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ABSTRACT

Physical mechanisms contributing to the isotopic structure of spectra of the insulating activated crystals induced by the isotopic disorder in the host crystal or in a system of the impurity optical centers have been considered. The microscopic theory of the geometrical anharmonic isotopic effect is presented. We have shown that the local deformation due to a mass defect in the crystal lattice is dominant in the formation of the fine specific spectral structure in crystals with the proper inhomogeneous isotopic composition (such as ${}^6\text{Li}_c{}^7\text{Li}_{1-c}\text{YF}_4\text{:Ho}$ with the natural abundance of $c = 7.42\%$ of the ${}^6\text{Li}$ isotope). It contributes essentially to the observed shifts of the spectral lines in the case of different masses of the active optical centers (such as ${}^{164}\text{Er}$, ${}^{166}\text{Er}$, ${}^{168}\text{Er}$ and ${}^{170}\text{Er}$ isotopes in the LiYF_4 crystal) as well. Detailed calculations of crystal field parameters and of their first and second derivatives with respect to the lattice strains for the impurity lanthanide ions in lithium-yttrium double fluorides were performed within the framework of the exchange charge model and used in the estimations of the different contributions to the isotope-induced shifts of the Stark sublevels.

1. INTRODUCTION

The dependence of the energy levels of optical centers in activated crystals on the isotopic composition is a topical problem of modern spectroscopy. From the theoretical point of view there are two main goals, namely, to derive a method for estimating possible values of the energy shifts and, secondary, to find an answer to the question what kind of information may be obtained from the measured isotopic spectral structure. Usually an isotopic disorder in crystals contributes to an inhomogeneous broadening and to a specific lineshape of optical transitions^{1,2}. Recently the isotope shifts of the $f-f$ transitions in the low-strain samples of the lithium-yttrium double fluorides activated by erbium and holmium have been directly resolved at liquid helium temperatures^{3,4}. Illustrations of the observed isotopic spectral structures are presented in Fig.1. Lanthanide ions substitute for yttrium in the LiYF_4 crystals and are in the crystal field of the tetragonal (S_4) symmetry. Part of the hyperfine structure of the singlet-doublet transition from the first excited state $\Gamma_2({}^5\text{I}_8)$ to the Γ_{34}^1 Stark sublevel of the ${}^5\text{I}_7$ multiplet of the Ho^{3+} ion observed at 5 K is shown in Fig.1(a). The fine approximately equidistant structure with a separation of 450 MHz of the hyperfine components is induced by the isotopic disorder in the 8 lithium sites nearest to the Ho^{3+} ion³. Another isotopic equidistant structure (with the 76 MHz shifts per unit isotope mass) of the absorption line corresponding to the transition between the ground state and the lowest Stark sublevel of the ${}^4\text{F}_{9/2}$ multiplet of the Er^{3+} even isotopes in LiYF_4 is shown in Fig.1(b)⁴. The relative absorption strengths of the individual components observed in isotopic structures are approximately in the ratio of the abundances of the even-mass Er isotopes and are consistent with the relative abundances of the ${}^6\text{Li}$ and ${}^7\text{Li}$ atoms in the $\text{LiYF}_4\text{:Ho}$ samples^{4,5}. Beginning with the works by Imbusch et al.¹ and by Hyang⁶ the isotopic spectral effects in the activated crystals are attributed to the interaction of the optical centers with the zero-point vibrations of the lattice, and the isotope shifts of the energy levels are assumed to be proportional to differences between the mean-square displacements of atoms with various masses. In our recent work we have carried out an analysis of the isotopic structure of the spectra of the Ho^{3+} ions in the ${}^6\text{Li}_c{}^7\text{Li}_{1-c}\text{HoF}_4$ crystals taking into account changes of the static crystal field caused by the random lattice deformations due to the isotopic disorder in the lithium sublattice⁷. The results obtained for the shifts of the Stark sublevels of the ground ${}^5\text{I}_8$ multiplet and the excited ${}^5\text{I}_7$, ${}^5\text{I}_6$, ${}^5\text{I}_4$ multiplets of the Ho^{3+} ion with an isolated ${}^6\text{Li}$ (${}^7\text{Li}$) ion in its nearest Li-surroundings in the perfect ${}^7\text{LiHoF}_4$ (${}^6\text{LiHoF}_4$) lattice were qualitatively consistent with the measured structures of the hyperfine components of the singlet-doublet and doublet-doublet transitions in the ${}^6\text{Li}_c{}^7\text{Li}_{1-c}\text{YF}_4\text{:Ho}$ (0.1%) crystals. However the direct comparison of the calculated line shifts with experimental data was incorrect due to the possible correlation between neighbouring mass defects in the Li

and Y sites and the corresponding influence of this correlation on the lattice deformation. Here are the results of a more reliable examination of the lattice local deformations induced by mass defects in real crystals and their contribution to the observed isotopic spectral effects.

