Isotope effect for the thermal expansion coefficient of germanium

V. I. Ozhogin,*) N. A. Babushkina, L. M. Belova, and A. P. Zhernov

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

E. E. Haller

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

K. M. Itoh

Department of Applied Physics, Keio University, Yokohama, 223-8522 Japan

The first experimental and theoretical investigation of the difference in the temperature behavior of the linear expansion coefficients of single crystals grown from isotopically highly enriched and natural germanium is reported. A comparison of the data for ^{70}Ge and ^{nat}Ge crystals reveals the significant influence of isotopic composition over a wide range of temperatures 30–230 K. © *1999 American Institute of Physics.* [S1063-7761(99)02101-0]

Many problems in the theory of the thermal expansion of crystal lattice have been thoroughly studied (see, e.g., Ref. 1). To the best of our knowledge, however, the thermal expansion coefficient α for crystals differing solely in their isotopic composition has not investigated. In this paper we report the first experimental and theoretical study of the behavior of the coefficient α as a function of the isotopic composition over a wide range of temperatures. We are specifically concerned with natural germanium (^{nat}Ge) and highly enriched (99.99%) germanium (^{70}Ge) samples.

The dependence of the thermal expansion coefficient α on the temperature T is dictated by the temperature behavior of the heat capacity in many cases. This is because the total Grüneisen factor γ (which is sensitive to the anharmonic interatomic force parameters) usually exhibits a weak dependence on T. For germanium, on the other hand, the dependence of γ on T is very strong. Here, since $\gamma(T)$ is a sign-indefinite function, the behavior of $\alpha(T)$ for Ge is qualitatively determined primarily by the Grüneisen factor and not by the heat capacity.[1]

In regard to kinetic phenomena two types of isotope effects are possible, which differ in that one depends linearly, and the other quadratically on the difference in the masses of the isotopes. Linear effects are governed by the variation of the phonon spectrum as the isotopic composition changes. Quadratic effects are associated with the irregular distribution of the isotopes and induce an additional relaxation mechanism of phonon (and electron) scattering. Their role has been investigated in application to the thermal conductivity of germanium in, for example, Refs. 2 and 3. As for thermal expansion, on the other hand, both the linear and the quadratic dependences on the isotopic mass are entirely the result of the variation of the phonon spectrum.

EXPERIMENTAL OBSERVATION OF THE ISOTOPE EFFECT IN THE THERMAL EXPANSION OF GERMANIUM

We have performed for the first time measurements of the temperature dependence of the difference in the linear expansion coefficients of chemically pure and structurally perfect germanium ^{70}Ge and ^{nat}Ge single crystals over a wide temperature range 30–230 K. According to mass-spectrometer measurements, the content of the primary isotope in ^{70}Ge single crystals is at least 99.99%. In this connection a measurement of the Hall conductivity in it has shown that the total concentration of electrically active impurities does not exceed 2×10^{12} cm^{-3} (Ref. 2). The ^{nat}Ge single crystal is a mixture of five isotopes having an average mass of 72.59.

The thermal expansion of the samples was investigated by means of a strain-gauge dilatometer. The recording part of the instrument was a bridge circuit. The customary approach in this method is to place the investigated sample and a standard sample on the instrument mounting, with identical standard resistance gauges (Ni–Cu–Cr wire of diameter 30 μm, $R = 100\,\Omega$) attached to them. As the temperature is varied, the deformation of the gauges differs because the samples expand differently, producing different variations of their resistances and thus creating a bridge unbalance. This method has a sensitivity of 5×10^{-7} cm. The temperature dependence of the thermal expansion was measured with the samples heated at a rate not greater than 0.3 K/min. The temperature sensor was a copper–iron (Cu + 0.05%Fe)–copper thermocouple. The mounting of the samples is shown in Fig. 1. In principle, the experimental error can depend on the gauge bonding technology and on the temperature interval in which the measurements are performed. Additional measurements have shown that the error is less than 5%.

