

Isotope effect on the phonon-drag component of the thermoelectric power of germaniumA. V. Inyushkin,^{1,*} A. N. Taldenkov,¹ V. I. Ozhogin,¹ K. M. Itoh,² and E. E. Haller^{3,4}¹*Institute of Molecular Physics, Russian Research Center Kurchatov Institute, 123182 Moscow, Russia*²*Department of Applied Physics and Physico-Informatics, Faculty of Science and Technology, Keio University, 3-14-1, Hiyoshi, Kohoku-ku, Yokohama 223, Japan*³*Materials Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720, USA*⁴*Department of Materials Science and Engineering, University of California at Berkeley, Berkeley, California 94720, USA*

(Received 4 August 2003; published 15 October 2003)

We have measured the thermoelectric power of several germanium single crystals with different isotopic compositions: natural, 96.3%, and 99.99% enriched ⁷⁰Ge. *N*- and *p*-type Ge samples with the net concentration of electrically active impurities $<2 \times 10^{13} \text{ cm}^{-3}$ were studied. Our experimental data show a decrease of thermopower with an increase in isotopic mass disorder. This isotope effect is evident at temperatures below approximately 70 K where a phonon-drag part of the thermopower dominates. At high temperatures, in the diffusion regime, the thermopower does not correlate with the isotopic composition within experimental error. The observed isotope effect can be explained with a special phonon-drag contribution induced by a momentum transfer from thermal phonons to low-energy phonons in the enriched samples.

DOI: 10.1103/PhysRevB.68.153203

PACS number(s): 72.20.Pa, 72.80.Cw

Investigations of perfect crystalline solids provide important information on intrinsic processes, such as anharmonic phonon-phonon interactions. Isotope disorder, a kind of imperfection common to most crystalline solids, has been shown to affect numerous properties.^{1,2} In this paper, we show that in nearly perfect, isotopically enriched crystals, intrinsic processes strongly enhance the drag of electrons by phonons which, in turn, dominates the thermoelectric power at low temperatures. In particular, this effect is expected to manifest itself in thermopower of carbon materials, which has found broad recent interest (see, e.g., Ref. 3 and references therein).

A theory of the phonon-drag thermopower in semiconductors was developed by Herring⁴ nearly 50 years ago. This theory captures the essential physics of the phonon drag in moderately pure crystals when the normal processes of phonon-phonon scattering (conserving the total quasimomentum) have an insignificant effect on the total lifetimes of thermal phonons as compared with other relaxation processes, such as phonon scattering from the crystal point and extended defects, crystal boundaries, and Umklapp phonon-phonon processes.

Isotopes, randomly distributed over the lattice sites in solids, disturb the translational symmetry of a crystal and reduce the phonon lifetimes by elastic phonon scattering. Because the phonon lifetimes directly govern the lattice thermal conductivity, the isotopic disorder may produce a strong suppression of thermal conductivity $\kappa(T)$ in chemically pure nonmetallic crystals at low temperatures. This effect was found theoretically by Pomeranchuk,⁵ who pointed out that the isotope scattering rate is proportional to the square of the mass differences of the isotopes. Later, within the Debye approximation, Klemens⁶ derived the Rayleigh type formula for the phonon relaxation rate due to mass fluctuation scattering:

$$\tau_{\text{iso}}^{-1}(\omega) = \frac{V g_2 \omega^4}{4 \pi v^3}, \quad (1)$$

where ω is the phonon frequency, V is the molar volume, v is the phonon group velocity, and the parameter

$$g_2 = \sum_i f_i (\Delta M_i / M)^2 \quad (2)$$

characterizes the isotopic disorder. Here f_i is the concentration of the i th isotope, whose mass M_i differs from the average mass $M = \sum_i f_i M_i$ by $\Delta M_i = M_i - M$. In germanium with natural isotopic composition ^{nat}Ge five stable isotopes of comparable abundance (see Table I below) give rise to a strong isotopic disorder: $g_2 = 5.89 \times 10^{-4}$. This makes germanium especially suitable for investigations of isotope disorder effects of different properties.^{1,2} In 1958, Geballe and Hall⁷ measured for the first time the effect of isotopic disorder on the thermal conductivity of germanium single crystals. They observed an almost threefold increase of the $\kappa(T)$ for an isotopically enriched sample of ⁷⁴Ge (95.8%) with $g_2 = 3.7 \times 10^{-5}$ over that of ^{nat}Ge near the thermal conductivity maximum at ≈ 15 K. Recently, precise and comprehensive data were obtained for the isotope effect on thermal conductivity of Ge (Refs. 8,9) with a nearly isotope-pure germanium single crystal ($\geq 99.99\%$ of ⁷⁰Ge) having $g_2 = 8.2 \times 10^{-8}$. The maximum value of the thermal conductivity of this isotopically pure ⁷⁰Ge (99.99%) crystal is eight times higher than that of ^{nat}Ge crystal. This result clearly demonstrates that phonon scattering by isotopes in natural

TABLE I. Isotopic parameters of Ge crystals.

