Physics of the Solid State, 2024, Vol. 66, No. 8

10,03

Effect of atomic mass and isotopic disorder on the phonon spectra of isotope-enriched germanium crystals

© *T.V. Kotereva*[1], *V.A. Gavva*[1], *V.A. Lipsky*[1], *A.V. Nezhdanov*[2], *V.G. Plotnichenko*[3], *A.D. Bulanov*[1,2]

[1] Devyatykh Institute of Chemistry of High-Purity Substances, Russian Academy of Sciences,
Nizhny Novgorod, Russia
[2] Lobachevsky State University,
Nizhny Novgorod, Russia
[3] Prokhorov General Physics Institute of the Russian Academy of Sciences,
Dianov Fiber Optics Research Center,
Moscow, Russia

E-mail: kotereva@ihps-nnov.ru

Received April 23, 2024
Revised April 23, 2024
Accepted June 20, 2024

Studied the influence of average atomic mass and isotopic disorder on the phonon spectra of lattice IR absorption and Raman scattering (RS) for single crystals of germanium isotopes ^{72}Ge, ^{74}Ge and ^{73}Ge in comparison with $^{72}\mathrm{Ge}_{0.5}{}^{74}\mathrm{Ge}_{0.5}$. At a temperature of 15 K, differences in the width and position of the two-phonon absorption bands in the IR spectra were observed for the monocrystalline germanium $^{72}\mathrm{Ge}_{0.5}{}^{74}\mathrm{Ge}_{0.5}$ and ^{73}Ge. In the first- and second-order RS spectra, a shift of phonon frequencies to the higher frequency region was found, associated with a decrease in the average atomic mass of germanium single crystals.

Keywords: Elemental semiconductors, stable germanium isotopes, isotopic effects, Raman scattering, IR absorption.

DOI: 10.61011/PSS.2024.08.59062.97

1. Introduction

Obtaining, studying the properties and practical application of substances with a high degree of chemical and isotopic purity is one of the dynamically developing areas of fundamental and applied research. The preparation of crystalline solid semiconductors and the study of the influence of isotopic composition on their properties,arouse particular interest. One of the promising objects for this research is germanium. The recently developed hydride technology for the production of stable isotopes of germanium with a high degree of chemical and isotopic purity [1] has made it possible to obtain samples in sufficient quantities for research. The principal possibility of obtaining germanium in the form of single- crystals with high chemical purity and the presence of five stable isotopes ^{70}Ge (20.57%), ^{72}Ge (27.45%), ^{73}Ge (7.75%), ^{74}Ge (36.50%), ^{76}Ge (7.73%) [2] allowed us to use it as a target for obtaining fundamental knowledge about the influence of isotopic composition on the properties of semiconductors.

The influence of isotopic composition on the properties of crystals is associated with two factors: changes in the average atomic mass and isotopic disorder. A change in atomic mass leads to a change in the lattice parameter of crystals and deformation of the phonon spectrum, which, in turn, can affect the electronic properties of solids through the mechanism of electron-phonon interaction. The study of the dependence of a number of properties on the atomic mass of the isotope Ge showed that in most cases it is well described within the framework of the virtual crystal model [3,4]. Isotopic disorder has a strong influence on the thermal conductivity [5] and thermoelectric power [6] of germanium in the low-temperature region.

Well-developed methods for studying isotope effects in the phonon spectrum of crystals are Raman scattering (RS) and absorption infrared (IR) spectroscopy. Previously, these methods were used to study the vibrational spectra of crystals of Ge and Si isotopes in works [7,8].

The IR absorption spectra of single crystals of germanium isotopes ^{70}Ge and ^{74}Ge in the region $520-1000\,\mathrm{cm}^{-1}$ were studied in [9]. A shift of the bands to the long-wavelength region with increasing atomic mass of the isotope was observed. The effect of an alloying impurity on the attenuation coefficient in the absorption region of the crystal lattice is shown. Tabular data on the position of the maxima of the IR absorption bands of the crystal lattice of isotopes ^{72}Ge, ^{73}Ge, ^{74}Ge, ^{76}Ge were obtained in [10]. In [11], the effect of isotopic disorder on the IR absorption spectra of germanium was investigated using ^{76}Ge and Ge samples with natural isotopic compositions. The studied samples differed both in their average atomic mass and in the degree of isotopic disorder, which makes it difficult to isolate the influence of each factor. Thus, the detection of effects caused only by isotopic disorder is possible by comparing the spectra of samples with the same atomic mass.

