19,03

Thermal Conductivity of Single-Crystals Isotopically Enriched ^{70}Ge, ^{72}Ge, ^{74}Ge in the Temperature Range of 80–310 K

© A.M. Gibin[1], N.V. Abrosimov[2], A.D. Bulanov[1], V.A. Gavva[1]

[1] Devyatykh Institute of Chemistry of High-Purity Substances, Russian Academy of Sciences, Nizhny Novgorod, Russia
[2] Leibniz-Institut für Kristallzüchtung (IKZ), 12489, Berlin, Germany

E-mail: gibin@ihps-nnov.ru

Received April 19, 2023
Revised April 19, 2023
Accepted April 20, 2023

The temperature dependence of the thermal conductivity $\kappa(T)$ of single crystals isotopically enriched ^{70}Ge (99.926%), ^{72}Ge (99.980%), ^{74}Ge (99.921%) has been measured in the temperature range 80–310 K. In the studied temperature range, the thermal conductivity is determined by anharmonic processes of phonon scattering; a decrease in the thermal conductivity with increasing mass of the germanium isotope is experimentally observed.

Keywords: thermal conductivity, single-crystal, germanium isotope, isotopically enriched, isotope effect, thermal resistance.

DOI: 10.61011/PSS.2023.08.56589.65

1. Introduction

A change of the isotopic composition of a chemical element results in the change of the physical properties of a solid, which can be caused both by the degree of isotopic disorder of the crystalline lattice and by a change in the mass of the isotope. The thermal conductivity of $\kappa(T)$ nonmetallic crystals strongly depends on their isotopic composition: the change of the isotopic composition results in significant change of the degree of isotopic disorder of the crystalline lattice characterized by the parameter

$$g_2 = \sum_i c_i[(M_i - M_{av})/M_{av}]^2,$$

where M_i and c_i — mass and concentration i-th isotope, M_{av} — average atomic mass. In most experimental works devoted to the study of the thermal conductivity of isotopically modified crystals, this effect was studied — the dependence of thermal conductivity on the degree of isotopic disorder. These papers study thermal conductivity of isotope-enriched diamond [1–3], silicon-28 [4–7], germanium [8–10]. There are practically no studies of the dependence of $\kappa(T)$ on the mass of the isotope in the case when the isotopic disorder does not play a significant role. This is due to the fact that the masses of isotopes of one chemical element differ slightly, and the isotopic effects associated with the change in mass are small, which requires high-precision measurements of thermal conductivity. The measurement of the dependence of thermal conductivity on the average mass of an isotope, provided that phonon scattering on isotopic disorder plays an insignificant role, allows for a correct comparison of the theory with experiment, since changes of elastic constants and lattice constants with the mass of the isotope can be neglected in the first approximation [11]. The thermal conductivity of highly enriched ^{29}Si (99.919%) was measured and compared with the thermal conductivity of ^{28}Si in [12]. It is shown that for silicon with isotopic enrichment above 99.9% at low and high temperatures, the thermal conductivity depends on the average mass of the isotopes and does not depend on the isotopic disorder.

The isotopic effect in the thermal conductivity of germanium was first studied in [8]: the thermal conductivity of the sample ^{74}Ge was measured (with 95.8% enrichment) in the range 2–300 K. The thermal conductivity of samples ^{70}Ge with enrichment by the main isotope of 99.99% and 96.3% was measured in the interval 2–300 K in [9]. Except for those measured in [9] samples ^{70}Ge, the results of measurements of thermal conductivity ^{76}Ge (with 86% enrichment) and isotopically modified sample $^{70/76}$Ge with a content of 43% ^{70}Ge and 48% ^{76}Ge are provided in [10].

The thermal conductivity of single crystals of isotopically pure germanium ^{70}Ge, ^{72}Ge, ^{74}Ge with an enrichment of over 99.9% by the main isotope was measured in the range 80–310 K in this paper.

