Isotopic disorder effect in the infrared reflection spectra of $^6Li_x{}^7Li_{1-x}YF_4$ single crystals

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Abstract

Polarized infrared reflection spectra of $LiYF_4$ single crystals with different compositions of ^7Li and ^6Li isotopes were measured and analysed using the model of independent oscillators. Lattice dynamics calculations were performed. It was found that, for some modes, the contribution of the isotopic disorder to the damping constant is comparable to the anharmonic width. Results of simulations agree qualitatively with the experimental data. Possible reasons for the remaining discrepancies are discussed.
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1. Introduction

Isotopic disorder is the simplest type of disorder in crystal lattices. It contributes only to a random variation of atomic masses, while interactions between atoms remain unaltered. In some cases the isotopic disorder affects physical properties of materials significantly. One of the recently discovered isotope effects that is important for modern and future microelectronics is a large increment in the thermal conductivity of Si crystals after isotopic purification (about eight times at $T = 26$ K, and ∼10% at room temperature) [1]. Though isotope effects in solids have been studied for a long time, the recent interest in them is motivated by novel applications and the improvement in experimental facilities. Comprehensive reviews on isotope effects in solids and on their applications can be found, for example, in Refs. [2,3].

Different isotope effects have been observed in optical spectra of crystals, in particular in infrared spectra of bulk NaCl and LiF crystals [4–6], infrared spectra of donor and acceptor impurities in Si [7,8], Raman spectra of bulk semiconductor crystals [9], in optical spectra of transition metal [10] and rare-earth [11,12] ions embedded in crystal lattices.

Here we report results of measurements and simulations of isotope effects in the infrared (IR) reflection spectra of $LiYF_4$ single crystals due to mass disorder in the lithium sublattices. The crystal $LiYF_4$ is widely used as a host matrix for rare-earth ions in solid-state lasers [13]. It has been shown that pseudo-splittings of optical lines in rare-earth-doped $LiYF_4$ crystals due to isotopic disorder in Li sublattices may be as much as 0.03 cm^{-1} [12,14]. In this context, our study is important for the purposes of solid-state quantum electronics. We should emphasize that the IR spectra of $LiYF_4$ were studied comprehensively in Ref. [15], however the isotope effects have not been addressed.

2. Experimental

The $LiYF_4$ crystal belongs to the space group C_{4h}^6 with two formula units in the unit cell. Lattice vibrations at the Brillouin zone centre are classified by irreducible representations of the C_{4h} factor group. There are 12 IR active modes, namely four

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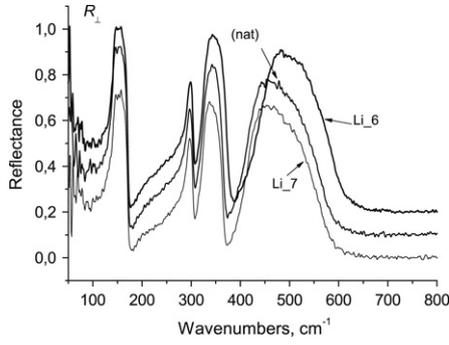*E-mail address:* boris.malkin@ksu.ru (B.Z. Malkin).

Fig. 1. The reflection coefficients $R_\perp$ (E_u) for radiation polarized orthogonally to the c-axis. The curves for the samples with natural Li isotope abundances and enriched in ^{6}Li are shifted up by 0.1 and 0.2, respectively.

modes of the A_u symmetry (polarized along the optical axis c) and four double degenerate modes of the E_u symmetry (polarized perpendicularly to c).

The reflection spectra were taken at room temperature for three samples of ^{6}Li$_x$^{7}Li$_{1-x}$YF$_4$, with natural abundances of ^{6}Li and ^{7}Li ($x = 0.0742$, nat), enriched in ^{6}Li ($x = 0.9$, Li_6), and pure in ^{7}Li ($x \sim 0$, Li_7). The samples were grown using the Bridgman–Stockebarger method. Reflectivity measurements have been performed using an IFS66v (Bruker) infrared Fourier-transform spectrometer with a reflection unit at near normal incidence.

