



Modeling and decoding of fine structure of electron-vibrational 5d – 4f luminescence spectra in $\text{LiRF}_4:\text{Ce}^{3+}$ (R = Y, Lu) crystals

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ABSTRACT

The 5d-4f luminescence spectra in the $\text{LiYF}_4:\text{Ce}^{3+}$, $\text{LiLuF}_4:\text{Ce}^{3+}$ crystals at zero temperature are simulated using a microscopic model of electron-phonon interaction and realistic phonon spectrum of host crystal lattices. Calculations show that three vibrational peaks with the energies 65 cm^{-1} , 223 cm^{-1} and 420 cm^{-1} with respect to zero-phonon transition energy dominate in vibrational structure in these spectra. Comparison of simulation results with available experimental data allows to identify zero-phonon lines and vibrational peaks in the measured spectra and thus determine energies of several $4f^1$ electronic configuration levels: 514, 2221 and 2316 cm^{-1} for $\text{LiYF}_4:\text{Ce}^{3+}$ and 514, 2188, 2283 and, possibly, 3134 cm^{-1} for $\text{LiLuF}_4:\text{Ce}^{3+}$ with respect to the ground 4f level energy.

1. Introduction

In recent years there has been a considerable interest in $4f^n-4f^{n-1}5d$ spectra of rare earth (RE) compounds, lying generally in the ultraviolet region, as a part of effort to design new lasers, phosphors and scintillator materials. Both absorption and emission spectra for the $4f^n-4f^{n-1}5d$ transitions have been obtained for most RE ions in several host crystals. In particular, LiYF_4 is an example of a crystal with intermediate electron-phonon coupling in 4f-5d transitions in impurity RE ions, when along wide vibrational bands the narrow phonon lines are observed in spectra [1,2].

Impurity Ce^{3+} ions substitute for Y^{3+} ions in LiYF_4 crystal in sites with S_4 point symmetry. Spectra of Ce^{3+} ground ($4f^1$) and excited ($5d^1$) configurations consist of 7 Kramers doublets (${}^2F_{5/2}$ and ${}^2F_{7/2}$ multiplets splitted by S_4 symmetry crystal field) and 5 Kramers doublets (${}^2D_{3/2}$ and ${}^2D_{5/2}$ multiplets), respectively. The absence of safe values of crystal field energies for the 4f electron in Ce^{3+} ion in LiYF_4 and LiREF_4 crystals is a well-known problem in literature. The authors of papers [3,4] independently made an attempt to determine several of the Ce^{3+} 4f crystal field levels from the measured with high spectral resolution 5d-4f luminescence spectrum in the $\text{LiYF}_4:\text{Ce}^{3+}$ crystal at low temperatures (and also in the $\text{LiLuF}_4:\text{Ce}^{3+}$ crystal in [3]): peaks observed in the luminescence spectrum were interpreted as zero-phonon lines (ZPLs) corresponding to transitions from the lowest 5d state to different 4f levels of the Ce^{3+} ion. However, it is possible that some of the observed peaks can origin from vibrational maxima but not from ZPLs

(and vice versa, some peaks that have been left unidentified in [3,4] can indeed origin from ZPLs). No modeling of vibrational structure of these luminescence spectra was performed in [3,4] or elsewhere in literature, that could allow distinguishing zero-phonon and electron-vibrational transitions. As for electron-phonon interaction in other Ce^{3+} -doped compounds, an original semi-empirical "degenerate model" of vibronic 4f-5d transitions has been developed for $\text{Y}_3\text{Al}_5\text{O}_{12}$ [5] and $\text{Na}_3\text{LuSi}_2\text{O}_7$, $\text{NaSr}_4(\text{BO}_3)_3$ hosts [6].

