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Isotopic shifts of the low-energy excitations of interstitial oxygen in germanium

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Abstract

The rotational states of O_i in natural Ge as determined by phonon spectroscopy are found to be shifted in isotopically enriched Ge:O_i crystals. These shifts are larger than compatible with the line width in natural Ge if only the motion of the quasi-free Ge–O–Ge molecule is considered. Because of the reduced isotope scattering of the phonons in the enriched Ge the position of higher excited states could be determined. This allows to estimate the height of the axial potential barrier by extending to Ge:O the Yamada–Kaneta model for Si:O. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Ge:O_i; Isotope shift; Phonon spectroscopy

1. Introduction

Phonon scattering resonances between 0.18 and 4.08 meV in Ge:O can be associated with rotational states of interstitial oxygen $E(l) \propto l^2/I$ up to $l = \pm 5$ [1]. I is the momentum of inertia of the rotating entity. The state $l = \pm 3$ is split into states $3^{\downarrow}$ and $3^{\uparrow}$ by 0.28 meV through modulation of the angular potential ditch due to the neighbouring Ge-tripods. It follows that the axial barrier against radial oscillation must be much higher and the radial distance of the potential minimum determining the rotation larger (93 pm) than for Si:O_i (22 pm, [2]). However, from such measurements in natural Ge (^{n}Ge) it cannot be decided, to which extent and how the nearest Ge neighbours or the lattice are involved in the rotational states. We have therefore determined the O- and Ge-related isotope shifts of the resonances in isotopically enriched, quasi-monoisotopic (qmi) Ge crystals doped with ^{16}O as well as in ^{n}Ge implanted with ^{18}O (and ^{16}O). The reduced isotope scattering of high-frequency phonons in qmi Ge allows to detect

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states at energies higher than in ^{nat}Ge, which is important for an estimate of the height of the central barrier.

2. Experimental

One ^{74}Ge:O sample (87.7% enrichment, $[O_i] = 6.7 \times 10^{21}$ m^{-3}) was Czochralski-grown at the University of Kiev [3], three other samples: ^{76}Ge:O [$\approx$ 89.1%, $\approx 5 \times 10^{22}$ m^{-3}], ^{73}Ge:O [96.7%, 5.5×10^{22} m^{-3}], ^{70}Ge:O [95.7%, 15×10^{22} m^{-3} ($[O_i]$ reduced to 3.4×10^{22} m^{-3} by annealing)], were grown by the vertical Bridgman method at the Lawrence Berkeley National Laboratory [4]. The oxygen concentrations and the isotopic enrichments were determined by high-resolution IR-spectroscopy from the integrated and relative intensity of the isotopic components of the oxygen absorption in the 860 cm^{-1}-band [5]. For the investigation of the oxygen isotope effect ^{nat}Ge was doped by implantation with similar parameters as used for oxygen implantation to produce insulating GaAs layers [6]. Tunnelling junctions of evaporated Al- and Sn-films were used for phonon emitters and detectors, respectively. Temperature was varied between about 0.4 K and 1.0 K in a ^{3}He-bath cryostat to determine the temperature dependence of the line width and to distinguish transitions starting from thermally occupied levels. At higher oxygen concentrations the apparent line widths of the resonances are larger than the true line widths due to multiple phonon scattering.

3. Results and discussion

Ge-isotopic shifts are found in all qmi samples as shown in Fig. 1 specifically for the resonance near 4 meV. The shifts depend linearly on the average Ge-mass as shown in Fig. 2 for the transition $l = 0$ to $l = 5$. The linear interpolation allows to predict a hypothetical line shape for ^{nat}Ge by superposing line positions and intensities of the 15 nearest Ge-neighbour isotopical combinations. The resultant line shape in ^{nat}Ge is distinctly broader than the experimental one (Fig. 2).

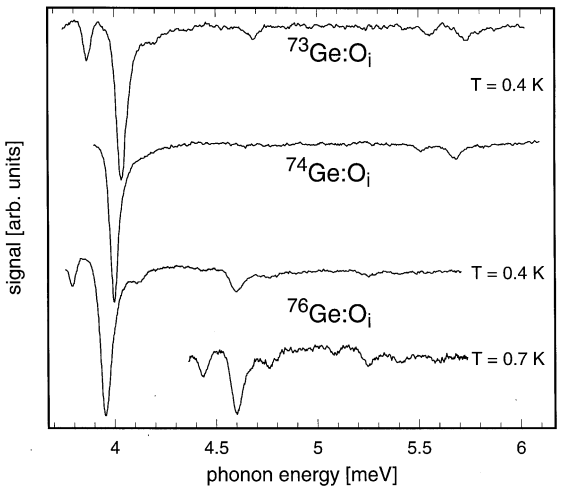

Fig. 1. Transmission spectra (baseline subtracted) at higher energies through qmi Ge:O$_i$. The doublets around 4 meV belong to $l = \pm 5$ [1] and those around 5.8 meV (detected only in qmi Ge) to $l = \pm 6$ of the ground state series. Weak doublets around 4.6 meV (previously also found in a thin sample of ^{nat}Ge [7]) and 5.2 meV are ascribed to transitions to the first excited radial states.