The reflection coefficients,

$$R_\perp(\omega) = \left| \frac{\sqrt{\varepsilon_\perp(\omega)} - 1}{\sqrt{\varepsilon_\perp(\omega)} + 1} \right|^2, \quad R_\parallel(\omega) = \left| \frac{\sqrt{\varepsilon_\parallel(\omega)} - 1}{\sqrt{\varepsilon_\parallel(\omega)} + 1} \right|^2 \quad (1)$$

(where $\varepsilon(\omega)$ is the frequency-dependent dielectric permeability) were measured at a resolution of 2 cm^{-1} in the wave number range from 50 to 7000 cm^{-1} using linearly polarized radiation with the electric field vectors orthogonal ($R_\perp$) and parallel ($R_\parallel$) to the crystal symmetry axis c, respectively. The main peculiarities of the spectra are represented in Figs. 1 and 2. It is seen that both experimental spectra contain four specific features, in accordance with the four phonon modes driven by the radiation. The high-frequency band in the $R_\perp$ (E_u) spectrum (Fig. 1) remarkably shifts to higher frequencies as the mass of the Li ions diminishes, whereas in the $R_\parallel$ (A_u) spectrum this effect is more pronounced for the next peak with lower frequency. A similar transfer of the spectral weight to higher frequencies was found in the IR reflectivity spectra of LiF upon substitution of ^{6}Li for ^{7}Li [6], and a shift to lower frequencies was observed in the IR reflectivity spectra of La$_2$NiO$_{4+\delta}$ upon substitution of ^{18}O for ^{16}O [16].

The spectra obtained were fitted by the standard expression for the dielectric permeability of the system of independent oscillators:

$$\varepsilon_\perp(\omega) = \varepsilon_\perp(\infty) + \sum_k \frac{M_k^2(E_u\text{TO})}{\omega_k^2(E_u\text{TO}) - \omega^2 - 2i\omega_k\gamma_k(E_u\text{TO})}, \quad (2)$$

$$\varepsilon_\parallel(\omega) = \varepsilon_\parallel(\infty) + \sum_k \frac{M_k^2(A_u\text{TO})}{\omega_k^2(A_u\text{TO}) - \omega^2 - 2i\omega_k\gamma_k(A_u\text{TO})}, \quad (3)$$
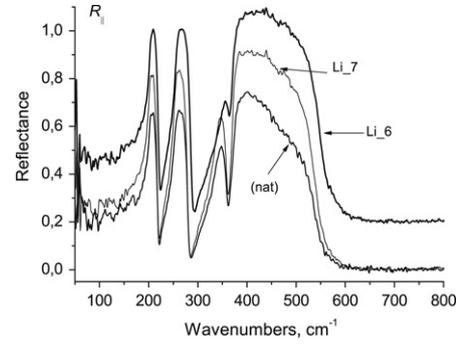

Fig. 2. The reflection coefficients $R_\parallel$ (A_u) for radiation polarized parallel to the c-axis. The curve for the sample enriched in ^{6}Li is shifted up by 0.2.
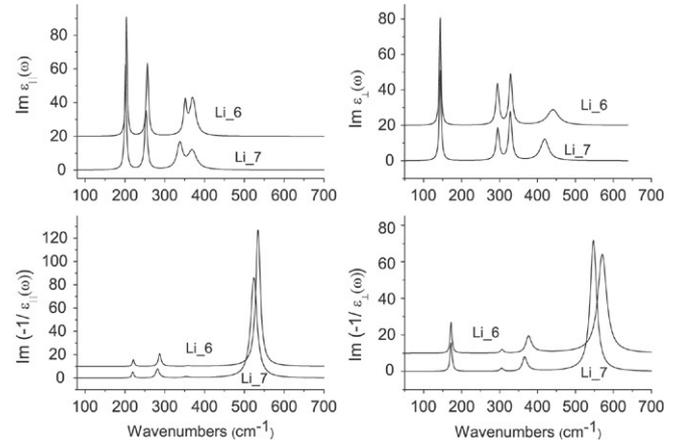

Fig. 3. Absorption and loss functions calculated with the parameters obtained from the measured reflectances in the samples enriched in ^{6}Li and ^{7}Li.