The purposes of the present theoretical study are: 1) to perform modeling of vibrational structure in the low-temperature 5d-4f luminescence spectrum in the $\text{LiYF}_4:\text{Ce}^{3+}$ crystal using a microscopic model of electron-phonon interaction and realistic phonon spectrum of the host crystal lattice; 2) to interpret available experimental data on this spectrum [3,4] and consider an opportunity of establishing values of the 4f crystal field levels for the Ce^{3+} ion based on this interpretation; 3) to perform similar analysis of experimental data on luminescence for the $\text{LiLuF}_4:\text{Ce}^{3+}$ crystal and several other double fluorides crystals with sheelite structure; on this basis, to make a comparison of electron-phonon interaction in these compounds.

2. Simulation details

To simulate interconfigurational 5d-4f luminescence spectrum in $\text{LiYF}_4:\text{Ce}^{3+}$, we use the microscopic model of electron-phonon interaction that we derived in [7] for simulating the 4f-5d absorption spectrum in this crystal. Simulation involves calculation of 5d crystal

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field parameters and 5d electron-phonon coupling constants in the framework of the exchange charge model [8] (interaction of the 4f electron with phonons is weak and is neglected in our model); numerical diagonalization of the effective impurity Ce^{3+} ion Hamiltonian containing spin-orbit and crystal field interactions for the ground 4f and excited 5d electronic configurations; calculation of integral intensities of the 5d-4f transitions given by squared matrix elements of the effective electric dipole moment of the Ce^{3+} ion; simulation of band shapes in adiabatic approximation using realistic phonon spectrum of the host crystal lattice: frequencies and polarization vectors of vibrations for 8870 wave vectors distributed uniformly over the irreducible part of the Brillouin zone are calculated using parameters of the rigid-ion model of the LiYF_4 crystal lattice established in [9], perturbation of phonon spectrum by the impurity ion is neglected, lattice vibrations are considered in harmonic approximation.

In crystallographic axes crystal field interaction Hamiltonian for the ground 4f electronic configuration of the Ce^{3+} ion is determined by seven crystal field parameters as follows [7]

$$H_{\text{CF}} = B_0^2 C_0^{(2)} + B_0^4 C_0^{(4)} + B_4^4 C_4^{(4)} + B_{-4}^4 C_{-4}^{(4)} + B_0^6 C_0^{(6)} + B_4^6 C_4^{(6)} + B_{-4}^6 C_{-4}^{(6)},$$

where crystal field parameters satisfy the equation $B_k^{p*} = (-1)^k B_{-k}^p$, $C_k^{(p)}$ are components of one-electron spherical tensor operators $C^{(p)}$. Spin-orbit interaction for the 4f electron is determined by a spin-orbit coupling constant ζ , so there are only eight independent real quantities defining the effective Hamiltonian for the 4f electron in our model. Similarly, the effective Hamiltonian for the 5d electron of the impurity Ce^{3+} ion is defined by a spin-orbit coupling constant $\zeta(5d)$ and four crystal field parameters $B_0^2(5d)$, $B_0^4(5d)$, $B_{\pm 4}^4(5d)$, calculated as explicit functions of lattice ion's coordinates in the framework of the exchange charge model utilizing three phenomenological fitting parameters [8]. Hamiltonian of electron-phonon interaction for the 5d electron, linear in dynamic displacements of lattice ions, is considered within cluster approximation: only vibrations of ligands (eight fluorine ions forming two deformed tetrahedrons) is taken into account. The electron-phonon coupling constants are calculated consistently with the 5d crystal field parameters by direct differentiation of the latter with respect to the host ion's coordinates.

Procedure of the Hamiltonian parameters fitting can be divided into two stages.