A number of works are devoted to the study of Raman scattering of light in germanium crystals. In [12] the first-

Table 1. Values of the average atomic mass and factor of isotopic disorder of germanium samples

Sample	$^{\mathrm{nat}}$Ge	^{72}Ge	^{73} ^{74}Ge	^{72}Ge$_{0.5}$^{74}Ge$_{0.5}$	
Average atomic mass	72.605	72.0002	73.0002	73.9991	72.9999
The isotopic factor disorder g	$5.87 \cdot 10^{-4}$	$5.27 \cdot 10^{-8}$	$1.93 \cdot 10^{-7}$	$3.53 \cdot 10^{-7}$	$1.88 \cdot 10^{-4}$

order Raman spectra of natural germanium, its isotopes ^{70}Ge (95.9%), ^{73}Ge, ^{74}Ge (95.8%), ^{76}Ge (86.0%) and an alloy containing 42.7% ^{70}Ge and 48% ^{76}Ge at a temperature of 10 K were investigated. It was found that the magnitude of the shift increases with decreasing atomic mass of the isotope. An additional shift and broadening of the Raman band at a temperature of 77 K was detected for isotopically disordered samples of natural germanium and the ^{70}Ge^{76}Ge alloy. In work [13], a comparison of the band shape of the Raman isotope of germanium ^{70}Ge, natural germanium and alloy ^{70}Ge^{76}Ge was carried out. For natural Ge crystals and the ^{70}Ge^{76}Ge alloy, additional scattering was observed in the low-energy part of the ground band of the Raman associated with isotopic disorder, no line broadening was reported.

In [14] the second-order Raman spectrum of germanium of natural isotopic composition was studied. The correlation of the Raman spectrum with the density of phonon states measured by the neutron scattering method [15] has been established.

The phonon spectra of germanium with different values of the isotopic disorder factor have been studied by the authors of many works [12,13,16–19]. However, the results of comparative analysis of an isotopically disordered crystal with a germanium sample with the same average atomic mass are rarely found in the literature.

In [16,17], comparative data on the effect of the isotopic composition of germanium on the spectrum of second-order Raman for the isotope ^{70}Ge,(95.9%), alloy ^{70}Ge$_{0.5}$^{76}Ge$_{0.5}$ and germanium with natural isotopic composition are presented. There is no information about the second-order Raman spectra for other germanium isotopes in the literature.

The purpose of this work — is to conduct a comparative analysis of the effect of isotopic disorderliness and average atomic mass on the phonon spectra of the first and second order enriched germanium crystals with a higher degree of enrichment than previously studied samples.

Samples of single crystals of the germanium isotopes ^{72}Ge, ^{73}Ge, and ^{74}Ge with a higher degree of isotopic enrichment (greater than 99.9%) were used to study the effect of average atomic mass. For a comparative study of the contribution of isotopic disorderliness, a single crystal of the ^{72}Ge$_{0.5}$^{74}Ge$_{0.5}$ alloy was grown for the first time, having almost the same (difference ~ 0.0004, at.%) average atomic mass with ^{73}Ge.

2. The experimental part

2.1. Characteristics of the studied germanium isotope samples

Isotopes ^{72}Ge, ^{73}Ge, ^{74}Ge were obtained by the hydride method described in detail in [1]. To obtain the ^{72}Ge$_{0.5}$^{74}Ge$_{0.5}$ sample, equimolar amounts of ^{72}Ge and ^{74}Ge isotopes were fused in a crucible made of high-purity quartz glass coated with amorphous SiO$_2$. After melting the charge, it was kept for 1 h in the alternating electromagnetic field of the inductor to homogenize the melt. The melt was then subjected to directional solidification using the Bridgman method.

To study the IR absorption and Raman spectra, plane-parallel plates with a thickness of 1.3 mm were cut from the middle part of the single-crystals. Both sides of the plates have been polished.

The content of chemical impurities in isotopically enriched germanium according to mass spectrometric analysis — less than $10^{-4}-10^{-6}$ wt%. The isotopic composition of the studied germanium samples was analyzed by inductively coupled plasma mass spectrometry (ICP-MS).

Isotopic disorder was characterized by the value of the factor g, which was determined by the formula (1) [17]:

$$g = \sum\nolimits_i C_i[(M_i - M_{\mathrm{av}})/M_{\mathrm{av}}]^2, \qquad (1)$$

where M_i and C_i — the mass of the i-isotope and its concentration.

