═══════════ **PHYSICS** ═══════════

Dependence of the Position of Phonon IR Absorption Bands of Germanium Isotopes on Their Mass Number

G. I. Kropotov[a],*, Corresponding Member of the RAS A. D. Bulanov[b], V. E. Rogalin[c],**, I. A. Kaplunov[d],***, and A. A. Shakhmin[a]

Abstract—For the first time, in a single experiment, the dependence of the position of the phonon absorption peaks in the IR spectrum (range 11−40 µm) for all five stable monoisotopic germanium single crystals was studied. The dependence obtained can be used to study the mass composition of germanium of various isotopic purity.

Germanium, both crystals and its compounds, is widely used in science and technology for various purposes. The most significant areas of application are optics (parts of transmission optics and acousto-optics of the infrared range, glasses for various purposes, fiber optics), the semiconductor industry (sensors, photodetectors, gamma radiation detectors, photoelectric converters), and the chemical industry [1, 2, 4, 6].

Natural germanium contains stable isotopes with mass numbers 70, 72, 73, 74, 76 (^{70}Ge 20.57%, ^{72}Ge 27.45%, ^{73}Ge 7.75%, ^{74}Ge 36.50%, ^{76}Ge 7.73%) [3]. The use of isotopically pure crystals is associated with the possibility of technologies for their production [4−6] and opens up a number of new uses for the material. New, previously unknown properties are revealed in monoisotopic single crystals. There is a significant anomaly in the temperature dependences of thermal conductivity for isotopically pure single crystals [6−9]. At low temperatures (from 100 K and below), monoisotopic Ge has not only higher thermal conductivity, but also thermo-emf [10]. An assumption is made about a "giant" contribution to the attenuation coefficient of hypersound from the scattering of sound waves on isotopic disorder in single crystals ^{nat}Ge, compared to monoisotopic crystals. Monoisotopic crystals differ in the physical and structural characteristics from crystals of natural composition (phase transition temperature, crystal lattice parameters, and absorption and reflection coefficients) [11−14].

Directions for research into isotopically pure Ge crystals are driven by new applications of the material in micro- and nanoelectronics, infrared optics, terahertz optics, nanophotonics, and other fields.

Monoisotopic Ge may be promising for the creation of spintronics elements, quantum computers, and other nanoelectronics problems [15]. To use germanium isotopes with even atomic mass (which have zero nuclear spin) as a matrix in quantum computers, it is necessary to minimize the content of odd isotopes in the matrix (^{73}Ge).

Currently, single crystals of the isotope ^{76}Ge are already used as a detector material for studies of double beta decay processes and a number of fundamental physical processes [6, 16, 17]. The use of isotopically pure germanium makes it possible to control the process of neutron transmutation doping of semiconductors, control the degree of compensation of impurities in germanium, ensure a uniform distribution of impurities, and achieve high concentrations of impurities during doping [18].

Previously in works [19, 20] when studying the IR absorption spectra of isotopically pure single crystals of ^{70}Ge and ^{74}Ge, obtained at the Kurchatov Institute of Atomic Energy, a shift of several phonon absorption bands was discovered with a change in the mass com-

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[a] *Tydex LLC, St. Petersburg, Russia*

[b] *Devyatykh Institute of Chemistry of High-Purity Substances, Russian Academy of Sciences, Nizhny Novgorod, Russia*

[c] *Institute of Electrophysics and Electric Power, Russian Academy of Sciences, St. Petersburg, Russia*

[d] *Tver State University, Tver, Russia*

*e-mail: grigorykropotov@tydex.ru

**e-mail: v-rogalin@mail.ru

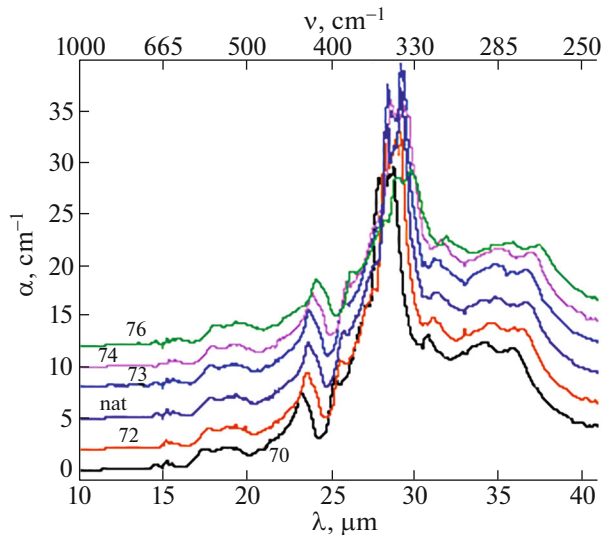****e-mail: kaplunov.ia@tversu.ru*

Fig. 1. Absorption (attenuation) spectrum of monoisotopic germanium samples.

