freeze-out of three-phonon processes with umklapp. This result indicates unequivocally that to describe the inherent phonon relaxation processes in germanium the strong dispersion of the transverse acoustic phonons must be taken into account. This in turn requires that the generalized expression (1) be used for the rate of scattering of phonons by isotopes instead of the Rayleigh-type formula used previously, which was derived on the basis of the theory of a continuous medium:

$$\tau_{\text{iso}}^{-1}(\omega) = \frac{V_0 g \omega^4}{4 \pi v_D^3}. \quad (3)$$

Calculations of isotopic scattering of dispersive phonons in germanium performed by Tamura⁷ show that large deviations of τ_{iso}^{-1} from the expression (3) arise even for phonons with frequencies above approximately 1 THz, i.e., with energy above 50 K (in the temperature equivalent). At temperatures corresponding to and above the maximum of the thermal conductivity the energies of the phonons which dominate in the thermal conductivity exceed 50 K, and therefore expression (1) must be used to describe the isotopic scattering of the phonons. This agrees with our qualitative conclusion.

Our measurements have revealed a feature in the temperature dependence of the thermal conductivity of germanium at temperatures ranging from approximately 20 up to 60 K: At these temperatures kinks occur in the temperature dependence of the thermal conductivity. This is seen more clearly in the temperature dependence of the double-logarithmic derivative $d \ln K / d \ln T$ of the thermal conductivity (see Fig. 2), where a feature in the form of a smooth step appears at $T \approx 20\text{--}30$ K. We note that the measurements were performed on two different ^{70}Ge samples enriched to 99.99%, and the data for these samples agreed to within the experimental error. Since the feature is observed for Ge samples with different isotopic composition, for which the rate of scattering of phonons by isotopes differs by almost four orders of magnitude, apparently it is not associated with the above-indicated specific nature of the isotopic scattering. It can be conjectured that the feature is due to the substantially different temperature dependences of the contributions of different branches of the phonon spectrum to the thermal conductivity.⁸ To explain the experimental results, detailed calculations of the thermal conductivity must be performed taking into account the characteristic features of the phonon spectrum of germanium.

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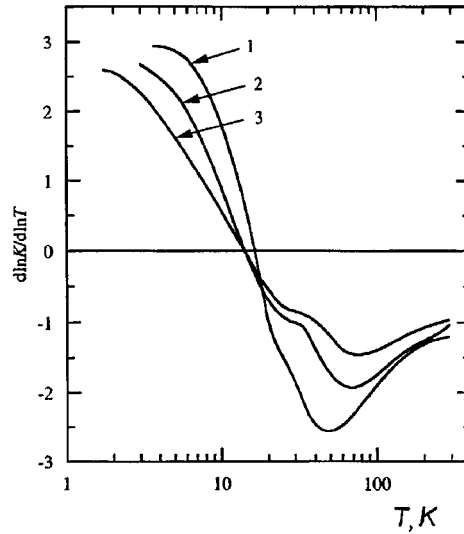


FIG. 2. Temperature dependences of the double-logarithmic derivative of the thermal conductivity ($d \ln K / d \ln T$) for the experimental samples: 1 — 99.99% ^{70}Ge ; 2 — 96.3% ^{70}Ge ; 3 — natural Ge.

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^{a)}Present address: Department of Instrumentation Engineering, Keio University, Yokohama, 223 Japan.

¹I. Pomeranchuk, J. Phys. USSR **6**, 237 (1942).

²T. H. Geballe and G. W. Hull, Phys. Rev. **110**, 773 (1958).

³R. Berman and J. C. F. Brock, Proc. R. Soc. London Ser. A **289**, 46 (1965).

⁴T. R. Anthony, W. F. Banholzer, J. F. Fleischer *et al.*, Phys. Rev. B **42**, 1104 (1990).

⁵P. G. Klemens, Proc. Phys. Soc. London A **68**, 1113 (1955).

⁶J. Callaway, Phys. Rev. **113**, 1046 (1959).

⁷S. Tamura, Phys. Rev. B **27**, 858 (1983).

⁸M. G. Holland, Phys. Rev. **132**, 2461 (1963).

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