2.1. Fitting of the 5d Hamiltonian parameters [7]

In [7] we fulfilled the simulation of the low-temperature 4f-5d absorption spectrum in the $\text{LiYF}_4:\text{Ce}^{3+}$ crystal using the values of the effective 4f Hamiltonian parameters extracted from estimations made in literature [1,4]. Exchange charge model parameters, determining crystal field interaction and electron-phonon interaction for the 5d electron of the Ce^{3+} ion, were varied to fit experimental data [1,3]: 1) 5d crystal field levels; 2) distribution of intensity between the ZPL and the vibrational sideband for a 4f-5d band corresponding to a transition from the ground 4f state to the lowest 5d state. The calculated [7] Huang–Rhys parameters S_{HR} for the 4f-5d transitions equal, in the order of the 5d energy increase, 2.92, 17.4, 5.98, 5.97 and 16.44, with the smallest value for the lowest 5d state, thus explaining why the ZPL is observed in experiment only in optical bands which involve this 5d state [1,3]. The calculated [7] 5d crystal field levels 34088 cm^{-1} , 41098 cm^{-1} , 48548 cm^{-1} , 49308 cm^{-1} and 53723 cm^{-1} also agree well with experimental results, with the exception of the underestimated splitting between the third and fourth 5d levels: 760 cm^{-1} versus experimentally observed $\sim 1900 \text{ cm}^{-1}$; in [10] we showed that such a large splitting between these sublevels of an orbital doublet can be explained taking into account non-adiabatic mixing of these electronic states by phonons (the Jahn-Teller effect). We should also note that the three highest 5d levels seem to be situated above the bottom of

the LiYF_4 conduction band, which is approximately 15000 cm^{-1} above the lowest Ce^{3+} 5d level according to [11]. Therefore, autoionization processes and hybridization of the localized 5d states with the delocalized states in the conduction band may contribute significantly to homogeneous broadening of corresponding 4f-5d bands.

Let us stress that no high resolution measurements of the low-temperature 4f-5d absorption or excitation spectra in the $\text{LiYF}_4:\text{Ce}^{3+}$ crystal are available in literature, that would resolve the vibrational structure in the band corresponding to a transition to the lowest 5d state, and no direct fitting of this vibrational structure was made during the 5d Hamiltonian fitting procedure in [7].

2.2. Fitting of the 4f Hamiltonian parameters

No parameters of the 5d Hamiltonian, established in [7], are additionally fitted in the present study. The shape of the 5d-4f luminescence spectrum in $\text{LiYF}_4:\text{Ce}^{3+}$ is calculated for zero temperature within the adiabatic and Condon approximations. Unlike the case of excited 5d states of the Ce^{3+} ion, the use of adiabatic approximation is fully justified here since the lowest 5d level, being itself a Kramers doublet, is separated from the first excited 5d level by a gap exceeding eight maximum LiYF_4 crystal phonon energies, equaling 560 cm^{-1} [9]. The calculated band shape is convoluted with a Gaussian distribution with the width of 23.5 cm^{-1} to take into account inhomogeneous broadening induced by random lattice strains.

In preliminary simulation of the 5d-4f luminescence spectrum in $\text{LiYF}_4:\text{Ce}^{3+}$, the same literature parameters for the effective 4f Hamiltonian were used that we had exploited earlier in [7] in modeling of absorption spectrum in this compound. Comparing the vibrational structure of a single band, corresponding to a transition from the lowest 5d state to a 4f level, with the fine structure of the measured with high resolution 5d-4f luminescence spectrum in $\text{LiYF}_4:\text{Ce}^{3+}$ crystal [3,4], we gave interpretation to the latter and determined a few of the 4f crystal field energies. On this basis, and also taking into account g-factors values for the ground 4f Ce^{3+} state available in literature [12,13], we found an appropriate set of 4f Hamiltonian parameters and fulfilled the final simulation of the 5d-4f luminescence spectrum in $\text{LiYF}_4:\text{Ce}^{3+}$. For details of simulation of the 5d-4f luminescence spectrum in the $\text{LiLuF}_4:\text{Ce}^{3+}$ crystal – see Section 3.2.