position. In works [13, 14] the optical characteristics of isotopes were studied: ^{72}Ge, ^{73}Ge, ^{74}Ge, and ^{76}Ge.

In this work, this study was, for the first time, in a single experiment, continued for all five stable isotopes of germanium, and the position of all main phonon absorption bands in the IR region of the spectrum was considered.

EXPERIMENTAL

The experiments were carried out on samples of isotopically pure germanium single crystals ^{70}Ge, ^{72}Ge, ^{73}Ge, ^{74}Ge, and ^{76}Ge. Germanium was obtained by the hydride method at the Devyatykh Institute of Chemistry of High-Purity Substances, Russian Academy of Sciences, then purified to obtain isotopically enriched polycrystalline germanium by the zone melting method [3, 5].

Single crystals were grown in the ⟨100⟩ crystallographic direction in the laboratory of the Institute for Crystal Growth (IKZ, Berlin) using the Czochralski method from a quartz crucible in a high-purity argon environment [5, 21]. Undoped crystals with high electrical resistivity were grown.

Samples for research were cut from grown single crystals and then polished using a specially developed technology of chemical–mechanical optical processing.

Transmission spectra were measured on a Bruker Vertex 70 Fourier spectrometer in the spectral range of 1.3–670 μm. The error in measuring the wave number was ~1 cm^{-1}, and the transmittance is 0.5%. Optically processed Ge single crystal plates of natural isotopic composition (^{nat}Ge) were grown at Tver State University.

RESULTS AND DISCUSSION

In Fig. 1 the spectral dependence of the absorption (attenuation) coefficient of natural germanium is given (^{nat}Ge) with five monoisotopic germanium samples in the range of 10–40 μm. The nature of each spectrum is approximately the same, with minor differences in the absorption coefficient observed. For a more visual visualization of the specific nature of the spectra, the curves are shifted upward by correcting the values of the attenuation coefficient (isotope ^{70}Ge without correction, ^{72}Ge with the correction +2 cm^{-1}, natural germanium +5 cm^{-1}, isotopes ^{73}Ge +8 cm^{-1}, ^{74}Ge +10 cm^{-1}, and ^{76}Ge +12 cm^{-1}). The main difference is the correspondence of the absorption bands to the corresponding wavelength (frequency). It is clearly seen that the isotopic composition of the crystals affects the position of the characteristic absorption bands of Ge in the spectral range under consideration. In the spectral range of 11–40 μm, we identified 16 absorption bands, which corresponds to the data of [13, 14, 22]; for the isotope ^{70}Ge, the position of a number of characteristic bands was revealed for the first time.

In Table 1 the corresponding values of the position of the maximum of the identified absorption bands and a comparison of the measurement results with known data are presented. These bands are interpreted as two-phonon absorption at critical points of the Brillouin zone [23]. The density of states is expressed by the maxima of absorption bands, the isotopic shift of which relative to the spectrum of natural germanium is associated with a change in the average atomic mass of the sample. The most intense bands are observed in the region of 23–38 μm. In the region of 11–23 μm, bands with low intensity were detected. The stripes are small, but precisely defined, and their recorded position significantly exceeds the instrument error. The presence of an isotope shift clearly indicates that these bands are associated with the phonon structure of single crystals of germanium isotopes.

Previously in works [19, 20], when studying the IR absorption spectra of isotopically pure single crystals ^{70}Ge and ^{74}Ge, a shift in the phonon absorption bands was discovered with a change in the mass composition, and this shift was generally approximated by the expression

$$\nu = 1.6\nu_0 e^{-kM}, \qquad (1)$$

where ν_0 is the frequency of the maximum of the corresponding phonon absorption band of natural germanium, M is the mass number of the isotope, and k is the power coefficient in the range 0.0062–0.0072.