According to the data on the isotopic composition of the studied samples, their average atomic mass M_{av} and the isotopic disorder factor g were calculated (Table 1).

It can be seen that the value of the factor g for the alloy ^{72}Ge$_{0.5}$^{74}Ge$_{0.5}$ is about 3 orders of magnitude higher than for pure isotopes.

2.2. Registration of IR transmission and Raman spectra of germanium

IR transmission spectra were recorded in the region of $200-700\,\mathrm{cm}^{-1}$ at temperatures of 298 and 15 K using an IFS-113v IR Fourier transform spectrometer equipped with a DTGS detector with a polyethylene window. The resolution was $0.5\,\mathrm{cm}^{-1}$. Lavsan film was used as a beam splitter. Radiation source — globar (SiC rod). To cool the samples to a temperature of 15 K, a closed-cycle cryostat refrigerator RGD 210 from Leybold with windows made of KRS-5 was used. The number of accumulated scans for subsequent averaging was 250.

The Raman spectra of single-crystal isotopically enriched germanium samples were obtained using the INTEGRA Spectrum complex (NT-MDT, Russia) at room temperature 295 K in the reflection scheme. The excitation was carried out by HeNe laser radiation with a wavelength of 632.8 nm. The radiation was focused by a 100x aperture lens NA = 0.95. The power of unfocused laser radiation, measured using a flint photodetector 11PD100-Si (Standa Ltd), was 1.9 mW. The detection of Raman spectra was carried out by a cooled ANDORTM CCD camera in the range of 150−1000 cm^{-1} with a resolution of 0.9 cm^{-1}.

3. Results and discussion

3.1. IR transmission spectra

Results of comparative study of IR spectra in the region of phonon lattice vibrations of germanium isotopes ^{72}Ge, ^{73}Ge, ^{74}Ge and alloy $^{72}\mathrm{Ge}_{0.5}{}^{74}\mathrm{Ge}_{0.5}$ are presented in Figure 1 The phonon frequencies for the isotopes ^{72}Ge, ^{73}Ge and ^{74}Ge increase with a decrease in their average atomic mass. The dependence of the phonon frequency on the atomic mass is well described in frames of the virtual crystal model. Comparison of the IR spectra of ^{73}Ge and the alloy $^{72}\mathrm{Ge}_{0.5}{}^{74}\mathrm{Ge}_{0.5}$ showed that the position and half-width of the IR absorption bands coincide within the experimental error, which was $< 0.1\,\mathrm{cm}^{-1}$, i. e. the effect of the isotopic disorder factor on the IR absorption of germanium at room temperature was not detected at a resolution of 0.5 cm^{-1}.

In the IR spectra of ^{73}Ge single-crystals and $^{72}\mathrm{Ge}_{0.5}{}^{74}\mathrm{Ge}_{0.5}$ alloy obtained at low temperature (15 K), it can be seen that the structure of some bands in the two-phonon absorption region is different (Figure 2). In the phonon absorption region $(\mathrm{TO}+\mathrm{TA})_\mathrm{X}$, $(\mathrm{TO}+\mathrm{TA})_\mathrm{L}$ at 350 cm^{-1} the positions of the maxima coincide within the experimental error, a broadening is observed in isotopically disordered $^{72}\mathrm{Ge}_{0.5}{}^{74}\mathrm{Ge}_{0.5}$ compared to isotopically pure ^{73}Ge. The broadening value measured at the locations indicated by the arrows in Figure 2 was 1.5−3.5 cm^{-1}. In the absorption region of phonons $(\mathrm{LO}+\mathrm{LA})_\mathrm{K}$, $(\mathrm{LO}+\mathrm{LA})_\mathrm{L}$ at 500−400 cm^{-1} no differences in the shape of the bands were revealed. This is consistent with the results of the work of [11], where it is shown that the additional line broadening caused by isotopic disorder strongly depends on the energy of phonons; and only transverse optical phonons at points L, K, W and X in the Brillouin zone are significantly influenced by isotopic disorder.