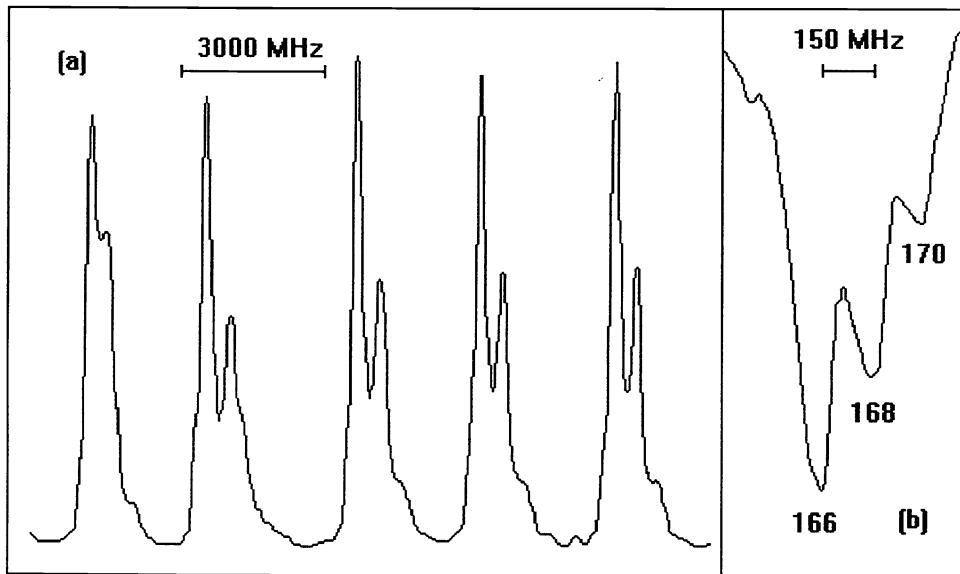


Fig.1. Isotopic structure in the optical absorption spectra of the LiYF₄:Ho (a) and LiYF₄:Er (b) activated crystals with the natural abundance of the ⁶Li and ⁷Li and of the Er isotopes^{3,4}.

2. GEOMETRICAL ISOTOPIC EFFECT

The potential energy of a crystal lattice does not depend on the atomic mass numbers. In the framework of the harmonic approximation a change in isotopic composition results only in changes of the vibration spectrum of the lattice and of the mean-square displacements of the atoms from their equilibrium positions. The spacing between the atoms, as in thermal expansion, experiences changes only as a consequence of the anharmonicity of vibrations. Let us expand the potential energy Φ of the complex lattice containing isotope (mass) defects in a series in the static (\mathbf{u}) and dynamic (ξ) displacements of the atoms from their equilibrium positions in a regular lattice (a matrix form for contractions over the atom labels and coordinates is used):

$$\Phi = \Phi_0 + (1/2!) \Phi'' (\mathbf{u} + \xi)^2 + (1/3!) \Phi''' (\mathbf{u} + \xi)^3 + \dots \quad (1)$$

The condition for an equilibrium of a lattice $\partial \langle \Phi \rangle / \partial \mathbf{u} = 0$ brings about a system of equations for the static displacements $\Phi'' \mathbf{u} + (1/2!) \Phi''' \langle \xi \xi \xi \rangle + \dots = 0$, where the angular brackets $\langle \dots \rangle$ denote averaging over the canonical ensemble of a harmonic lattice. With a similar system of equations for the perfect lattice with the same matrices Φ'' and Φ''' of the second and third order force constants respectively we can put down the shifts of the atoms induced by the mass defects as follows

$$\delta \mathbf{u} = (1/2) \mathbf{G}(\omega = 0) (\langle \xi \xi \xi \rangle - \langle \xi \xi \xi \rangle_0), \quad (2)$$

where $\langle \dots \rangle_0$ denotes the canonical averaging for the regular lattice, and the Green's function of the defect lattice (the generalized lattice susceptibility at the frequency ω) is introduced:

$$\mathbf{G}(\omega) = [(\mathbf{m} + \delta \mathbf{m}) \omega^2 - \Phi'']^{-1}. \quad (3)$$