The quality of the measurement system was tested using a standard sample of pure copper, for which the values of the
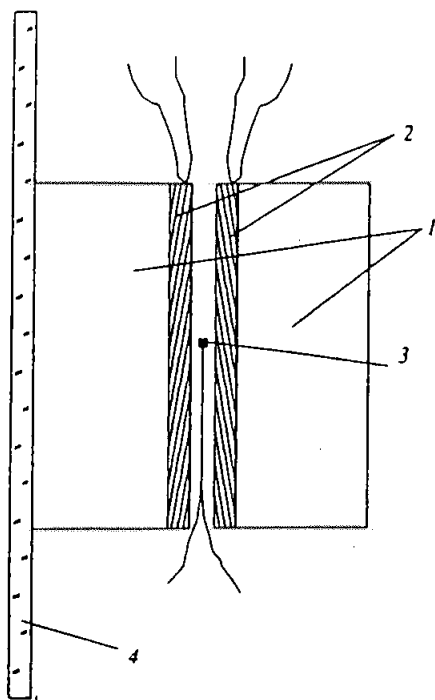
thermal expansion coefficient are well known. Our data for copper (in measurement relative to quartz) differ by at most 5% from established data at temperatures of 20–80 K (Ref. 1).

To improve the reliability of the results in the present study, we performed direct measurements of the difference in the thermal expansion coefficients of chemically pure ^{nat}Ge and ^{70}Ge single crystals. The samples of natural and isotopically pure germanium were mounted in two arms of the measurement bridge. The measured bridge unbalance in this case is proportional to the difference in the thermal expansions of the two samples, ^{nat}Ge and ^{70}Ge.

The samples were cut from germanium single crystals in the shape of $5 \times 4 \times 2$-mm parallelepipeds with their longest edges parallel to the [100] axis of the crystal.

This setup was used to measure the relative thermal elongation $\Delta l/l$ of the sample. Our object of interest, the thermal expansion coefficient $\alpha = (1/l)(dl/dT)$, was calculated by numerical differentiation of the graph of $\Delta l/l$ as a function of T.

The results of measurements of the difference $\Delta \alpha$ in the thermal expansion coefficients of the two single crystals are shown in Fig. 2. The scatter of the values of $\Delta \alpha$ as a function of T was found to be $\sim 20\%$ after differentiation of the experimental data with respect to T. The scatter of $\Delta \alpha(T)$ is large because the measured quantity is the temperature dependence of the small difference between the thermal expansions $\Delta l/l$ of the two single crystals (^{nat}Ge and ^{70}Ge). The $\Delta \alpha(T)$ curve in Fig. 2 is smoothed by a polynomial. The absolute rms error of the values so obtained for $\Delta \alpha(T)$ is $\sim 20\%$ in the temperature range 60–200 K and $\sim 30-40\%$ in the low-temperature range. Errors can also be attributed to

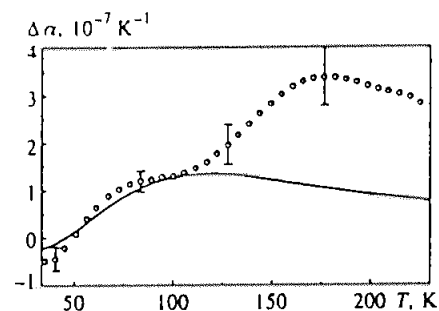
FIG. 2. Temperature dependence of the factor $\Delta \alpha = \alpha_c(M_{c1}) - \alpha_c(M_{c2})$, where $M_{c1} = 72.59$ and $M_{c2} = 70$, theoretical (solid curve) and experimental (dots).

limited capabilities for regulating the temperature regime of the experimental setup, for example, an insufficiently slow temperature scanning rate in measuring the temperature dependence of the relative thermal expansion of germanium.