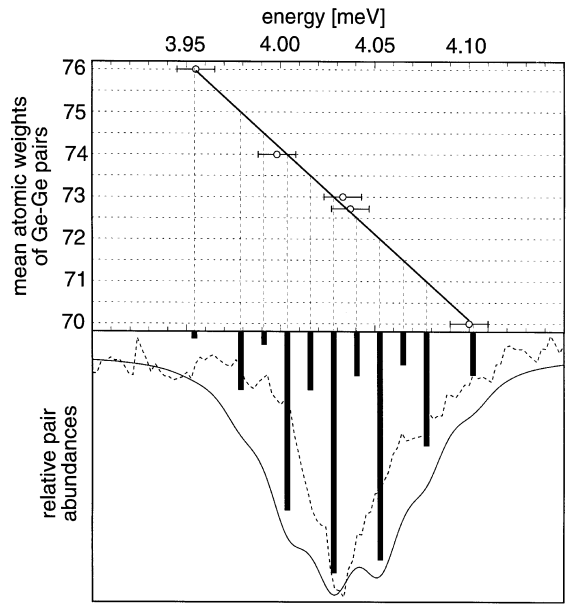

Fig. 2. Position of the transition $l = 0$ to $l = \pm 5$ for various Ge-isotopes and ^{nat}Ge. Lower part: Hypothetical line shape in ^{nat}Ge by superposition of Lorentzians (line width 25 μeV) according to the relative abundances of the possible Ge-pair combinations in ^{nat}Ge as compared to the experimental line width in ^{nat}Ge at low oxygen concentration (broken line).

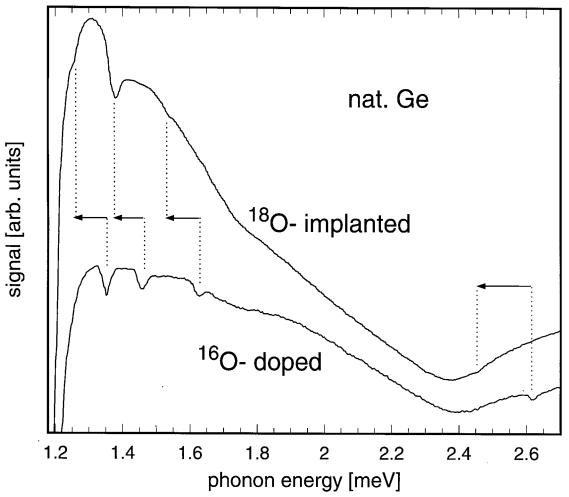

Fig. 3. Transmission spectrum of ^{18}O-implanted Ge.

In "Ge ^{18}O-doped by implantation the strongest transition $l = \pm 1$ to $l = 3$[†] and three of the weaker transitions were detected at ^{3}He temperatures (Fig. 3). If only the oxygen would rotate a value of $E/E' = m'/m = 18/16 = 1.125$ would be expected in the rigid rotator approximation whereas the observed ratio for all resonances is only 1.07. This small O-isotope shift also suggests a contribution of the Ge-neighbourhood to the rotation.

For a quasi-free Ge–O–Ge molecule the Ge–Ge-axis may be displaced from the rotation axis by a positive or negative value of r for co- or counterrotation of Ge–Ge and O [8]. The displacements obtained from the observed shifts are as large as $\approx 20\%$ of the Ge–Ge distance [9,13]. One would then expect a large perturbation of the rotation through the tight binding to the tripods of the next-nearest Ge, whereas, the splitting of the $l = \pm 3$ state by the sixfold perturbation corresponds to an angular hindering potential amplitude of the rotating entity of only 0.28 meV [1]. The hindering might be reduced by the in-phase motion of a larger neighbourhood which could be included by replacing the Ge-mass M by $M(1 + x)$ in the case of monoisotopic Ge. This will also reduce r. However, assuming that r and x do not depend on M does not lead to a compatible set of equations for the determination of these parameters. A large lattice interaction, though, could by an averaging lead to the observed narrow line width of the resonances in "Ge. A contribution of the lattice might also be mediated via anharmonic coupling to the IR-modes of the complex where the motion of the Ge-neighbours is intrinsic. Coupling between the low-energy rotational states and the ν_3 mode is evident from the fine structure of the 860 cm^{-1} band also with different isotopic shifts of the band for the various Ge-isotopic pair combinations in "Ge as compared to qmi-Ge [3,5,8,10] which has been ascribed to coupling with lattice phonons.

The observed higher resonances can be fitted by the level scheme calculated with a model potential [11]. The levels at 4.60 and 5.25 meV in ^{76}Ge are then due to the transitions to the first excited 2D radial states and the line near 5.8 meV is the transition to the rotational state $l = \pm 6$ of the ground state series. The weakness of the $l = \pm 1$ state of the excited radial series near 5.1 meV may be due to the small phonon transition probability. (See Refs. [12,14] for a discussion of phonon interaction in the case of Si : O$_i$.) From the fit within this model one would obtain 12 meV for the height of the axial barrier.

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