Composition	⁷⁰ Ge (%)	⁷² Ge (%)	⁷³ Ge (%)	⁷⁴ Ge (%)	⁷⁶ Ge (%)	g_2 10^{-6}	M (a.m.u.)
^{nat} Ge	21.23	27.66	7.73	35.94	7.44	589	72.59
⁷⁰ Ge96	96.3	2.1	0.1	1.2	0.3	77.5	70.04
⁷⁰ Ge99	≥ 99.99	≤ 0.01	0	0	0	0.08	69.92

germanium is the primary process that limits the lifetimes of thermal phonons at temperatures near the conductivity maximum.

The phonon lifetimes control other kinetic coefficients, e.g., thermoelectric power described by the Seebeck coefficient $S(T)$. The thermopower has two additive independent components: diffusion $S_d(T)$ and phonon-drag $S_g(T)$. The former arises from a diffusion of charge carriers opposite to a temperature gradient in the electronic system. The latter results from a quasimomentum transfer from the phonons to the charge carriers in the presence of a temperature gradient in the phonon system.

The effect of phonon lifetime is most evident at low temperatures where the phonon-drag thermopower dominates. In a sufficiently pure (nondegenerate) semiconductor the phonon-drag $S_g(T)$ depends upon electron-phonon scattering and phonon relaxation processes. According to the laws of crystal momentum- and energy-conservation, only acoustic phonons with very small wave vectors \mathbf{q} can participate in electron-phonon scattering events. Thus, the lifetimes of these low- q phonons (so-called “electronic” phonons) determine the magnitude of $S_g(T)$, in contrast to the thermal conductivity where *thermal* phonons dominate. In the framework of Herring’s theory of phonon-drag,⁴ the electron drag by phonons, which acts as a phonon low-pass filter, is sensitive to the phonon relaxation processes having relatively weak frequency dependencies ($\sim \omega^p, p < 4$). For pure ^{nat}Ge crystals the magnitude and temperature dependence of $S_g(T)$ can be well described by using only two phonon relaxation processes: boundary scattering and phonon-phonon scattering.⁴ The frequency independent boundary scattering determines $S_g(T)$ at very low temperatures $T < 10$ K in samples with diameters of few millimeters. This scattering gives rise to the $T^{1/2}$ dependence of $S_g(T)$. In germanium, the influence of boundary scattering of phonons upon the phonon-drag thermopower $S_g(T)$ has been observed experimentally in Refs. 10,11. At relatively high temperatures, $50 < T < 100$ K, where phonon-phonon scattering dominates, $S_g(T) \sim T^{-n}$ with $n = 2.2 - 2.5$.¹⁰⁻¹³ Phonon scattering from point mass defects, which has a strong frequency dependence $\sim \omega^4$ weakly affects $S_g(T)$. As a consequence, in moderately pure semiconductors, the phonon-drag thermopower $S_g(T)$ is practically independent of impurity concentration in comparison with the thermal conductivity at temperatures near the maximum of $\kappa(T)$.⁴ Therefore, in this conventional approach to the phonon-drag effect in thermoelectric phenomena, the isotopic disorder produces only a very small reduction of the magnitude of thermoelectric coefficients.¹¹

To our knowledge, the only experimental study of the effect of isotopic disorder on the thermoelectric power has been performed by Oskotskii *et al.*¹⁴ They have measured the thermopower for two tellurium single crystals with different isotopic compositions: natural and enriched ¹²⁸Te (92%). The enriched crystal had an isotopic disorder parameter g_2 reduced by factor 7.5. These authors found that the isotopic composition did not influence the thermopower of Te crystals at low temperatures.

In this paper we present results of an experimental investigation of the thermoelectric power for high-purity Ge

TABLE II. Characteristics of the Ge samples. $\Delta N = |N_d - N_a|$ in 10^{12} cm^{-3} was estimated from electrical conductivity data at 77 K.