The results of this experiment showed (Table 2) that the lattice absorption peaks for the first six bands (Table 1) observed in germanium single crystals of natural isotopic composition and in samples of monoisotopic germanium crystals (^{70}Ge, ^{72}Ge, ^{73}Ge,

Table 1. Position of absorption band maximum, cm^{-1}

Germanium samples	Phononic designation lines [22]															
	3TO	2TO+LA	2TO+TA	2TO$_X$	(TO+LO)$_L$	(TO+L)$_X$	Q$_2$+Q$_2$(O)	(LO+LA)$_K$	(TO+TA$_2$)$_K$	Σ_1(O)+Σ_3(A)	(TO+TA)$_X$	(TO+TA)$_L$	Λ_3(O)+Λ_3(A)	(L+TA)$_Z$	(LA+TA)$_K$	(LA+TA$_1$)$_K$
^{nat}Ge	839.6	750.3	641.9	560.2	522.2	502.5	469.2	423.2	389.2	360.4	350.8	351.5	342.5	318.5	287.4	273.2
^{nat}Ge [14]	841.0	750.8	647.2	560.9	522.6	501.6	473.7	423.0	389.9	361.0	351.0	348.7	342.8	318.7	286.0	271.5
^{70}Ge	856.9	763.2	655.6	571.4	532.2	506.6	471.0	429.2	390.3	367.0	354.4	352.0	347.2	324.7	292.8	278.9
^{70}Ge [19], [20]	855.0	760.0	655.0	–	–	–	–	–	–	–	–	–	–	–	–	–
^{72}Ge	844.9	751.8	643.5	563.4	526.0	504.3	470.2	424.4	389.6	361.7	353.7	344.8	342.4	321.5	289.0	276.6
^{72}Ge [14]	844.0	754.0	649.8	564.5	525.0	504.4	476.5	426.3	392.3	361.5	353.0	349.9	343.3	320.7	286.0	272.0
^{73}Ge	839.5	750.2	641.5	558.7	521.6	502.4	469.0	421.0	388.8	360.2	351.4	346.2	341.3	319.5	287.4	272.9
^{73}Ge [14]	840.0	750.0	645.5	559.6	521.8	499.0	474.0	422.0	389.6	359.0	350.9	348.3	342.4	318.4	285.0	271.5
^{74}Ge	833.7	743.6	638.1	554.0	519.4	498.0	466.7	418.4	385.2	356.5	344.8	344.8	338.4	315.5	284.1	270.6
^{74}Ge [14]	833.5	744.6	640.2	555.7	517.3	497.0	469.1	419.9	387.2	356.4	348.0	345.4	339.8	316.0	284.0	270.6
^{74}Ge [19], [20]	830.0	740.0	635.0	–	–	–	–	–	–	–	–	–	–	–	–	–
^{76}Ge	822.9	736.2	629.5	548.9	512.6	492.3	466.2	414.1	380.8	352.7	344.2	342	335.6	313.5	278.6	266.7
^{76}Ge [14]	823.4	736.0	633.0	549.9	511.0	491.0	464.5	415.0	382.5	353.3	344.5	342	335.7	313.0	281.0	267.0

Table 2. Position of the maximum of absorption bands: experiment, calculation

Composition of germanium	Maxima of phonon absorption bands in germanium											
	ν_1, cm^{-1}		ν_2, cm^{-1}		ν_3, cm^{-1}		ν_4, cm^{-1}		ν_5, cm^{-1}		ν_6, cm^{-1}	
	Experiment	Formula (1) $k = 0.00645$	Experiment	Formula (1) $k = 0.00645$	Experiment	Formula (1) $k = 0.00645$	Experiment	Formula (1) $k = 0.00645$	Experiment	Formula (1) $k = 0.00645$	Experiment	Formula (1) $k = 0.0065$
^{70}Ge	856.9	856.0	763.2	762.9	655.6	653.9	571.4	570.7	532.2	532.0	506.6	510.0
^{72}Ge	844.9	845.0	751.8	753.2	643.5	645.5	563.4	563.4	526.0	525.1	504.3	503.5
$^{72.59}$Ge (nat)	839.6	841.8	750.3	750.3	641.9	643.1	560.2	561.2	522.2	523.1	502.5	501.6
^{73}Ge	839.5	839.6	750.2	748.4	641.5	641.4	558.7	559.7	521.6	521.7	502.4	500.3
^{74}Ge	833.7	834.2	744.6	743.5	638.1	637.2	554.0	556.1	519.4	518.4	498.0	497.0
^{76}Ge	822.9	823.5	736.2	734.0	629.5	629.1	548.9	549.0	512.6	511.8	492.3	490.6

^{74}Ge, ^{76}Ge) shift in accordance with dependence (1). The result is clearly illustrated in Fig. 2 at frequencies for the first six bands: dependences of the frequencies ν of the phonon absorption peaks of these crystals on M, the mass number of the isotope.