where $\varepsilon(\infty)$ is the electronic contribution to the dielectric constant, $\omega_k(\Gamma)$ is the frequency and $\gamma_k(\Gamma)$ is the damping constant of the transverse optical phonon mode at the Brillouin zone centre corresponding to the irreducible representation Γ of the lattice factor group, and the parameter $M_k(\Gamma)$ determines the effective dipole moment of the mode. For spectra fitting, we have used SCOUT — SpectrosCopic Objects and UTilities, a WINDOWS application written by Theiss [17,18]. The values of the fitting parameters ($\varepsilon(\infty)$, ω_j, M_j and $\gamma_j(\omega_j)$) are represented in Table 1. The calculated absorption spectra $Im[\varepsilon(\omega)]$ and the loss functions $Im[-1/\varepsilon(\omega)]$ for the E_u and A_u excitations are represented in Fig. 3. The maxima in these plots correspond to frequencies of optical transversal (TO) and longitudinal (LO) modes, which agree well with the data given in the literature (see Table 1) for crystals with natural abundances of Li isotopes [15]. It is seen in Fig. 3 that both TO and LO frequencies in the sample Li_6 are shifted to higher values relative to mode frequencies in the Li_7 sample. The high-frequency E_uTO and E_uLO modes exhibit the largest isotopic shifts up to 22 cm^{-1}. The broadening effect due to the isotopic disorder is also well pronounced for the same modes.

3. Calculations of the spectral parameters and discussion

The isotopic disorder, similarly to the anharmonic interactions in a perfect lattice, contributes to frequency shifts and the

Table 1

Measured and calculated frequencies, damping constants and oscillator strengths of IR active vibrational modes in $^6Li_x{}^7Li_{1-x}YF_4$ crystals

x	Symm. $\varepsilon(\infty)$	Mode j	ω_j, cm^{-1}			γ_j, cm^{-1}		M_j, cm^{-1}	
			Exper.		Theor.	Exper.	Theory (anharm. + isotope)	Exper.	Theory
			Ref. [15]	This work					
0.90 Li_6	A_u 1.979	1		203.6	189.5	2.2	4.7	257.4	141
		2		256.3	273.1	3.4	4.1	273.8	285
		3		351.6	341.1	4.5	3.4 + 1.5	241.2	245
		4		370.5	403.4	9.2	11.4	387.3	150
	E_u 1.918	1		143.6	155.1	2.6	3.8	214.9	195
		2		294.6	279.1	4.8	6.5	254.7	161
		3		329.5	321.6	5.1	14.2	308.7	217
		4		441.1	452.6	18.1	4.3 + 1.7	373.1	269
0 Li_7	A_u 1.979	1		202.8	186.6	3.3	4.3	247.3	150
		2		253.5	272.3	4.3	3.7	264.9	270
		3		340.2	322.8	6.7	2.5	302.	260
		4		371.6	403.12	11.2	10.8	339.6	142
	E_u 1.914	1		143.9	154.9	3.0	3.9	208.9	197
		2		295.3	278.1	5.0	6.8	230.6	153
		3		328.8	321.4	5.0	17.0	297.7	213
		4		419.0	422.9	12.8	5.6	360.5	275
0.074 (nat)	A_u 1.932	1	196 (219)[a]	201.4 (220)	186.8	2.6	4.4	259.5	150
		2	251 (278)	252.8 (281)	272.3	3.9	3.7	263.2	271
		3	341 (360)	338.2 (354)	324.1	8.5	2.7 + 1.3	295.1	259
		4	370 (534)	369.2 (524)	403.13	13.0	10.9	327.5	142
	E_u 1.930	1	137 (171)	142.3 (171)	154.9	2.5	4.1	211.7	197
		2	294 (308)	295.3 (306)	278.2	4.5	11.5	227.9	154
		3	325 (367)	330.4 (366)	321.4	5.6	15.5	330.4	213
		4	418 (560)	420.4 (549)	425.0	15.7	4.8 + 3.4	365.4	275

[a] Figures in brackets are the frequencies of longitudinal vibrations $\omega_j(\Gamma LO)$.