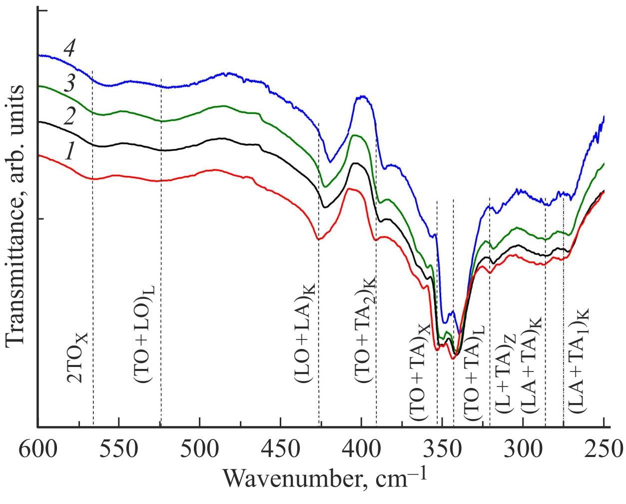

Figure 1. IR transmission spectra of single-crystals of germanium isotopes at $T = 298$ K: curve *1* — ^{72}Ge, *2* — ^{73}Ge, *3* — $^{72}\mathrm{Ge}_{0.5}{}^{74}\mathrm{Ge}_{0.5}$, *4* — ^{74}Ge. Phonon assignment [11]. The spectra are shifted along the ordinate axis for convenience.

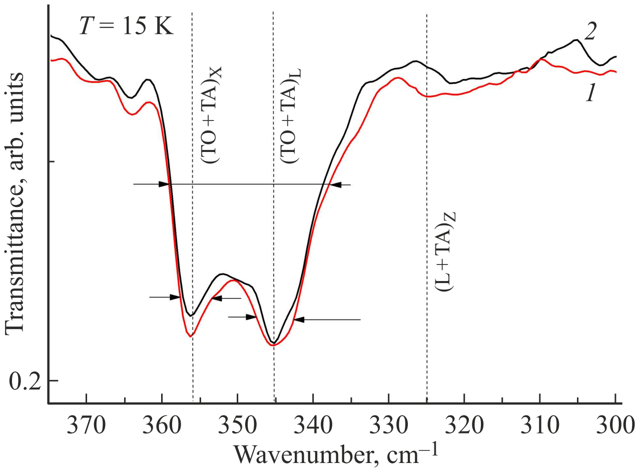

Figure 2. IR transmission spectra of ^{73}Ge and $^{72}\mathrm{Ge}_{0.5}{}^{74}\mathrm{Ge}_{0.5}$ alloy at $T = 15$ K. Curve *1* — $^{72}\mathrm{Ge}_{0.5}{}^{74}\mathrm{Ge}_{0.5}$, *2* — ^{73}Ge.

The band shift associated with isotopic disorder may be more pronounced in the long-wavelength part of the spectrum, as demonstrated in [11]; this is supported by our experimental data. The frequency shift to the short wavelength region in $^{72}\mathrm{Ge}_{0.5}{}^{74}\mathrm{Ge}_{0.5}$ compared to ^{73}Ge was determined by us from the IR spectra for the $(\mathrm{L}+\mathrm{TA})_\mathrm{Z}$ phonon, attributed according to [11] (and $(\mathrm{L}+\mathrm{TA})_\mathrm{W,X}$ according to [15,20]), at 320 cm^{-1} was $2.5 \pm 0.5\,\mathrm{cm}^{-1}$. This value exceeds the contribution calculated in [21] from anharmonicity in natural Germanium 0.08 cm^{-1} at a temperature of 10 K, therefore, it can be assumed that the nature of the shift is associated with the influence of isotopic disorder. It should be noted that the maximum detection accuracy was low for the $(\mathrm{L}+\mathrm{TA})_\mathrm{Z}$ phonon due to the noise level and weak intensity of the absorption bands.

3.2. Raman scattering spectra

For crystals with diamond-like crystal lattice, to which germanium belongs, are characterized by a threefold degeneracy of the phonon states in the center of the