2. Experiment

High-purity single crystals of isotopically enriched germanium ^{70}Ge, ^{72}Ge, ^{74}Ge were obtained by the method described in [13,14]. The single crystals were grown using Chokhralsky method. The content of impurities in the samples did not exceed the detection limit of the mass spectrometric method of analysis (10^{-5}–10^{-6} wt.%). The exception was an admixture of silicon, the content of which in germanium crystals — $2 \cdot 10^{-5}$ wt.%. The isotopic composition of the germanium samples studied

Table 1. Isotopic composition of germanium samples

Sample	Isotope content, at.%					M_{av}, a.m.u.	$g_2 \cdot 10^5$
	70	72	73	74	76		
Ge-70	**99.9260**	0.0067	0.00007	0.06722	0.00001	69.92707	0.225
Ge-72	0.00011	**99.97983**	0.01565	0.00435	0.00006	71.92232	0.0067
Ge-74	0.0051	0.0077	0.0617	**99.9207**	0.0048	73.92030	0.035
Ge-nat*	20.52	27.45	7.76	36.52	7.75	72.63	58.7

Comment. * Data from [15] were used for the isotopic composition of natural germanium Ge-nat.

is given in Table 1. The resistivity of germanium single crystals was 45–50 Ω cm at room temperature. Samples for measurements in the form of rectangular parallelepipeds with the same dimensions were cut out of initial single crystals: $4 \times 4 \times 40$ mm. The samples were cut along the growth axis: the long edge of the parallelepiped is directed along the crystallographic axis [100], and the lateral faces are parallel to the planes [100]. The sides of the sample were sanded using a corundum abrasive with a particle size of about 20 μm.

As can be seen from Table 1, the values of the isotopic disorder parameters g_2 for single crystals of isotopically enriched germanium used for measurements differ quite significantly. But, as it was found during measurements of the thermal conductivity of various samples of isotope-enriched silicon in [4–7], with enrichment by isotope ^{28}Si more than 99.8% in the temperature range 80–300 K, there is no experimentally significant difference, and the difference in the value of thermal conductivity is determined mainly by the mass of the isotope [12]. In [9] it was noted that at room temperature the thermal conductivity of the samples ^{70}Ge with an enrichment of 99.99% and 96.3% coincide within the measurement error (2%). Thus, in our case, the difference of thermal conductivity of isotope-enriched germanium single crystals will be determined only by the difference in isotope masses. Residual isotopic impurities in the highly enriched samples measured by us ^{70}Ge, ^{72}Ge, ^{74}Ge at temperatures above 80 K cannot make an experimentally noticeable contribution to the scattering of phonons.

Thermal conductivity was measured by the stationary longitudinal heat flow method using two resistance thermometers (platinum PT111 thermometers from LakeShore Cryotronics, Inc.) and one heater (thick-film resistor with a nominal value of 620 Ω) [4]. Thermometers were mechanically attached to the sample using beryllium bronze knives, and the heater was glued to the end of the sample using a thin layer of glue. The opposite end of the sample at a length of about 5 mm was clamped in a copper cooling pipe. The distance between thermometer mounting points was 23–26 mm. Measurements were carried out in high vacuum, to reduce the error caused by thermal losses due to radiation, a radiation shield was installed around the sample. The systematic error of the absolute value of thermal conductivity was about 2% at room temperature and no more than 4% in the region 90–200 K.

3. Results and discussion

Experimental data on the thermal conductivity of $\kappa(T)$ samples of isotopically enriched germanium ^{70}Ge, ^{72}Ge, ^{74}Ge in the entire studied temperature range are shown in Fig. 1.