Sample	Composition	Axis	Type	ΔN
S1	^{nat} Ge	[111]	<i>n</i>	4
Gn2	^{nat} Ge	[100]	<i>p</i>	0.5
G70	⁷⁰ Ge96	[100]	<i>p</i>	2
G2	⁷⁰ Ge99	[100]	<i>n</i>	2.7
G7	⁷⁰ Ge99	[111]	<i>n</i>	20

single crystals with different isotopic compositions including a highly enriched crystal with 99.99% ⁷⁰Ge. We find that the absolute value $|S(T)|$ increases significantly with a reduction in isotopic disorder at low temperatures. This surprising result cannot be accounted by the conventional theory of the phonon-drag thermopower.

To determine experimentally the effect of isotopes on the thermoelectric power, one compares $S(T)$ for samples with different isotopic compositions but with all the other important properties left identical. These include the sample shape and dimensions, its surface roughness, the crystal lattice defect concentration, the chemical impurity concentration, and the free charge carrier concentration. Fortunately, in chemically pure germanium crystals of both *n*- and *p*-type with the netconcentrations of electrically active donors and acceptors $\Delta N = |N_d - N_a| < 10^{14} \text{ cm}^{-3}$, the phonon-drag thermopower changes little, $< 5\%$, with increasing carrier concentration¹⁰ due to the saturation effect of Herring.⁴ In *n*- and *p*-type Ge, the maximum values of $|S_g(T)|$ appear to be very close to each other. This doping dependence of the phonon-drag $S_g(T)$ offers excellent conditions for the experimental determination of isotopic disorder effects in chemically pure Ge crystals.

Germanium single crystals of isotopically controlled composition were grown using the Czochralski method.¹⁵ In this work five crystals with three different isotopic compositions were studied: natural ^{nat}Ge, ⁷⁰Ge96 with 96.3% enrichment, and ⁷⁰Ge99 with $\geq 99.99\%$ enrichment. Their isotopic parameters are listed in Table I. Five different samples in the form of rectangular parallelepiped with typical dimensions $2.5 \times 2.5 \times 40 \text{ mm}^3$ were cut from these crystals. The sample surfaces were ground with $\sim 14 \mu\text{m}$ diamond powder slurry to ensure diffuse scattering of thermal and subthermal phonons from the sample surfaces at temperatures above 10 K. Two samples were of natural isotopic composition, while another two samples were nearly single isotope ⁷⁰Ge. Note that the samples with the same isotopic composition differed in crystal orientation and up to one order of magnitude in their impurity contents. The netconcentration of electrically active impurities ΔN was $< 2 \times 10^{13} \text{ cm}^{-3}$. Characteristics of the samples are given in Table II.

Differential thermoelectric power and thermal conductivity were measured simultaneously by a longitudinal steady-state technique. The heat flow was parallel to the long axis of the sample. Electrical contacts to the sample in the form of

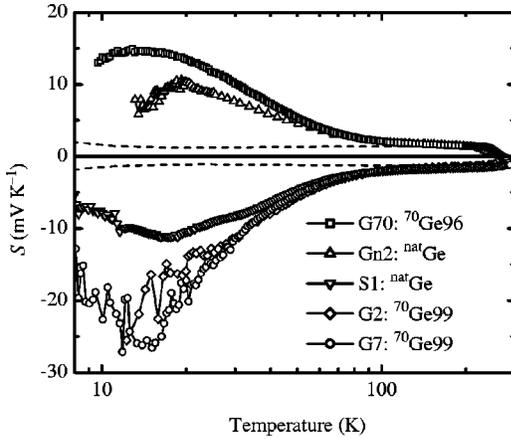


FIG. 1. Thermoelectric power as a function of temperature for Ge crystals with different isotopic composition. The dashed curves are calculated diffusion thermopower for n - and p -type Ge.

metallic stripes aligned across the long axis of the sample were made by tinning the sample surface with Pb/Sn alloy solder. Two small copper clamps carrying resistance thermometers were attached to the sample directly on the stripes. These thermometers were used to determine the mean temperature of the sample and the temperature drop along the sample. Manganin lead wires were electrically connected to the copper clamps. These wires were used to measure the Seebeck voltage across the sample. No corrections were made to the measured thermopower $S(T)$ relative to manganin, as its absolute thermopower is negligible, $<1 \mu\text{V/K}$ below 300 K.¹⁶ Thermal conductivity data obtained with this setup coincide with the data reported previously in Refs. 8,9 for the same samples to within an experimental error of 2%. The uncertainty in the absolute value of thermoelectric power is estimated to be less than 5% at high temperatures and $\approx 20\%$ below 20 K.