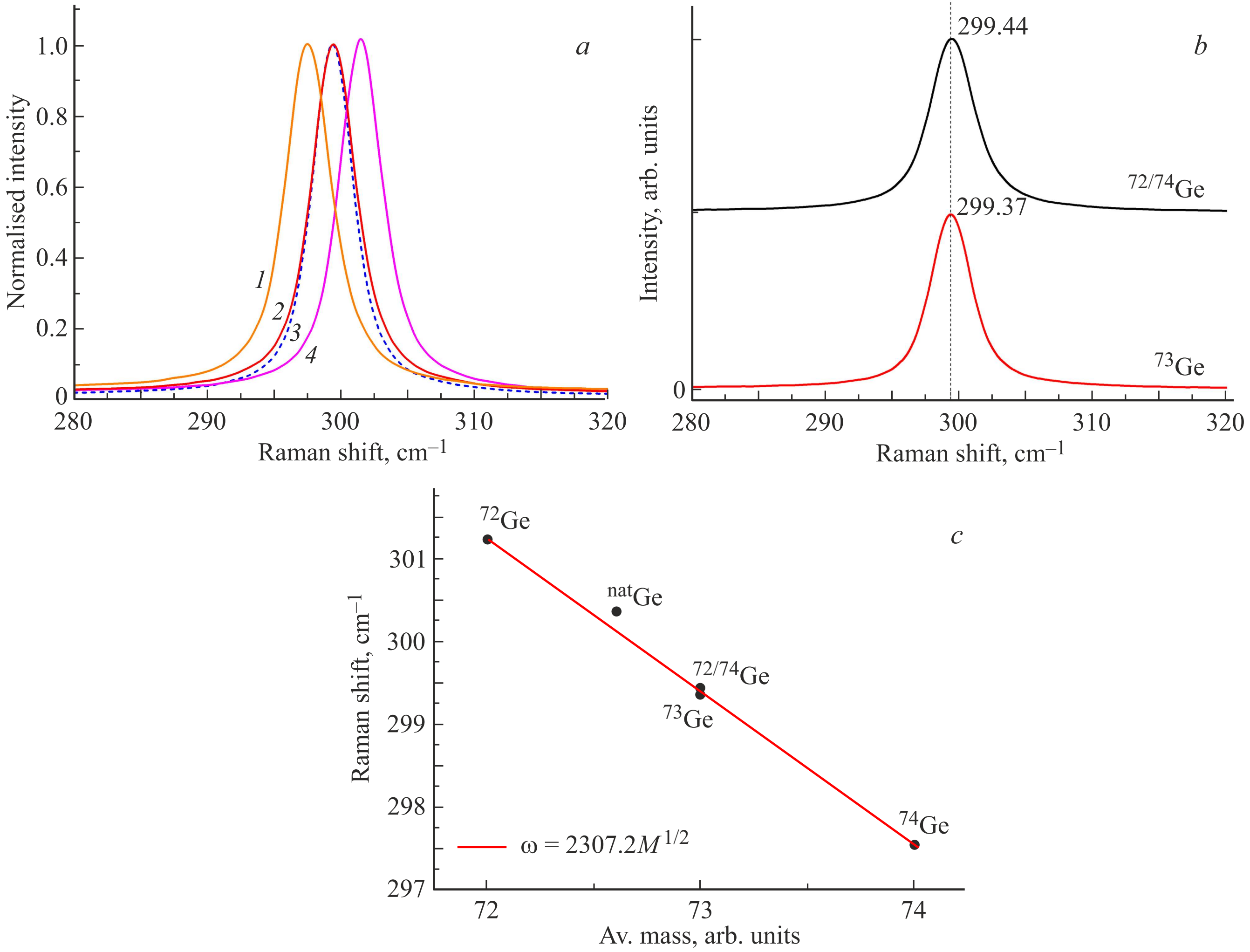

Figure 3. *a*) First-order Raman spectrum of germanium isotopes ^{72}Ge, ^{73}Ge, ^{74}Ge and alloy ^{72}Ge$_{0.5}$^{74}Ge$_{0.5}$. Curve *1* — ^{74}Ge, *2* — ^{72}Ge$_{0.5}$^{74}Ge$_{0.5}$, *3* — ^{73}Ge, *4* — ^{72}Ge; *b*) comparison of Raman spectra of ^{73}Ge and disordered ^{72}Ge$_{0.5}$^{74}Ge$_{0.5}$ alloy sample; *c*) Raman frequency as a function of average atomic mass, measured at 298 K, for isotopically pure and disordered samples Ge.

Brillouin zone ($\mathbf{k} = 0$), which are active in Raman scattering spectra. Figure 3 shows the first-order Raman spectrum for samples of single-crystal isotopes of germanium ^{72}Ge, ^{73}Ge, ^{74}Ge and alloy ^{72}Ge$_{0.5}$^{74}Ge$_{0.5}$. To obtain information on the frequency of the maximum and half-width of the bands, the intensity was normalized to unity and the line was approximated by the Lorentz function. The error in the determination of frequency and half-width in this processing of the spectra did not exceed 0.01 and 0.1 cm^{-1}, respectively. The accuracy of the position of the Raman band peaks was determined by the instrumental error of the device and was 0.3 cm^{-1}.