In the expression (3) \mathbf{m} is the diagonal (in the site representation) matrix of atom masses in a regular lattice and $\delta\mathbf{m}$ represents the mass changes due to the presence of impurity isotopes. The Green's function matrix for the perturbed crystal can be put down through the Green's function \mathbf{G}^0 for the perfect crystal:

$$\mathbf{G} = \mathbf{G}^0 - \mathbf{G}^0(\mathbf{1} + \delta\mathbf{m}\omega^2\mathbf{G}^0)^{-1} \delta\mathbf{m}\omega^2\mathbf{G}^0, \quad (4)$$

which, in the site representation, has elements

$$G_{\alpha\beta}^0\left(\begin{matrix} L & L' \\ k & k' \end{matrix} \middle| \omega\right) = \frac{1}{N} (m_k m_{k'})^{-1/2} \sum_{\mathbf{q}, j} \frac{e_{\alpha}\left(k \middle| \begin{matrix} \mathbf{q} \\ j \end{matrix}\right) e_{\beta}^*\left(k' \middle| \begin{matrix} \mathbf{q} \\ j \end{matrix}\right)}{\omega^2 - \omega_j(\mathbf{q})^2} \exp\left(i\mathbf{q}\mathbf{X}\left(\begin{matrix} L & L' \\ k & k' \end{matrix}\right)\right). \quad (5)$$

Here α, β label the Cartesian components of the phonon polarization vector $\mathbf{e}\left(k \middle| \begin{matrix} \mathbf{q} \\ j \end{matrix}\right)$ of the k -th ion with the mass m_k , \mathbf{q} is a wave-vector and $\omega_j(\mathbf{q})$ is the frequency of a phonon from the j -th branch of the vibration spectrum, L is the cell label, N is the number of cells in the lattice, and \mathbf{X} is the lattice vector. When going over from summation over wave-vectors to integration, we obtain correlation functions for dynamic displacements in the following form

$$\left\langle \xi_{\alpha}\left(\begin{matrix} L \\ k \end{matrix}\right) \xi_{\beta}\left(\begin{matrix} L' \\ k' \end{matrix}\right) \right\rangle = \frac{\hbar}{2\pi} \int \text{Im} G_{\alpha\beta}\left(\begin{matrix} L & L' \\ k & k' \end{matrix} \middle| \omega\right) (2n(\omega) + 1) \frac{d\omega^2}{\omega} \quad (6)$$

where $n(\omega)$ is the occupation number of the phonons. With an approximation of pair interactions, the relative shifts of the atoms in the perturbed lattice are obtained from the expressions (2) and (6) in the following form

$$\delta u_{\alpha}\left(\begin{matrix} L \\ k \end{matrix}\right) = -\frac{1}{2} \sum_{L' k' L'' k''} G_{\alpha\beta}\left(\begin{matrix} L & L' \\ k & k' \end{matrix} \middle| 0\right) \Phi_{\beta\gamma\zeta}\left(\begin{matrix} L' & L' & L'' \\ k' & k' & k'' \end{matrix}\right) \times \\ \left[\Phi_{\zeta\gamma}\left(\begin{matrix} L' & L' \\ k' & k' \end{matrix}\right) + \Phi_{\zeta\gamma}\left(\begin{matrix} L'' & L'' \\ k'' & k'' \end{matrix}\right) - \Phi_{\zeta\gamma}\left(\begin{matrix} L' & L'' \\ k' & k'' \end{matrix}\right) - \Phi_{\zeta\gamma}\left(\begin{matrix} L'' & L' \\ k'' & k' \end{matrix}\right) \right] \quad (7)$$

here and below repeated Greek indices are summed over, the differences of the correlation functions for the perturbed and perfect lattices $\phi = \langle \xi\xi \rangle - \langle \xi\xi \rangle_0$ can be calculated with the formula

$$\phi = -\frac{\hbar}{2\pi} \int (2n(\omega) + 1) \text{Im} \mathbf{G}^0(\mathbf{1} + \delta\mathbf{m}\omega^2\mathbf{G}^0)^{-1} \delta\mathbf{m}\mathbf{G}^0 \omega d\omega^2. \quad (8)$$

One of the infinite sums over the lattice sites in (7) can be easily truncated when taking into account the rapid decrease of the differences ϕ with the increase of the distance from the perturbed lattice site. The estimation of the second infinite sum demands a thorough examination of the anharmonic force constants and remains a challenging problem.