3. Results and discussion

3.1. Spectra of $\text{LiYF}_4:\text{Ce}^{3+}$ crystal

Let us consider in details the calculated vibrational structure of a band, corresponding to a 4f-5d transition in $\text{LiYF}_4:\text{Ce}^{3+}$ at zero temperature involving the lowest 5d state of the Ce^{3+} ion; let us remind that in our model this structure does not depend on a particular 4f state involved in the transition. In Fig. 1 such a band in the absorption spectrum is shown, with the energy of a zero-phonon transition put equal to 1000 cm^{-1} for illustrative purposes. The calculated one-, two-, three- and four-phonon envelopes are shown in Fig. 1, as well as the integral vibrational band for the transition; ZPL at 1000 cm^{-1} is not shown in Fig. 1 for simplicity. Only one- and two-phonon bands provide significant vibrational structure in the spectrum, in accordance with the Huang–Rhys parameter S_{HR} value of 2.92 for such a 4f-5d transition. Three most pronounced vibrational peaks in the calculated one-phonon band are observed at the energies 65 cm^{-1} , 223 cm^{-1} and 420 cm^{-1} with respect to the energy of a zero-phonon transition and are noted in Fig. 1 as 'a', 'b' and 'c', correspondingly. A two-phonon lineshape is proportional to a convolution of the one-phonon lineshape with itself [7], therefore three vibrational maxima in the calculated two-phonon envelope, noted in Fig. 1 as 'm' (288 cm^{-1} with respect to the energy of a zero-phonon transition), 'n' (485 cm^{-1}) and 'p' (643 cm^{-1}), can be interpreted as results of one-phonon peaks superimpositions 'a + b', 'a + c' and 'b + c', correspondingly. Other vibrational maxima were not

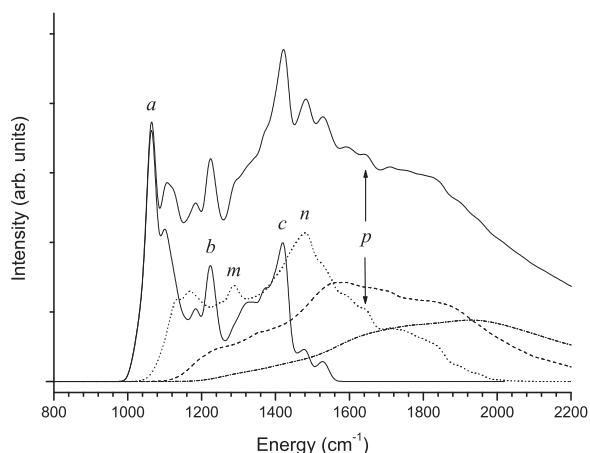


Fig. 1. Calculated vibrational band, corresponding to a $4f \rightarrow 5d$ transition to the lowest $5d$ state of the Ce^{3+} ion in the $LiYF_4$ crystal (upper solid curve); one-phonon (lower solid), two-phonon (dotted), three-phonon (dashed), four-phonon (dash dot) contributions to the band. ZPL at 1000 cm^{-1} is not shown. For vibrational maxima notion see text.

noted in Fig. 1 to avoid cluttering the figure.

According to our model, similar vibrational structure is expected to occur in absorption (excitation) and luminescence spectra of $4f^n - 4f^{n-1}5d$ transitions involving states in the low-energy region of the excited $4f^{n-1}5d$ configuration for different RE ions doped in $LiYF_4$ crystal (unless transition under consideration is spin- or symmetry-forbidden, and therefore Condon approximation is inapplicable and a non-Condon lineshape should be considered [14]). This proposition was confirmed in modeling of the low-temperature $4f^{14} - 4f^{13}5d$ absorption spectrum in the $LiYF_4:Lu^{3+}$ crystal [15].