The results of the measurements are presented in Fig. 1. The absolute values of $S(T)$ for all samples are identical within 20% at high temperatures, $T > 100$ K, in the regime of extrinsic conductivity, where the diffusion thermopower dominates. Small variations in $|S(T)|$ from sample to sample originate apparently from the variations in impurity content and type of dominant charge carriers that alter the diffusion part of thermopower. In this temperature range, we did not find a correlation between $|S(T)|$ and isotopic composition of a sample.

At low temperatures $T < 70$ K, in the regime dominated by phonon drag, the absolute values for different samples with the same isotopic composition are identical within experimental uncertainty in spite of very different doping levels. This is in accord with Herring's saturation effect. At these temperatures the experimental data clearly demonstrate the increase of thermopower with decreasing isotopic disorder. The isotope effect is present in samples of both n - and p -type conductivity and does not appear to depend upon the direction of a temperature gradient with respect to the crystallographic orientation. Note, that the highly enriched sample G7 has the highest level of residual impurities, however, it shows the largest absolute value of thermopower,

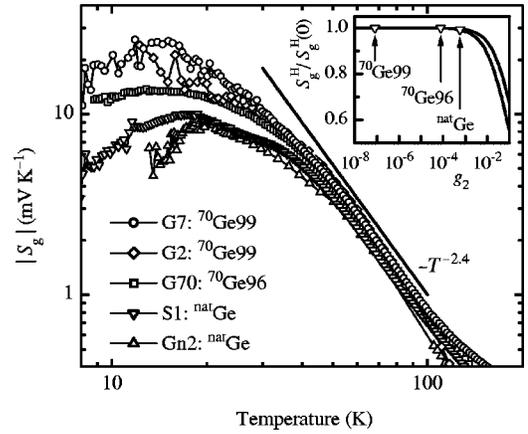


FIG. 2. Phonon-drag thermopower vs temperature for Ge crystals. The inset shows the calculated Herring phonon-drag thermopower as a function of isotopic disorder for $T=20$ K (lower curve) and 80 K (upper curve). Arrows show the values for isotopic compositions studied in this work.

which is about 2.5 times larger than for natGe sample S1 near the $S(T)$ maximum. The data strongly suggest that the mass-fluctuation phonon scattering due to the isotopic disorder suppresses the phonon-drag effect in pure Ge single crystals.

In Fig. 2 we present data on phonon-drag thermopower $|S_g(T)|$ obtained by subtracting the diffusion part $S_d(T)$ from the measured values. The diffusion thermopower $S_d(T)$ shown in Fig. 1 as the dashed line was calculated with the conventional Herring theory (see, for example, Refs. 4,12,11) taking into account the experimental data on electrical conductivity for our samples. It is seen from Fig. 2 that near the maximum of phonon-drag thermopower the effect of isotopic disorder is most pronounced. In the range $50 < T < 100$ K $|S_g(T)| \sim T^{-n}$, where $n \approx 2.4$, our data on $|S_g(T)|$ for natGe are in agreement with those of Refs. 10–13. We have also calculated the Herring phonon-drag thermopower $S_g^H(T)$ for germanium as a function of isotopic disorder parameter g_2 (the inset in Fig. 2). The experimentally observed isotope effect turns out to be larger by two order of magnitude than the theoretical estimates.

The enhanced phonon-drag thermopower is observed in isotopically pure samples. For these samples as it follows from the analysis of thermal conductivity data^{9,17} the isotope scattering of thermal phonons is reduced so much (by factor up to 7000) that the normal phonon-phonon processes dominate to an appreciable extent the nonequilibrium phonon distribution, which exists in the presence of a temperature gradient. Under these conditions not only the additional (or correction) term $\kappa_2(T)$ to the thermal conductivity, which is remarkably sensitive to the isotopic disorder, appears as was shown by Callaway,¹⁸ but an additional contribution $S_{2g}(T)$ to the phonon-drag thermopower can arise. Kozlov and Nagaev¹⁹ suggested a mechanism for the additional phonon-drag thermopower: a quasimomentum transfer from the thermal phonons to the low- q “electronic” phonons through the normal phonon-phonon processes, which increases the available phonon momentum that can be transferred to the charge carriers. This contribution $S_{2g}(T)$, which can be large in

comparison with Herring phonon-drag thermopower for pure crystals and has a similar temperature dependence, decreases linearly with increasing point defect concentration.²⁰ Consequently the isotopic disorder can produce a relatively strong reduction of $S_{2g}(T)$. The isotope effect, which we observed in the phonon-drag thermopower for germanium crystals is likely due to an additional contribution $S_{2g}(T)$. Note that in Ref. 21 a proper account of normal phonon-phonon processes has been proposed for the case of isotopically pure Ge crystals. In the framework of this model the qualitative account of the effect of isotopic disorder on the phonon-drag thermopower is obtained.²²

In summary, we have measured the thermoelectric power for germanium single crystals with different isotopic compositions at low temperatures. We have found a strong increase of the electron-phonon drag effect in isotopically pure Ge crystals. This result suggests an appearance of additional contribution to the Herring phonon-drag thermopower in the case when normal processes are the dominant phonon scattering mechanism.