3. LOCAL DEFORMATIONS IN THE ACTIVATED ${}^6\text{Li}_c{}^7\text{Li}_{1-c}{}^{89}\text{YF}_4: {}^{165}\text{Ho}$ AND ${}^7\text{Li}{}^{89}\text{YF}_4: {}^m\text{Er}$ ($m=164, 166, 168, 170$) CRYSTALS

The theory presented in the preceding section was used to determine the changes of the coordinates of fluorine ions in the nearest surroundings of the impurity lanthanide ion in the tetragonal ${}^7\text{LiYF}_4$ crystal at 0 K due to the substitution of the ${}^7\text{Li}$ isotope by ${}^6\text{Li}$ in one of the eight nearest Li-sites (see Fig.2) or due to the substitution of a given lanthanide isotope by another one. We have considered the same lattice-dynamics rigid-ion model as in our previous work⁷ on isotope effects in ${}^7\text{LiHoF}_4$ when replacing the Ho mass by the mass of yttrium. However to increase the accuracy of calculations of the phonon spectral density the number of points in the irreducible part of the Brillouin zone, in which the lattice equations of motion were solved, was increased up to 1150. The potential energy of the lattice was represented by a sum of pair Coulomb and

non-Coulomb interactions, the latter taken into account when the interionic distances R are shorter than 3 \AA only with the exponential dependence on R . The crystallographic coordinate system was used at all stages of calculations including the generation of phonon frequencies and eigenvectors of the perfect crystal, the construction of imaginary parts of Green's functions by the Brillouin zone numerical integration and of real parts via dispersion relations, the calculation of real and imaginary parts of the perturbed Green's functions, of the correlation functions and their derivatives with respect to the mass of the isolated impurity isotope.

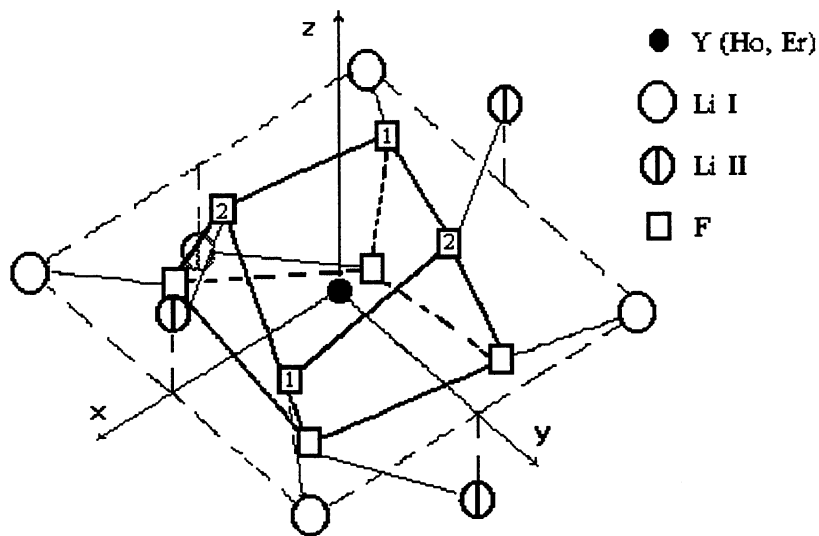


Fig.2. Fragment of the LiYF_4 crystal lattice structure. The fluorine and lithium ions nearest to the Y site are shown.