As can be seen from Fig. 1, in the entire studied temperature range for samples of isotope-enriched germanium, a decrease in the thermal conductivity of germanium samples is observed with an increase in the mass of the isotope. The thermal conductivity of ^{70}Ge is higher than the thermal conductivity of ^{72}Ge by 5% and ^{74}Ge by 10% at a temperature of 90 K. The difference decreases with the temperature increase, and at room temperature reaches 2% between the thermal conductivity of the samples ^{70}Ge and ^{72}Ge and 4% between ^{70}Ge and ^{74}Ge. Fig. 1 also shows the data of [9] for the sample ^{70}Ge with an enrichment of 99.99%. The data obtained that we obtained for the thermal conductivity of ^{70}Ge are well aligned with the data of [9]: the

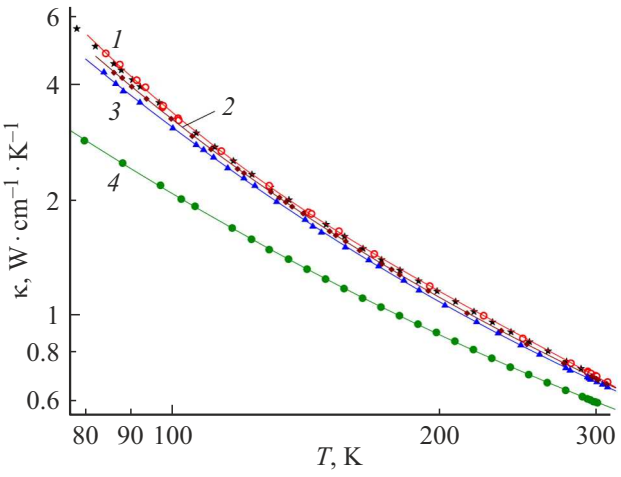

Figure 1. Temperature dependence of thermal conductivity of $\kappa(T)$ samples of isotope-enriched germanium ^{70}Ge (*1*), ^{72}Ge (*2*), ^{74}Ge (*3*) and germanium of natural isotopic composition (*4*); asterisks — data [9] for ^{70}Ge (99.99%).

Table 2. Values of thermal conductivity of isotopically enriched germanium and comparison with data for germanium of natural isotopic composition

T, K	Ge-*nat*	Ge-70		Ge-72		Ge-74	
	κ_{nat}, W/cm · K	κ_{70}, W/cm · K	κ_{70}/κ_{nat}	κ_{72}, W/cm · K	κ_{72}/κ_{nat}	κ_{74}, W/cm · K	κ_{74}/κ_{nat}
90	2.43	4.16	1.71	3.95	1.63	3.76	1.55
300	0.598	0.700	1.17	0.687	1.15	0.673	1.13

difference of the entire temperature range does not exceed the measurement error.

An increase in the thermal conductivity of isotopically enriched germanium compared to the thermal conductivity of germanium of natural isotopic composition (curve *4*) is associated with a significant decrease in isotopic disorder (coefficient g_2 in Table 1). The values of thermal conductivity ^{70}Ge, ^{72}Ge, ^{74}Ge, obtained at temperatures of 90 K and 300 K, are provided in Table 2 in comparison with data for germanium of natural isotopic composition.

Figure 2 shows a comparison of our data for the thermal conductivity of ^{74}Ge with the data of [8] for ^{74}Ge with an enrichment of 95.8%. A satisfactory agreement with the data of [8] is observed in interval 90–150 K. Above 150 K, with increase of temperature, the difference increases, which is most likely due to thermal losses due to radiation during measurements in [8], which may be attributable to the shape of the germanium sample.