With a decrease in the average atomic mass of the isotopes, a shift of the first-order Raman bands to the high-frequency region was observed. The dependence of the position of the band maxima on atomic mass is well described by the expression $\omega \propto M^{-1/2}$. It is known that the frequency shift due to isotopic disorder is proportional to the parameter g according to the expression [12]:

$$\Delta\omega = g\,\frac{\omega^2}{12}\int_0^\infty \frac{1}{(\omega^2-\omega_i^2)}\,N_{\mathrm{d}}(\omega_i)\,d\omega_i, \qquad (2)$$

where ω is the optical phonon frequency, $N_{\mathrm{d}}(\omega_i)$ is the density of states function.

The values of g for a sample of natural Ge are $5.87 \cdot 10^{-4}$, for the alloy ^{72}Ge$_{0.5}$^{74}Ge$_{0.5}$ — $1.88 \cdot 10^{-4}$. The magnitude of the shift in the Raman spectrum for a sample of natural isotopic composition according to [12] and our experimental data [7] was ~ 0.4 cm^{-1}, then the shift in the Raman frequency of the optical phonon at the point Γ, caused by isotopic disorder, should be in the alloy by 3.1 times less than in natural Ge, i.e. 0.13 cm^{-1}. The difference in the maximum position in Figure 3 in the spectra of ^{73}Ge and ^{72}Ge$_{0.5}$^{74}Ge$_{0.5}$ alloy samples having the same average mass in our work was 0.07 cm^{-1}, which is lower than the experimental error of 0.15 cm^{-1}.

Table 2. Values of the maxima of the wave numbers of phonons in the Raman spectra (Figure 4) of germanium isotopes and the alloy $^{72}\mathrm{Ge}_{0.5}{}^{74}\mathrm{Ge}_{0.5}$. Phonon assignment [17]

Phonons	The position of the maxima of the phonon bands, cm^{-1}			
	$^{72}\mathrm{Ge}$	$^{72}\mathrm{Ge}_{0.5}{}^{74}\mathrm{Ge}_{0.5}$	$^{73}\mathrm{Ge}$	$^{74}\mathrm{Ge}$
2TA(X)	160.8	159.4	159.4	158.5
2TA(W–K, L–W)	230.2	228.0	228.0	226.9
TO(Γ)	301.3	299.4	299.4	297.6
TO(X)+TA(X)	353.7	351.7	351.6	350.3
2LA(K–L)	378.4	378.3	378.3	377.7
2TO(W)	552.7	547.8	550.1	545.5
2TO(L)	574.9	570.0	570.6	567.3
2O(Γ)	596.7	593.6	593.2	588.1

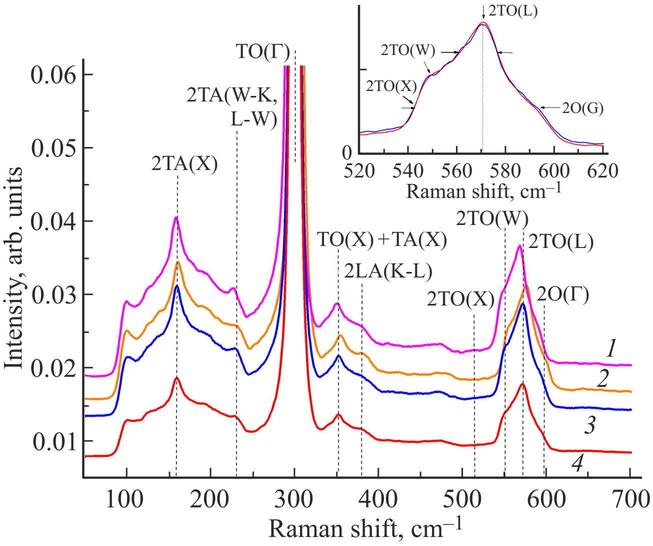

Figure 4. *a*) Second order Raman spectrum. The density of overtone states for optical branches is in the range 520–600 cm^{-1} (inset). The observed peak positions are listed in Table 2. Curve *1* — $^{74}\mathrm{Ge}$, *2* — $^{72}\mathrm{Ge}$, *3* — $^{73}\mathrm{Ge}$, *4* — $^{72}\mathrm{Ge}_{0.5}{}^{74}\mathrm{Ge}_{0.5}$.