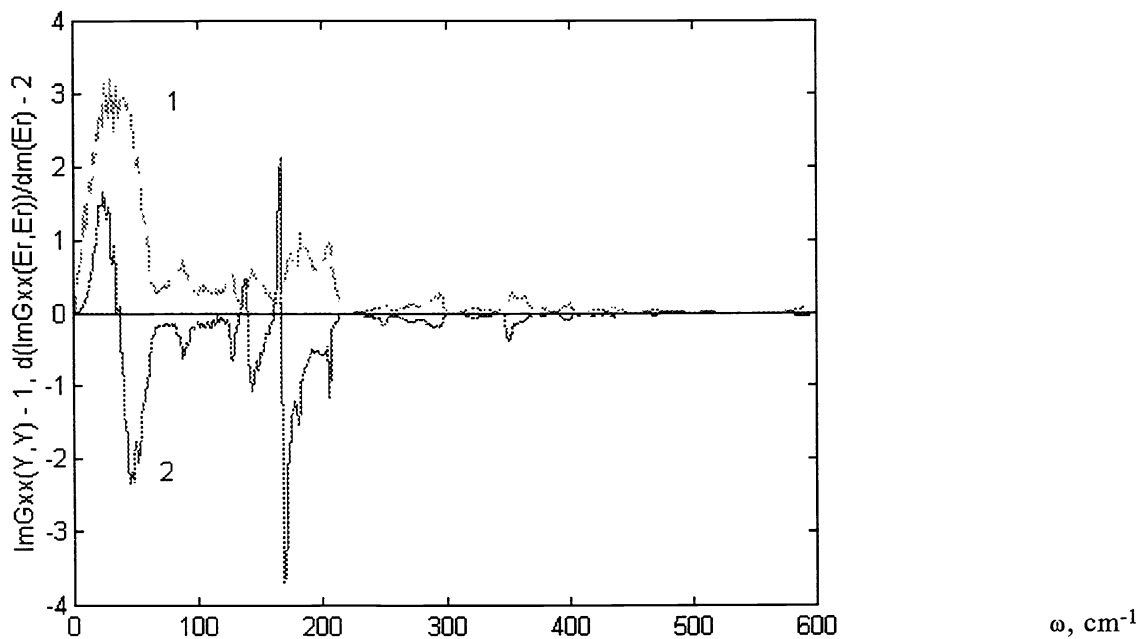


Fig.3. The spectral density of the Y ion vibrations along the $[100]$ axis (dashed line) and an increment of the same density per unit Er isotope mass (solid line, in arbitrary units).

Results of calculations of the correlation functions for ion displacements are given in Table 1. As an illustration of a redistribution of the spectral density of vibrations due to the lanthanide ion substitution for yttrium the derivative of the spectral density of the Er ion vibrations in the (0 0 1) plane with respect to its mass is plotted in Fig.3. In the case of the impurity lanthanide ion vibrations along the lattice [0 0 1] symmetry axis we have found a strong resonance mode of $\sim 229 \text{ cm}^{-1}$ frequency near the narrow gap in the vibrational spectrum with the width to be less than one cm^{-1} . However it is quite possible that these gap and resonance mode are artefacts of the lattice-dynamics model. For the isolated mass defect in the Li- or Y-site the treatment of the dynamics of the perturbed lattice reduces to a simple one-dimensional problem. We have also strictly resolved the six-dimensional problem for complexes consisting of an impurity holmium ion in the Y-site (0 0 0) and ^6Li impurity isotope in one of its neighbouring non-equivalent positions in the $^7\text{LiYF}_4$ lattice (see Fig.2): Li I (-0.5 -0.5 0) and Li II (0 -0.5 0.25). The corresponding differences

Table 1. Correlation functions of ion displacements at 0 K in $^7\text{LiYF}_4$ and their changes in $^7\text{LiYF}_4\cdot^{166}\text{Er}$, $^7\text{LiYF}_4\cdot^6\text{Li}$, ^{165}Ho crystals (in units of 10^{-6} \AA^2)