According to the theory of Leibfried–Schleman [16], in the high temperature range (of the order of the Debye temperature Θ_D, which for germanium is 374 K [17]), the thermal conductivity of the crystal due to anharmonic phononphonon processes with transfer, determined by the formula

$$\kappa(T) = A \cdot (M_{av} V_0^{1/3} \Theta_D^3)/(\gamma^2 T), \qquad (1)$$

where A — a numerical constant independent of the average mass of M_{av} atoms in a crystal, V_0 — atomic volume, γ — the Gruneisen parameter characterizing the degree of anharmonicity of the crystal lattice. From the above formula (taking into account that $\Theta_D \propto M_{av}^{-1/2}$) it follows that the thermal conductivity depends on the mass of the atom as $M_{av}^{-1/2}$. The ratio of thermal conductivity values at high temperatures should be $\kappa(^{70}\text{Ge})/\kappa(^{72}\text{Ge}) = (72/70)^{1/2} = 1.014$ and $\kappa(^{70}\text{Ge})/\kappa(^{74}\text{Ge}) = (74/70)^{1/2} = 1.028$ for germanium crystals with atomic masses of 70, 72 and 74. Our experimental data show that the ratio of the thermal conductivity of Ge-70 to Ge-72 at room temperature is 1.02, and the ratio of the thermal conductivity of Ge-70 to Ge-74 is 1.04. Taking into account the systematic measurement error (2%), the experimental data obtained do not contradict the theoretical assessment of the isotope effect. The lower values of thermal conductivity in comparison with the experiment when calculated using the formula (1) can also be explained by the fact that the experimental data were obtained at a temperature of 300 K are lower than the Debye temperature.

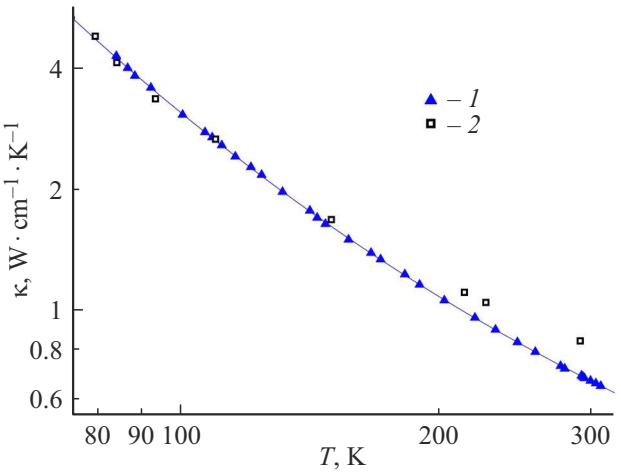

Figure 2. Temperature dependence of thermal conductivity of $\kappa(T)$ samples of isotopically enriched germanium ^{74}Ge: *1* — data of this paper, *2* — data of [8].

At temperatures close to Θ_D, the thermal resistance of the germanium crystal lattice W (the inverse of thermal conductivity) can be represented as the sum of [18]:

$$W = 1/\kappa(T) = W_3 + W_4 + W_{iso}, \qquad (2)$$

where the first term displays three-phonon anharmonic scattering, the second —four-phonon scattering, and the third — thermal isotopic resistance W_{iso}, which is due to isotopic disorder in crystals and is determined by the formula [19]:

$$W_{iso} = 4\pi^2 \cdot g_2 \cdot V_0 \cdot \Theta_D/h\upsilon^2, \qquad (3)$$

where υ is average phonon velocity. At high temperatures (near Θ_D) W_{iso} does not depend on temperature. For natural germanium, the theoretically calculated value is $W_{iso} = 0.20\,\text{cm} \cdot \text{K} \cdot \text{W}^{-1}$. The expression $(\text{cm} \cdot \text{K} \cdot \text{W}^{-1})$ is proposed in [20] for the temperature dependence of the thermal resistance of natural germanium in the temperature range $0.5\Theta_D < T < 1.6\Theta_D$):

$$W(T) = 3.95 \cdot 10^{-3} T + 3.38 \cdot 10^{-6} T^2 + 0.17, \qquad (4)$$

i.e. $W_{iso} = 0.17\,\text{cm} \cdot \text{K} \cdot \text{W}^{-1}$. From experimental data for ^{70}Ge and natural germanium obtained in [9.10], it is calculated that at 300 K the value of W_{iso} is $0.26\,\text{cm} \cdot \text{K} \cdot \text{W}^{-1}$ [21].