The half-width of the phonon bands in Ge is determined by their lifetime (anharmonic disintegration into two or more low-energy phonons) and the broadening associated with isotopic disorder. The contribution to the half-width of the line arising from isotopic disorder, according to [15], is two orders of magnitude less than the broadening due to anharmonic scattering for phonons at the point Γ, since the density of phonon states approaches zero in the center of the zone. For the first-order band broadening caused by isotopic disordering, the half-width increase in the alloy should be $\sim 0.005\,\mathrm{cm}^{-1}$ [10].

$$\Gamma_{\mathrm{isotope}} = g\,\frac{\pi\omega^2}{12}\,N_{\mathrm{d}}(\omega), \qquad (3)$$

where g — disorder factor, ω — optical phonon frequency, $N_{\mathrm{d}}(\omega) = D(\omega)$ — state density function.

The first-order Raman spectra of isotopically-enriched single-crystal Ge samples, in Figure 3, showed that the dependence of the Raman line width on the average atomic mass in the room temperature region is not detected, in contrast to that observed in work 12 at a temperature of 10 K. The broadening of the Raman band found by us for the $^{72}\mathrm{Ge}_{0.5}{}^{74}\mathrm{Ge}_{0.5}$ alloy sample, measured relative to the monoisotopic $^{73}\mathrm{Ge}$, was $0.33\,\mathrm{cm}^{-1}$. This value exceeds the value calculated by us and predicted in [12], and may include, in addition to the anharmonicity-related additive, part of the isotopic heterogeneity of the samples, and may also be due to various measurement effects such as the influence of oxide film thickness, wavelength, and laser penetration depth discussed in [12]. Therefore, it is not possible to determine more precisely the mechanisms of broadening the phonon lines of the optical zone in our experiment.

The second-order Raman spectra for single-crystals of germanium isotopes, shown in Figure 4, associated with the scattering of photons through two-phonon processes, were studied. In such processes, either two photons with identical but oppositely directed wave vectors are formed, or one phonon is formed and the other is destroyed. Since two-phonon processes occur much less frequently than single-phonon processes, the intensity of the second-order overtones in the Raman spectrum is tens of times weaker than that of the main band. Because of this, the signal-to-noise ratio deteriorates, making it difficult to observe and interpret second-order spectra. In addition, many bands represent a combination of frequencies of several two-phonon states and have a complex shape, which makes it difficult to isolate the band maxima. The second order Raman spectrum is shown in Figure 4.

Figure 4 shows the frequencies of the 2nd-order overtone in the Raman spectra of isotopically pure Ge in comparison with disordered germanium alloy, the designations of which are taken from [17]. As for the first-order Raman light scattering bands, in the second-order spectra a shift of the band maxima to the short-wavelength region is observed with a decrease in atomic mass. The highest ratio of isotopic shift to atomic mass change of $\Delta\omega/\Delta M$ was observed in the high-frequency part of the spectrum.

For samples ^{73}Ge and ^{72}Ge$_{0.5}$^{74}Ge$_{0.5}$ with the same atomic mass, the position of the band maxima within the measurement error coincides, as shown in Figure 4 (inset). The numerical values of the phonon frequency maxima for single-crystals of germanium isotopes and ^{72}Ge$_{0.5}$^{74}Ge$_{0.5}$ alloy are presented in Table 2.

4. Conclusion

Comparative studies of the influence of isotopic disorder on the IR transmission spectra in the region of phonon lattice vibrations of single crystal samples of isotopically pure ^{72}Ge, ^{73}Ge, ^{74}Ge and the ^{72}Ge$_{0.5}$^{74}Ge$_{0.5}$ alloy were carried out at room (298 K) and low (15 K) temperatures. It was shown that at room temperature the dependence of phonon frequencies on atomic mass corresponded to the virtual crystal model as $\omega \propto M^{-1/2}$, without changing the shape of the bands, thus, the influence of isotopic disorder was not detected.

In the low-temperature IR transmission spectra, a broadening of the two phonon absorption bands $(\mathrm{TO}+\mathrm{TA})_{\mathrm{x}}$ and $(\mathrm{TO}+\mathrm{TA})_{\mathrm{L}}$ was observed in the isotopically disordered single-crystal alloy ^{72}Ge$_{0.5}$^{74}Ge$_{0.5}$ compared to the isotopically pure single-crystal ^{73}Ge by $1.5-3.5\,\mathrm{cm}^{-1}$. The found frequency shift of the $(\mathrm{L}+\mathrm{TA})_{\mathrm{Z}}$ phonon by $2.5 \pm 0.5\,\mathrm{cm}^{-1}$ to the short wavelength region for ^{72}Ge$_{0.5}$^{74}Ge$_{0.5}$ with respect to ^{73}Ge is presumably associated with the influence of isotopic disorder.