THEORETICAL ANALYSIS OF THERMAL EXPANSION TO FIRST ORDER IN THE DIFFERENCE IN ISOTOPIC MASSES

In the quasiharmonic approach to the linear isotopic mass-difference approximation for cubic crystals the linear expansion coefficient α is given by the relations[4]

$$\alpha(T) = \frac{1}{3\Omega_0 B_0} \sigma(T), \tag{1}$$

$$\sigma(T) = \sum_l \gamma(l) C_l(T), \quad C_l(T) = \frac{1}{T^2} \omega^2(l) n(\omega(l))$$

$$\times [n(\omega(l)) + 1]. \tag{2}$$

Here $\omega(l)$ is the phonon frequency of the lth mode with quasimomentum f and polarization j, i.e., $l = \{f, j\}$, $n(\omega)$ is the Planck distribution, $\gamma(l)$ is the partial (mode) Grüneisen factor, i.e., by definition

$$\gamma(l) = -\frac{\partial \ln \omega(l)}{\partial \ln \Omega} \bigg|_{\Omega = \Omega_0}, \tag{3}$$

C_l denotes the heat capacity of the lth mode, Ω_0 is the equilibrium unit cell volume of the lattice, and B_0 is the hydrostatic compression modulus at $T = 0$. The Boltzmann and Planck constants are set equal to unity.

Equation (1) can be written in the form

$$\alpha(T) = \frac{1}{3\Omega_0 B_0} \gamma(T) C_L(T), \tag{1'}$$

where $\gamma(T)$ is the total Grüneisen factor, and $C_L(T) = \Sigma_l C_l(T)$ is the lattice heat capacity.

Note the following relation, which holds for any isotopic composition in any mode:

$$M_c \omega^2(l) = \varphi(l), \tag{4}$$

where the effective force parameter $\varphi(l)$ does not depend on the average mass M_c. By definition,

$$M_c = \sum_i c_i M_i,$$

where c_i is the concentration and M_i is the mass of isotopes of the ith species.

We now fix a specific isotopic composition by the index c_0. Making use of Eqs. (1) and (4), we then have a universal relation for an arbitrary isotopic composition, which we label with the index c:

$$\alpha_c(T) = \alpha_{c_0}(T'), \quad T' = T\sqrt{M_c/M_{c_0}}. \tag{5}$$

We close this section with a few words about the general case of an anharmonic crystal lattice. In such a lattice the mode frequency $\tilde{\omega}(l)$ consists of the sum of the harmonic and anharmonic contributions:

$$\tilde{\omega}(l, T) = \omega(l, \Omega) + \Delta^{(a)}(l, \Omega). \tag{6}$$

The increment $\Delta^{(a)}$ is determined by standard third- and fourth-order anharmonic processes.[5,6] The expression for the anharmonic correction to the Grüneisen factor $\gamma(l)$ now has the form

$$\Delta\gamma^{(a)}(l, T) \approx \Delta\Omega(T)\frac{\partial\gamma(l)}{\partial\Omega_0} - \frac{\partial\{\Delta^{(a)}(l)/\omega(l)\}}{\partial\Omega_0}. \tag{7}$$

Here $\Omega(T) = \Delta\Omega(T) + \Omega_0$ is the unit cell volume.

Second-order effects with respect to the difference in the isotopic masses are not discussed in this paper, because an estimate shows that their role is of little consequence in application to germanium.

COMPARISON OF THEORY WITH EXPERIMENT

Using relations (1)–(3) and (5), we calculate the coefficients $\alpha(T)$ for germanium crystals with average masses of 72.59 and 70. Here we determine the frequencies of the phonon modes $\omega(l)$ from the Born–von Kármán theory. We use the force parameters obtained previously[7] by the fitting of experimental inelastic neutron scattering data. We also use the partial Grüneisen factors γ_l determined in Ref. 8 in the microscopic bond-charge model. In addition, we assign the following values to the lattice constant a_0 and the compression modulus B_0: $a_0 = 5.658$ Å; $B_0 = 0.772 \times 10^{12}$ dyn/cm^2 (Ref. 9).