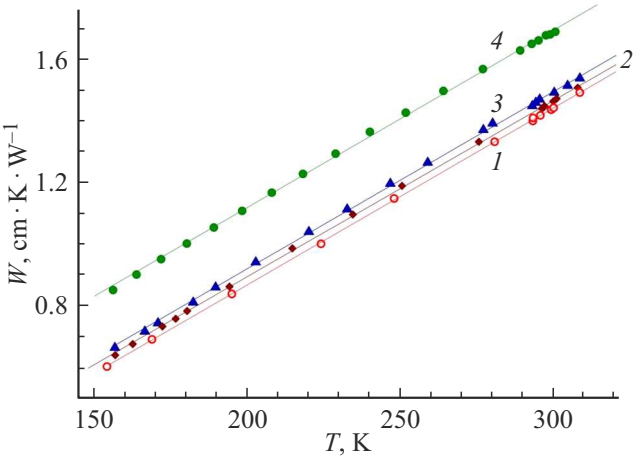

Figure 3. Temperature dependence of thermal resistance of germanium samples ^{70}Ge (*1*), ^{72}Ge (*2*), ^{74}Ge (*3*) and germanium of natural isotopic composition (*4*).

Figure 3 shows the temperature dependence of the thermal resistance of germanium samples studied by us in comparison with the data for natural germanium. As can be seen from the figure, the temperature dependence of the thermal resistance for all germanium samples in the range 160−310 K ($0.4\Theta_D < T < 0.8\Theta_D$) is close to linear, and the dependences themselves in this range are almost parallel. The difference in thermal resistance of isotope-enriched samples compared to natural germanium is $0.25\,\mathrm{cm}\cdot\mathrm{K}\cdot\mathrm{W}^{-1}$ for ^{70}Ge, $0.22\,\mathrm{cm}\cdot\mathrm{K}\cdot\mathrm{W}^{-1}$ for ^{72}Ge and $0.20\,\mathrm{cm}\cdot\mathrm{K}\cdot\mathrm{W}^{-1}$ for ^{74}Ge and is kept constant from 170 to 300 K. This difference in thermal resistance corresponds to the value W_{iso}. Thus, based on the experimental data obtained by us, the value of the isotopic resistance of natural germanium is $W_{iso} = 0.22 \pm 0.03\,\mathrm{cm}\cdot\mathrm{K}\cdot\mathrm{W}^{-1}$. This value satisfactorily conforms with the theoretically calculated value [19] and experimental data [9,10,20].

4. Conclusion

Experimental data obtained as a result of measurements of the thermal conductivity of single crystals of isotopically pure germanium ^{70}Ge, ^{72}Ge, ^{74}Ge show that for germanium with isotopic enrichment above 99.9% thermal conductivity in the region of 80−310 K depends on the average mass of the isotopes. Thermal conductivity decreases with the increase of isotope mass. The conclusions of the theory of phonon thermal conductivity on the dependence of the value $\kappa(T)$ on the mass arising from the fact that the average speed of phonons is inversely proportional to the square root of the average mass of lattice atoms are consistent with the experimental results obtained.

Funding

The paper was supported by the Ministry of Science and Education of the Russian Federation within the framework of the state task of the Institute of Chemistry of High-Purity Substances of the Russian Academy of Sciences, the topic FFSR-2022-0003.

Conflict of interest

The authors declare that they have no conflict of interest.