widths of phonon modes [19,20]. Although, in general, the effects due to the anharmonic interactions and the isotopic disorder cannot be separated [20], the combined non-separable part is small for crystals with ionic-type bonding like LiYF$_4$. Both effects are accounted for in the ionic susceptibility $\chi(\omega)$ that contributes to the reflectance (1) through the relation $\varepsilon(\omega) = \varepsilon(\infty) + 4\pi\chi(\omega)$. Usually, the susceptibility $\chi(\omega)$ is evaluated using Matsubara [21,22] or retarded [23] Green's functions. Because of ionic-type coupling in LiYF$_4$, the major contribution to the susceptibility comes from induced dipole moments, linear in atomic displacements. Therefore, the susceptibility tensor is [23]

$$\chi_{\alpha\beta}(\omega) = \frac{1}{\hbar}\sum_j \frac{2\omega_j d_\alpha(j) d_\beta(j)}{\omega_j^2 - \omega^2 + 2\omega_j[\Delta_j(\omega) - i\gamma_j(\omega)]}, \qquad (4)$$

where $d(j)$ is the dipolar moment that corresponds to the IR active phonon mode with the frequency ω_j, and $\Delta_j(\omega)$ is the shift and $\gamma_j(\omega)$ is the width of this mode caused by the mode coupling due to the lattice anharmonicity and the isotopic disorder. In the crystallographic system of coordinates with the z-axis parallel to the c-axis, the susceptibility tensor of LiYF$_4$ has two non-zero components, $\chi_\parallel$ and $\chi_\perp$, that correspond to polarizations of the incident light parallel and orthogonal to the c-axis.

We have calculated widths of the transversal modes with the zero wave vector of A_u and E_u symmetry due to the isotopic disorder in Li sublattices using a microscopic model of lattice

dynamics. To check the validity of the model, we also evaluated contributions to damping due to cubic anharmonic terms in the lattice Hamiltonian. Because of weak ionic polarizabilities in LiYF$_4$, the model of the lattice dynamics can be simple enough with a small number of adjustable parameters. We utilized a rigid ion model with long-range Coulomb and short-range non-Coulomb interactions. For the nearest-neighbor ions A and B at a distance r, the non-Coulomb energy is taken in the form of the Born–Mayer potential, $V_{AB} = V_{0,AB}\exp(-r/R_{AB})$, with phenomenological parameters $V_{0,AB}$ and R_{AB}. There are minor variations in the sets of short-range force constants and effective ion charges used by different authors [24–26]. We used the set of coupling parameters from Ref. [25], which were fitted to experimental results on inelastic neutron scattering. In this model, the effective ion charges equal $Z(Li^+) = 0.757$, $Z(F^-) = -0.77$, and $Z(Y^{3+}) = 2.323$, in units of the proton charge $|e|$.

The effect of Li mass disorder on the shifts and widths of IR lines has been taken into account in the following way. Shifts of phonon lines due to different isotopic compositions were obtained by using different average masses of Li atoms in calculations of lattice dynamics. The isotopic line broadening due to phonon elastic scattering was calculated according to Refs. [19,20]. The lattice dynamics database, which contains frequencies and polarization vectors of phonons for 8000 wave vectors in the irreducible part of the Brillouin zone, was used in simulations. We emphasize that we have also carried out similar

simulations with 27 000 wave vectors in the irreducible part of the Brillouin zone. However, the changes in the results are negligible, while the simulation time has increased appreciably.

The calculated frequencies of the IR active phonon modes for different samples are given in Table 1. The major isotopic shifts are obtained for mode 3 of A_u symmetry and mode 4 of E_u symmetry, which is consistent with the results of the measurements. The large isotopic shift in the mode frequency indicates that the corresponding vibrational mode involves significant lithium ion displacements. The relative weights of lithium displacements can be characterized by the components of the normalized polarization vector, $e_\alpha(\text{Li}_\sigma, qj)$, corresponding to the phonon mode with the frequency $\omega_j(q)$ and the wave vector q (there are two lithium sites in the unit cell, $\sigma = 1, 2$). In particular, the calculated weights in the $^7\text{LiYF}_4$ crystal, $\sum_{\alpha,\sigma} |e_\alpha(\text{Li}_\sigma, 0A_u j \text{TO})|^2 = 0.22, 0.05, 0.68,$ 0.01 and $\sum_{\alpha,\sigma} |e_\alpha(\text{Li}_\sigma, 0E_u j \text{TO})|^2 = 0.02, 0.06, 0.01, 0.87$ for $j = 1, 2, 3, 4$ respectively, correlate precisely with the responses of the mode frequencies and damping constants to the substitution of ^6Li for ^7Li (see Table 1).