The results of the calculations are shown in the same figure as the experimental data (Fig. 2). The difference curves $\Delta\alpha = \alpha(M_{c1}) - \alpha(M_{c2})$ are shown for germanium crystals with masses $M_{c1} = 72.59$ and $M_{c2} = 70$, respectively. It is evident at once that theory and experiment are in reasonably good agreement in the temperature range $\sim 30 - 100$ K. The agreement is unsatisfactory at higher temperatures.

In our work we have observed that the isotope effect is large in the thermal expansion of germanium. In the temperature interval from 75 K to 125 K the relative difference $\Delta\alpha/\alpha$ reaches 10%. The data for α in ^{nat}Ge are borrowed from Ref. 1. According to the above calculations, $\Delta\alpha$ should not be more than a few percent at higher temperatures.

We also estimate the anharmonic corrections to the partial Grüneisen factors in the model of Ref. 8 on the basis of

Eqs. (6) and (7). We note that for the majority of the modes the parameters $\gamma^{(a)}(l) = \gamma(l) + \Delta\gamma^{(a)}(l)$ increase with the temperature. The anharmonicity-induced renormalizations, for example, at $T \approx 150$ K, are approximately 4%. On the other hand, a nonstandard situation is encountered for soft transverse modes. The corresponding values of $\gamma^{(a)}$ are approximately 1.3 times smaller in absolute value as a result of anharmonicity at the same temperature of 150 K. Here the calculations yield $\Delta\alpha = \alpha_c(M_{c1}) - \alpha_c(M_{c2}) = 0.142 \times 10^{-6}$ K^{-1} instead of the value of 0.121×10^{-6} K^{-1} obtained in the quasiharmonic approach. Consequently, when anharmonicity is taken into account, the quantitative description of the experimental data improves, but the discrepancy is still substantial.

We note that the theoretical calculations give results too low in comparison with the experimental data. The disparity could stem from the small difference in the chemical purity of the germanium ^{nat}Ge and ^{70}Ge single crystals. According to Ref. 10, the thermal expansion coefficient for Ge can differ for samples having different impurity concentrations. Moreover, the model in Ref. 8 is also in need of further development and refinement.

To summarize, for the first time we have measured the temperature dependence of the difference in the linear expansion coefficients of chemically pure germanium ^{nat}Ge and ^{70}Ge single crystals. We have found that theory and experiment concur reasonably well in the temperature range $\sim 30 - 100$ K. The agreement falls short at higher temperatures. Allowance for the anharmonicity of interaction between phonon modes brings theory and experiment somewhat closer together.

*)E-mail: ozhogin@imp.kiae.ru

[1] S. I. Novikova, Thermal Expansion of Solids [in Russian], Nauka, Moscow (1974).

[2] V. I. Ozhogin, A. V. Inyushkin, A. N. Taldenkov et al., JETP Lett. 63, 490 (1996).

[3] M. Asen-Palmer, K. Bartkowski, E. Gmelin et al., Phys. Rev. B 56, 9431 (1997).

[4] G. Leibfried, "Gittertheorie der mechanischen und thermischen Eigenschaften der Kristalle (Lattice theory of the mechanical and thermal properties of crystals)," in Handbuch der Physik, S. Flügge (Ed.), Vol. 7, Part 1, Springer-Verlag, Berlin (1955), pp. 104–324.

[5] M. A. Krivoglaz, Theory of X-Ray and Thermal Neutron Scattering by Real Crystals, Plenum Press, New York (1969).

[6] J. A. Reissland, The Physics of Phonons, Wiley, New York (1973).

[7] A. D. Zdetsis and C. S. Wang, Phys. Rev. B 19, 2999 (1979).

[8] R. Eryigit and I. P. Herman, Phys. Rev. B 53, 7775 (1996).

[9] G. Leibfried and N. Breuer, Point Defects in Metals, I: Introduction to the Theory, Springer-Verlag, Berlin (1978).

[10] V. V. Zhdanova, Fiz. Tverd. Tela (St. Petersburg) 5, 3341 (1963) [Sov. Phys. Solid State 5, 2451 (1963)].

Translated by James S. Wood