References

[1] T.R. Anthony, W.F. Banholzer, J.F. Fleischer, L. Wei, P.K. Kuo, R.L. Thomas, R.W. Pryor. Phys. Rev. B **42**, *2*, 1104 (1990).
[2] L. Wei, P.K. Kuo, R.L. Thomas, T.R. Anthony, W.F. Banholzer. Phys. Rev. Lett. **70**, *24*, 3764 (1993).
[3] J.R. Olson, R.O. Pohl, J.W. Vandersande, A. Zoltan, T.R. Anthony, W.F. Banholzer. Phys. Rev. B **47**, *22*, 14850 (1993).
[4] A.V. Gusev, A.M. Gibin, O.N. Morozkin, V.A. Gavva, A.V. Mitin. Inorganic materials **38**, *11*, 1100, (2002).
[5] A.V. Inyushkin, A.N. Taldenkov, A.M. Gibin, A.V. Gusev, H.-J. Pohl. Phys. Status Solidi C **1**, *11*, 2995 (2004).
[6] R.K. Kremer, K. Graf, M. Cardona, G.G. Devyatykh, A.V. Gusev, A.M. Gibin, A.V. Inyushkin, A.N. Taldenkov, H.-J. Pohl. Solid State Commun. **131**, *8*, 499 (2005).
[7] A.V. Inyushkin, A.N. Taldenkov, J.W. Ager III, E.E. Haller, H. Riemann, N.V. Abrosimov, H-J. Pohl, P. Becker. J. Appl. Phys. **123**, *9*, 095112 (2018).
[8] T.H. Geballe, G.W. Hull. Phys. Rev. **110**, *3*, 773 (1958).
[9] V.I. Ozhogin, A.V. Inyushkin, A.N. Taldenkov, A.V. Tikhomirov, G.E. Popov, E.E. Haller, K. Ito. JETP Letters **63**, *6*, 490 (1996).
[10] M. Asen-Palmer, K. Bartkowski, E. Gmelin, M. Cardona, A.P. Zhernov, A.V. Inyushkin, A. Taldenkov, V.I. Ozhogin, K.M. Itoh, E.E. Haller. Phys. Rev. B **56**, *15*, 9431 (1997).
[11] A.P. Zhernov, A.V. Inyushkin. UFN **171**, *8*, 827 (2001). (in Russian).
[12] A.V. Inyushkin, A.N. Taldenkov, A.V. Gusev, A.M. Gibin, V.A. Gavva, E.A. Kozyrev. Phys. Solid State *55*, *1*, 235 (2013).
[13] M.F. Churbanov, V.A. Gavva, A.D. Bulanov, N.V. Abrosimov, E.A. Kozyrev, I.A. Andryushchenko, V.A. Lipskii, S.A. Adamchik, O.Yu. Troshin, A.Yu. Lashkov, A.V. Gusev. Cryst. Res. Technol. **52**, *4*, 1700026. (2017).
[14] V.A. Gavva, O.Yu. Troshin, S.A. Adamchik, A.Yu. Lashkov, N.V. Abrosimov, A.M. Gibin, P.A. Otopkova, A.Yu. Sozin, A.D. Bulanov. Inorganic materials **58**, *3*, 246 (2022).
[15] J. Meija, T.B. Coplen, M. Berglund, W.A. Brand, P. De Bièvre, M. Gröning, N.E. Holden, J. Irrgeher, R.D. Loss, T. Walczyk, T. Prohaska. Pure Appl. Chem. **88**, *3*, 293 (2016).
[16] G. Leibfried, E. Schlömann. Nach Ges.Wiss. Goettingen Math. Phys. K1, **IIa**, *4*, 7193 (1954).
[17] P. Flubacher, A.J. Leadbetter, J.A. Morrison. Phil. Mag. **4**, *39*, 273 (1959).
[18] B.M. Mogilevsky, A.F. Chudnovsky. Teploprovodnost poluprovodnikov. Nauka, M., (1972). P. 396. (in Russian).
[19] V. Ambegaokar. Phys. Rev. **114**, *2*, 488 (1959).
[20] C.J. Glassbrenner, G.A. Slack. Phys. Rev. **134**, *4A*, A1058 (1964).
[21] A.V. Inyushkin. Inorganic materials **38**, *5*, 427 (2002).

Translated by A.Akhtyamov