Thus, the dependence of the position of the maxima of the phonon absorption bands on the composition of the germanium isotope is registered (Eq. (1)). A shift was observed from mass number 76 to 70 (within ~34 cm^{-1} for the first peak, within ~26– 27 cm^{-1} for the second and third peak, ~22 cm^{-1} for the fourth peak, ~19 cm^{-1} for the fifth peak, and ~14 cm^{-1} for the sixth peak). The frequency shift of the absorption bands decreases in magnitude with increasing wavelength of the incident radiation.

In single crystals ^{70}Ge and ^{72}Ge, an increase in the frequency of the absorption band (ν) is observed, and in single crystals ^{73}Ge, ^{74}Ge, and ^{76}Ge, the frequency decreases compared to single crystals of natural isoto-
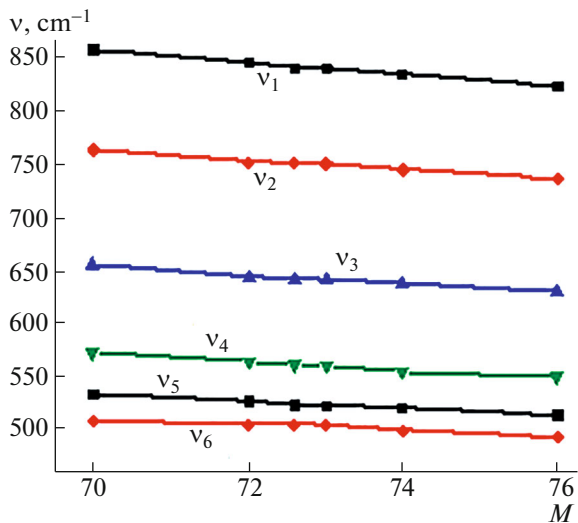
Fig. 2. Frequency dependencies ν of the phonon absorption peaks of isotopically pure germanium single crystals on M, the mass number of the isotope for the peaks in Table 2.

pic composition ($^{72.59}$Ge). Thin samples of single crystals were used in the work (thickness was 1.55 mm), which provided an accurate quantitative determination of the differences in the shifts of the absorption bands of the spectra of samples of natural (^{nat}Ge) and monoisotopic crystals of germanium (^{70}Ge, ^{72}Ge, ^{73}Ge, ^{74}Ge, and ^{76}Ge) in all frequency regions of the spectrum.

Previously in works [19, 20] using a Hitachi-225 dual-beam IR spectrophotometer, the IR absorption spectra of isotopically pure single crystals ^{70}Ge and ^{74}Ge were studied. Isotopes were obtained by the centrifugal separation method at the Institute of Molecular Physics of the Russian Research Center Kurchatov Institute with an enrichment of 99.99%. In the Lawrence Berkeley National Laboratory, their fine chemical cleaning was carried out using the method of multiple zone melting (33 passes). Polycrystalline ingots of ^{70}Ge and ^{74}Ge purified in this way were used as a feedstock for growing single crystals of the Ge n-type by the Czochralski method. The technology for producing these isotopes, as well as the crystal growth described in [7, 23], differed significantly from the methods for obtaining the samples studied in this work.

However, the values of isotopic shifts of the IR absorption bands obtained in this case were completely correlated with each other and corresponded to dependence (1), experimentally obtained from measurements carried out on samples of isotopically enriched germanium obtained by various methods.

CONCLUSIONS

For the first time, in a unifield experiment, the dependence of the position of IR absorption bands in the range of $11-40$ μm on the mass composition for all five stable isotopes of germanium was studied.

The results of this work showed clearly that even a slight change in the mass of the isotope noticeably affects the position of the phonon absorption peaks.

The data obtained can be used to study the mass composition of germanium crystals of various isotopic purities.

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CONFLICT OF INTEREST

The authors of this work declare that they have no conflicts of interest.

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