The authors thank Dr. I. G. Kuleev for helpful discussion. This work was supported by the CRDF (Project No. RP2-2274) and RFBR (Project No. 01-02-17469).

*Email address: inyushkin@imp.kiae.ru

¹E.E. Haller, J. Appl. Phys. **77**, 2857 (1995).

²A.P. Zhernov and A.V. Inyushkin, Phys. Usp. **44**, 785 (2001); **45**, 527 (2002).

³J. Vavro, M.C. Llaguno, J.E. Fischer, S. Ramesh, R.K. Saini, L.M. Ericson, V.A. Davis, R.H. Hauge, M. Pasquali, and R.E. Smalley, Phys. Rev. Lett. **90**, 065503 (2003).

⁴C. Herring, Phys. Rev. **96**, 1163 (1954).

⁵I. Pomeranchuk, J. Phys. (Moscow) **6**, 237 (1942).

⁶P.G. Klemens, Proc. Phys. Soc., London, Sect. A **68**, 1113 (1955).

⁷T.H. Geballe and G.W. Hull, Phys. Rev. **110**, 773 (1958).

⁸V.I. Ozhogin, A.V. Inyushkin, A.N. Taldenkov, A.V. Tikhomirov, G.E. Popov, E. Haller, and K. Itoh, Pis'ma Zh. Éksp. Teor. Fiz. **63**, 463 (1996) [JETP Lett. **63**, 490 (1996)].

⁹M. Asen-Palmer, K. Bartkowski, E. Gmelin, M. Cardona, A.P. Zhernov, A.V. Inyushkin, A.N. Taldenkov, V.I. Ozhogin, K.M. Itoh, and E.E. Haller, Phys. Rev. B **56**, 9431 (1997).

¹⁰T.H. Geballe and G.W. Hull, Phys. Rev. **94**, 1134 (1954).

¹¹E. Kaden and G.-L. Günter, Phys. Status Solidi B **126**, 733 (1984).

¹²C. Herring, T.H. Geballe, and J.E. Kunzler, Phys. Rev. **111**, 36 (1958).

¹³I.V. Mochan, Y.N. Obraztsov, and T.V. Smirnova, Fiz. Tverd. Tela (Leningrad) **1**, 1351 (1959) [Sov. Phys. Solid State **1**, 1239 (1960)].

¹⁴V.S. Oskotskii, A.M. Pogarskii, I.M. Timchenko, and S.S. Shalyt, Fiz. Tverd. Tela (Leningrad) **10**, 3247 (1968) [Sov. Phys. Solid State **10**, 2569 (1968)].

¹⁵K. Itoh, W.L. Hansen, E.E. Haller, J.W. Farmer, V.I. Ozhogin, A. Rudnev, and A. Tikhomirov, J. Mater. Res. **8**, 1341 (1993).

¹⁶K.D.D. Rathnayaka, J. Phys. E **18**, 380 (1985).

¹⁷A.P. Zhernov and D.A. Zhernov, Zh. Éksp. Teor. Fiz. **114**, 1757 (1998) [JETP **87**, 952 (1998)].

¹⁸J. Callaway, Phys. Rev. **113**, 1046 (1959).

¹⁹V.A. Kozlov and E.L. Nagaev, Pis'ma Zh. Éksp. Teor. Fiz. **13**, 639 (1971) [JETP Lett. **13**, 455 (1971)].

²⁰A.A. Belchik and V.A. Kozlov, Fiz. Tekh. Poluprovodn. (S.-Peterburg) **20**, 53 (1986) [Sov. Phys. Semicond. **20**, 31 (1986)].

²¹I.G. Kuleev and I.I. Kuleev, Zh. Éksp. Teor. Fiz. **120**, 649 (2001) [JETP **93**, 568 (2001)].

²²I.G. Kuleev, I.I. Kuleev, A.N. Taldenkov, A.V. Inyushkin, V.I. Ozhogin, K.M. Itoh, and E.E. Haller, Zh. Éksp. Teor. Fiz. **123**, 1227 (2003) [JETP **96**, 1078 (2003)].