$k\alpha, k'\beta^*$	$^7\text{LiYF}_4$ $\langle \xi_\alpha(k) \xi_\beta(k') \rangle_0$	$^7\text{LiYF}_4\cdot\text{Er}$ $\phi_{\alpha\beta}(k, k')$	$^7\text{LiYF}_4\cdot\text{Ho}, ^6\text{Li I}$ $\delta\phi_{\alpha\beta}(k, k')$	$^7\text{LiYF}_4\cdot\text{Ho}, ^6\text{Li II}$ $\delta\phi_{\alpha\beta}(k, k')$
1x,1x 1y,1y	1988	-378	0.5	0.4
1z,1z	1534	-304	-0.3	0.8
2Ix,2Ix 2Ily,2Ily	7420	-54 -43	532	532
2Iy,2Iy 2IIx,2IIx	7420	-57 -40	531	528
2Iz,2Iz 2IIz,2IIz	8944	18 -64	751	683
2Ix,2Iy -2IIx,2Ily	0	-6 5	-5	-2
2Ix,2Iz -2Ily,2IIz	0	-9 1	15	3
2Iy,2Iz 2IIx,2IIz	0	6 -2	-1	2
3x,3x 4y,4y	4633	-64 -59	1	6
3y,3y 4x,4x	4492	-55 -67	-6	8
3z,3z 4z,4z	4074	-27 -10	10	-27
3x,3y -4x,4y	-757	-9 -10	-1	4
3x,3z -4y,4y	-709	11 -1	8	2
3y,3z 4z,4z	810	5 10	-8	-18
2Ix,3x 2Ily,4y	1232	-56 -46	12	12
2Iy,3y 2IIx,4x	1238	-50 -41	13	14
2Iz,3z 2IIz,4z	1004	26 -62	-21	24
2Ix,3y -2Ily,4x	-55.3	-9 -2	-2	0.5
2Iy,3x -2IIx,4y	-85.2	-13 1	-3	-2
2Ix,3z -2Ily,4z	-106.7	13 -11	-1	0
2Iz,3x -2IIz,4y	-31.8	-11 5	18	-2
2Iy,3z 2IIx,4z	104.7	7 2	1	0.2
2Iz,3y 2IIz,4x	178.8	23 -14	-7	10
1x,3x 1y,4y	997 998	-104 -100	0.6	1
1y,3y 1x,4x	952 972	-95 -99	0.9	0
1z,3z 1z,4z	701 767	-72 -85	0.9	1.4
1x,3y -1y,4x	40 -19	-17 2	-0.6	0
1y,3x -1x,4y	158 -70	-34 11	0.3	0
1x,3z -1y,4z	-83 90	14 -19	-0.8	-0.4
1z,3x -1z,4y	-67 9	2 -1	1.1	-0.1
1y,3z 1x,4z	-86 12	21 0	0.4	0
1z,3y 1z,4x	-53 43	0 -9	2.0	1.5

*Notes: coordinates of ions, in units of the lattice constants a, c , are Y(Ho,Er) [0 0 0], $k = 1$; Li I [-0.5 -0.5 0], $k = 2\text{I}$; Li II [0 -0.5 0.25], $k = 2\text{II}$; F [x-0.5 y-0.5 z], $k = 3$; [-y x-0.5 0.25-z], $k = 4$; $x = 0.282$; $y = 0.164$; $z = 0.0815$; $a = 5.168 \text{ \AA}$, $c = 10.731 \text{ \AA}$.

$\delta\phi_{\alpha\beta}(k,k')$ between the correlation functions for the displacements of ions in these two types of complexes, including the fluorine ion F₃ or F₄ respectively (marked by labels 1 and 2 in Fig.1, see also notes to Table 1), which is the common nearest neighbour of the defect sites, are given in the two last columns of Table 1. The mutual influence of the two neighbouring mass defects lowers the symmetry of the lattice perturbation and brings about small but significant differences between the corresponding correlation functions of ion displacements in complexes with different geometry. Considering in the double lattice sums in the expression (7) only the third order force constants and the differences between the correlation functions ϕ and $\delta\phi$ of the ion displacements, corresponding to the impurity isotopes and their nearest neighbours, we obtained parameters of the local lattice deformation near the lanthanide ions, which are presented in Table 2. It should be emphasized that in the absence of correlation between the mass defects in the neighbouring lithium and yttrium sites displacements δu_α of the fluorine ions F I and F II in Table 2 could differ only in sign.

Table 2. Displacements of fluorine ions in the nearest surroundings of the impurity lanthanide ion in (0 0 0)-site due to a change of its mass and ⁶Li isotope substitution for ⁷Li in one of the nearest Li-sites in ⁷LiYF₄.

axis	F I			F II		
	coordinates	δu_α (10 ⁻⁴ Å) ⁶ Li (-0.5 -0.5 0) Ho (0 0 0)	$d(\delta u_\alpha)/dm_{Er}$ (10 ⁻⁶ Å/unit mass)	coordinates	δu_α (10 ⁻⁴ Å) ⁶ Li (0.5 0 0.25) Ho (0 0 0)	$d(\delta u_\alpha)/dm_{Er}$ (10 ⁻⁶ Å/unit mass)
x	x - 0.5	2.26	1.2	0.5 - x	- 3.15	- 8.1
y	y - 0.5	2.94	5.9	- y	- 2.29	5.0
z	z	3.26	- 4.1	0.25 - z	- 3.38	- 6.8