The first and second order Raman spectra of single crystals of germanium isotopes were studied at $T = 295$ K. The frequencies of the Raman bands are determined; the maxima of the first and second order bands shift depending on the average atomic mass of the sample. The highest ratio of isotopic shift to atomic mass change of $\Delta\omega/\Delta M$ was observed in the high-frequency part of the spectrum. The frequencies of the phonon bands in the first- and second-order Raman spectra of the ^{73}Ge and ^{72}Ge$_{0.5}$^{74}Ge$_{0.5}$ alloy samples with the same average atomic mass coincided within the measurement error.

Funding

This study was financially supported by the Ministry of Education and Science of the Russian Federation (state assignment 2022-0003).

Conflict of interest

The authors declare that they have no conflict of interest.

References

[1] 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).

[2] M. Berglund, M.E. Wieser. Pure Appl. Chem. **83**, *2*, 397 (2011).

[3] A.V. Gusev, A.M. Gibin, I.A. Andryushchenko, V.A. Gavva, E.A. Kozyrev. Phys. Solid State **57**, *9*, 1917 (2015).

[4] C. Parks, A.K. Ramdas, S. Rodriguez, K.M. Itoh, E.E. Haller. Phys. Rev. B **49**, *20*, 14244 (1994).

[5] T.H. Geballe, G.W. Hull. Phys. Rev. **110**, *3*, 773 (1958).

[6] A.V. Inyushkin, A.N. Taldenkov, V.I. Ozhogin, K.M. Itoh, E.E. Haller. Phys. Rev. B **68**, *15*, 153203 (2003).

[7] V.A. Lipskiy, V.O. Nazaryants, T.V. Kotereva, A.D. Bulanov, V.A. Gavva, V.V. Koltashev, M.F. Churbanov, V.G. Plotnichenko. Appl. Opt. **58**, *27*, 7489 (2019).

[8] V.G. Plotnichenko, V.O. Nazaryants, E.B. Kryukova, V.V. Koltashev, V.O. Sokolov, A.V. Gusev, V.A. Gavva, T.V. Kotereva, M.F. Churbanov, E.M. Dianov. Appl. Opt. **50**, *23*, 4633 (2011).

[9] I.A. Kaplunov, V.E. Rogalin, M.Yu. Gavalyan. Opt. Spectrosc. **118**, *2*, 240 (2015).

[10] V.A. Gavva, T.V. Kotereva, V.A. Lipskiy, A.V. Nezhdanov. Opt. Spectrosc. **120**, *2*, 255 (2016).

[11] H.D. Fuchs, C.H. Grein, M. Bauer, M. Cardona. Phys. Rev. B **45**, *8*, 4065 (1992).

[12] J.M. Zhang, M. Giehler, A. Göbel, T. Ruf, M. Cardona, E.E. Haller, K. Itoh. Rev. B **57**, *3*, 1348 (1998).

[13] H.D. Fuchs, P. Etchegoin, M. Cardona, K. Itoh, E.E. Haller. Phys. Rev. Lett. **70**, *11*, 1715 (1993).

[14] B.A. Weinstein, M. Cardona. Phys. Rev. B **7**, *6*, 2545 (1973).

[15] G. Nilsson, G. Nelin. Phys. Rev. B **3**, *2*, 364 (1971).

[16] P. Etchegoin, H.D. Fuchs, J. Weber, M. Cardona, L. Pintschovius, N. Pyka, K. Itoh, E.E. Haller. Phys. Rev. B **48**, *17*, 12661 (1993).

[17] H.D. Fuchs, C.H. Grein, C. Thomsen, M. Cardona, W.L. Hansen, E.E. Haller, K. Itoh. Phys. Rev. B **43**, *6*, 4835 (1991).

[18] H.D. Fuchs, C.H. Grein, R.I. Devlen, J. Kuhl, M. Cardona. Phys. L Rev. **44**, 16–15, 8633 (1991).

[19] M. Cardona, P. Etchegoin, H.D. Fuchs, P. Molinas-Mata. J. Phys.: Condens. Matter **5**, *33A*, A61 (1993).

[20] F.A. Johnson, R. Loudon. Proc. R. Soc. London, Ser. A **281**, *1385*, 274 (1964).

[21] R.A. Cowley. J. Phys. (Paris) Colloq. **26**, 659 (1965).

Translated by D.Safin