The effect of the isotopic disorder on the line broadening has been evaluated according to [19,20]

$$\gamma_{j,\text{isot}}(\omega) = \frac{1}{2} m_{\text{Li}} \left(\frac{\Delta m_{\text{Li}}}{\bar{m}_{\text{Li}}} \right)^2 \omega^3 x(1-x) \sum_{\alpha\beta\sigma} e_\alpha^*(\text{Li}_\sigma, 0j)$$
$$\times Im G_{\alpha\beta}(0\text{Li}_\sigma; 0\text{Li}_\sigma |\omega) e_\beta(\text{Li}_\sigma, 0j), \qquad (5)$$

where $\Delta m_{\text{Li}} = m(^7\text{Li}) - m(^6\text{Li})$ is the difference between the isotope masses, m_{Li} and $\bar{m}_{\text{Li}}$ are lithium atomic masses in crystals without and with isotopic disorder, respectively; x is the concentration of an admixed isotope (for Li_7 and (nat) samples the reference perfect lattice is composed of the ^7Li isotopes, while for the Li_6 sample the perfect lattice is composed of the ^6Li isotopes); and $G_{\alpha\beta}(0\text{Li}_\sigma; 0\text{Li}_\sigma |\omega)$ is the lattice Green's function at a lithium site σ [27]. The calculated contributions $\gamma_{j,\text{isot}}(\omega_j)$ to the widths of the IR active modes caused by the isotopic disorder are, as a rule, less than 0.02 cm^{-1}, which is much less than the measured damping constants. Exceptions are two modes that experience the largest isotopic shifts (see Table 1).

To verify parameters and approximations involved in the microscopic model that is utilized, we have calculated the line broadening due to cubic anharmonic interactions according to the standard formula [28]

$$\gamma_j(\omega) = \frac{18\pi}{\hbar^2} \sum_{Q} \sum_{q_1 j_1} \sum_{q_2 j_2} |V(0j; q_1 j_1; q_2 j_2)|^2$$
$$\times \{(n_1 + n_2 + 1)[\delta(\omega - \omega_1 - \omega_2)$$
$$- \delta(\omega + \omega_1 + \omega_2)] + (n_1 - n_2)[\delta(\omega + \omega_1 - \omega_2)$$
$$- \delta(\omega - \omega_1 + \omega_2)]\} \delta(q_1 + q_2 + Q), \qquad (6)$$

where Q is a reciprocal lattice vector, n_1 and n_2 are the phonon occupation numbers, and $V(0j; q_1 j_1; q_2 j_2)$ is the Fourier transform of a cubic force constant. The explicit form of $V(0j; q_1 j_1; q_2 j_2)$ can be found, for example, in Ref. [29]. Cubic force constants were evaluated within the microscopic model without any additional adjustable

parameters. In calculations, we have taken into account the non-Coulomb interactions and also the nearest-neighbor Coulomb interactions. The average atomic mass of Li was different for different samples. This results in small variations in $\gamma_j(\omega_j)$; see Table 1. Though the simulated line broadenings are qualitatively comparable with the experimental results, there is still considerable discrepancy for modes 3 and 4 of the E_u symmetry. A similar discrepancy is observed for the dipolar moments, M_j, that were evaluated through the ionic charges and polarization vectors of the corresponding vibrational modes. The most probable reason for the shortcomings of the theoretical analysis, besides some evident oversimplifications of the model utilized (in particular, accounting for the nearest-neighbor anharmonic interactions only), is the neglect of mixing of the IR active phonon modes of the same symmetry in the electromagnetic field of the incident radiation.

4. Conclusions

We have measured polarized infrared reflection spectra of LiYF_4 single crystals with different isotopic compositions of Li atoms. The obtained spectra were analysed using the model of independent oscillators. It was found that the isotopic disorder due to about 10% concentration of an impurity isotope induces remarkable broadening of the highest-frequency E_u mode, which demonstrates the largest isotopic shift. The widths and shifts of the IR active phonon modes due to both isotopic disorder and anharmonic interactions have been calculated. The calculations revealed that the contribution of the isotopic disorder to the damping constant is comparable with the anharmonic width for those vibrational modes whose frequencies depend markedly on the isotopic composition. The results of simulations agree qualitatively with the experimental data. However, some quantitative discrepancies remain.

Acknowledgements

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