4. ISOTOPE SHIFTS OF THE STARK SUBLEVELS OF THE IMPURITY Ho³⁺ AND Er³⁺ IONS IN LiYF₄ CRYSTALS

The energy of interaction of the lanthanide ion with the crystal lattice is described by the Hamiltonian

$$H = \sum_{p,q} B_p^q(\mathbf{u} + \xi) O_p^q, \quad (9)$$

where O_p^q are Stevens operators, and its dependence on displacements of the lattice ions from their equilibrium positions in the perfect static lattice is shown explicitly. Isotopic effects in the energy spectrum of the electronic 4f-shell can be considered in the framework of the perturbation theory. With the series expansion of H up to second order in $(\mathbf{u} + \xi)$

$$B_p^q(\mathbf{u} + \xi) = B_p^q + B_p^{q'} \bullet (\mathbf{u} + \xi) + \frac{1}{2} B_p^{q''} \bullet (\mathbf{u} + \xi)^2, \quad (10)$$

we obtain the Hamiltonian of the lanthanide ion in the static crystal field of the lattice, containing different isotopes, in the following form

$$H_0 = \sum_{p,q} [B_p^q + \delta B_p^q] O_p^q, \quad (11)$$

where the first term corresponds to the crystal field in the perfect lattice, and the second term contains contributions from the lattice deformation, induced by the isotopes, and from the nonlinear electron-phonon interaction (EPHI):

$$\delta B_p^q = B_p^{q'} \bullet \delta \mathbf{u} + \frac{1}{2} B_p^{q''} \bullet \phi. \quad (12)$$

The linear EPHI $H_{e-ph} = \sum_{p,q} B_p^{q'} \cdot \xi O_p^q$, taken in second order, induces additional shifts of the eigenvalues of the Hamiltonian H_0 . The corresponding difference between the energies of the i -th Stark sublevel in the perturbed and perfect lattices can be recorded as follows:

$$\Delta E_i = -\frac{\hbar}{2\pi} \sum_j \sum_{LL'kk'} \sum_{pp'qq'} \left\langle i \left| B_{p,\alpha}^q \left(\frac{L}{k} \right) O_p^q \right| j \right\rangle \left\langle j \left| B_{p',\beta}^{q'} \left(\frac{L'}{k'} \right) O_{p'}^{q'} \right| i \right\rangle \int \frac{\text{Im}[G_{\alpha\beta} \left(\frac{L}{k} \frac{L'}{k'} \middle| \omega \right) - G_{\alpha\beta}^0 \left(\frac{L}{k} \frac{L'}{k'} \middle| \omega \right)]}{\omega(E_j - E_i + \hbar\omega)} d\omega^2 \quad (13)$$

The energy shifts (13) can be estimated without many difficulties when taking into account that the most significant difference between the spectral densities of the ion displacements is localised on the impurity isotope. However one has to conduct the integration carefully near the singular points (where $E_i - E_j = \hbar\omega$) using an analytical approximation for the integrand.

Thus there are three mechanisms, that is three contributions to the isotope-induced shift of the localized electron energy. Two of the short-range type are due to EPHI. They are directly connected with the differences between the spectral densities of the ion vibrations. The contribution from the geometrical effect is of the same range as the crystal field of the perfect lattice. To proceed further in the calculations we have to use the real estimates of the EPHI parameters.

Table 3. Crystal field parameters and their calculated changes upon isotopic substitution of lithium and lanthanide ions in the activated LiYF₄ crystals. The theoretical values of the crystal field parameters are given in brackets.

p	q	Ho ³⁺			Er ³⁺		
		B_p^q 7LiYF ₄ (cm ⁻¹)	δB_p^q 7LiYF ₄ : 6Li I (10 ⁻³ cm ⁻¹)	δB_p^q 7LiYF ₄ : 6Li II (10 ⁻³ cm ⁻¹)	B_p 7LiYF ₄ (cm ⁻¹)	static effect (MHz/unit Er mass)	quadr. EPHI (MHz/unit Er mass)
2	0	189.3	78	96	190 (177)	113.8	-39.5
4	0	-78.3	-31	-23	-80 (-85)	-15.3	22.3
6	0	-3.3	9.8	-7.1	-2.3 (-2.8)	-5.6	-2.0
4	4	-657	-56	-63	-771 (-699)	-156.1	173.5
4	-4	-568	-73	13	-667 (-604)	-118.3	185.6
6	4	-322	-76	-104	-363 (-333)	-77.9	11.0
6	-4	-253	-92	16	-222 (-279)	-38.3	17.7

Changes of the parameters of the fully symmetric component of the crystal fields due to the impurity ⁶Li isotope in the ⁷LiYF₄:Ho crystal and to an increase of mass by one unit of the Er ion, presented in Table 3, were calculated in the framework of the exchange charge model⁸ with allowance for the interaction of the 4f electrons with point charges and point electric dipoles of the lattice ions and with the parametrized exchange charges proportional to the squares of the overlap integrals of the wave functions of the lanthanide ion and ligands. When calculating the data in the last column of Table 3 only the changes in the autocorrelation functions of the Er isotope itself were taken into account: $d\phi_{xx}/dm = -3.41$ and $d\phi_{zz}/dm = -2.75 \text{ \AA}^2/\text{unit mass}$.

With the equation (13) and the data from Table 3 we get the following values of the isotope-induced shifts of the Er ion energy levels: ground state 0 (⁴I_{15/2}), -33.3+14.6+65.6=46.9; the lowest sublevel 1 in the ⁴F_{9/2} multiplet, -28.4+15.4+50.4=37.4; the first excited sublevel 2 in the ⁴F_{9/2}, -1.5+9.5-12.1=-4.1 MHz/unit mass, where the summands are of the same order of magnitude and correspond respectively to contributions due to static displacements of the neighbouring fluorine ions, nonlinear and linear EPHI. The calculated difference of -41.5 MHz/unit mass between the isotopic shifts of the transitions 0 → 2 and 0 → 1 is in qualitative agreement with the measured one (R. Meltzer, private communication) of -22 MHz/unit mass.

The theory developed can not be used for estimating directly shifts of the individual spectral lines because the possible displacements of the multiplet centers of gravity have not been considered.

The contributions from lithium ions to parameters of the crystal field, affecting lanthanide ions in the LiYF_4 crystal, and to the EPHI constants are small compared with the contributions from the fluorine ligands. Thus the isotopic disorder in the lithium sublattice affects the energy spectra of the impurity lanthanide ions mainly by means of static displacements of ligands which are pushed away from the ${}^6\text{Li}$ and are attracted by ${}^7\text{Li}$ isotopes. Data in Table 3 for the ${}^7\text{LiYF}_4: {}^6\text{Li}, \text{Ho}$ crystal are obtained with the displacements of the fluorine ions induced by the impurity ${}^6\text{Li}$ isotope, presented in Table 2. Calculated with these data shifts of the hyperfine components of the Ho^{3+} ion doublet states in the ${}^5\text{I}_J$ ($J = 8, 7, 6$) multiplets (from -0.04 up to 0.04 cm^{-1}) are in good agreement with the measured intervals in the isotopic spectral structures.

5. CONCLUSION

In this work numerical estimates of the isotopic spectral effects in crystals doped with the lanthanide ions have been obtained without any fitting parameters except those used in the description of the lattice dynamics and of the crystal field in a perfect lattice. Though some of the calculated spacings in the isotopic structures of the optical transitions differ from those measured by a factor of almost three, the relative importance of various mechanisms (linear and quadratic EPHI, geometrical effect), contributing to the shape and the inhomogeneous broadening of the spectral lines in crystals with the mixed isotopic composition, is get clear. In some cases the local lattice deformation is a dominant mechanism. Theoretical results are in agreement with rather simple physical arguments: in the case of a heavy isotope its vibration amplitude decreases, ligands approach an optical center due to the anharmonic nature of the interionic interaction, and the crystal field increases. On the other hand, the same decrease of the vibration amplitude diminishes the strength of the crystal field. The redistribution of the spectral density of vibrations of the impurity isotope affects the repulsion between the Stark sublevels through the phonon field. Due to the strong localization of a lattice perturbation by a mass defect this effect is essentially dependent on the contribution of the corresponding ion into the crystal field affecting an optical center.

6. ACKNOWLEDGEMENTS

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