Let us also notice that vibrational structure of bands, corresponding to $4f-5d$ transitions in $LiYF_4:Ce^{3+}$ involving the excited $5d$ states of the Ce^{3+} ion, is significantly different. In Fig. 2 we compare the normalized calculated one-phonon bands of $4f-5d$ transitions for the four out of five $5d$ levels of the Ce^{3+} ion in $LiYF_4$ crystal; the only omitted level is the fourth $5d$ level which is almost identical to the third $5d$ level as far as interaction with phonons is concerned. The energies of zero-phonon transitions were put equal to 1000 cm^{-1} for all bands for illustrative purposes. It is interesting to note that the only vibrational peak present in all one-phonon bands in Fig. 2 is the 'a' peak (see Fig. 1). Another conclusion is that only the one-phonon band corresponding to transition to the lowest Ce^{3+} $5d$ state includes a pronounced vibrational peak with the energy higher than 400 cm^{-1} with respect to the energy of a zero-phonon transition – a 'c' peak (see Fig. 1).

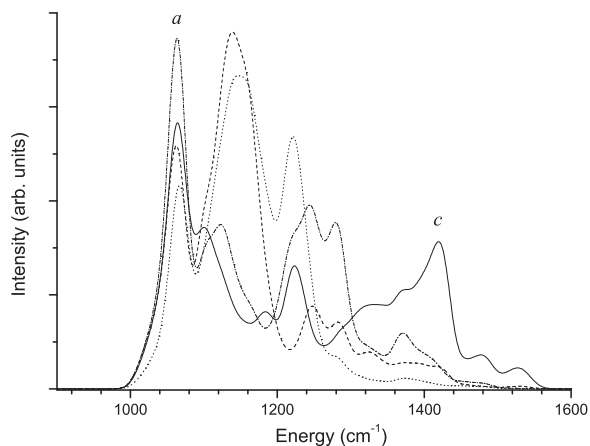


Fig. 2. Calculated normalized one-phonon bands in the spectra of $4f \rightarrow 5d$ transitions to the lowest (solid curve), first excited (dotted), second excited (dashed) and fourth excited (dash dot) $5d$ states of the Ce^{3+} ion in the $LiYF_4$ crystal. The bands were shifted to a unified onset at 1000 cm^{-1} . Vibrational maxima notion is in accordance with Fig. 1.

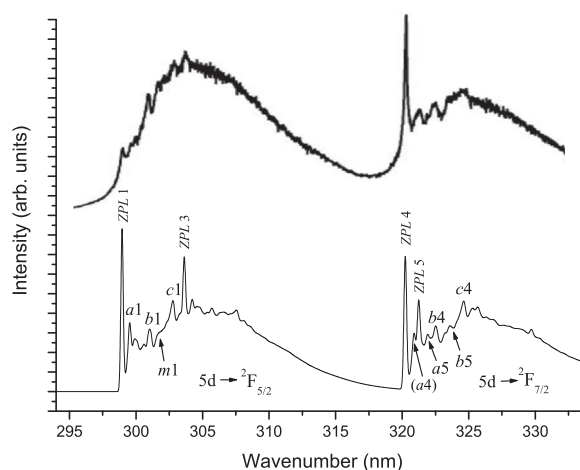


Fig. 3. Calculated for 0 K (lower curve) and measured at 10 K [4] (upper curve, reprinted with permission from [4], copyright (2005) by the American Physical Society) $5d-4f$ luminescence spectra in the $LiYF_4:Ce^{3+}$ crystal. For peaks identification notion see text and Fig. 1.

Within the established model of electron-phonon interaction, the $5d-4f$ luminescence spectrum in $LiYF_4:Ce^{3+}$ at zero temperature can be obtained as a superimposition of bands with the identical vibrational structure, shown in Fig. 1 (with a ZPL added!), but with different onsets (given by zero-phonon transition energies) and intensities. Let us now introduce a uniform notion for the spectra discussed below. The $4f$ crystal field levels will be numerated in the order of energy ascending, from 1 to 7. Zero-phonon lines will be noted as "ZPL i ", where i is a number of a $4f$ crystal field level. Similarly, vibrational maxima will be noted as "x i ", where 'x' is a symbolic notion of the vibrational maximum established in Fig. 1.

In Fig. 3 the calculated non-polarized $5d-4f$ luminescence spectrum in $LiYF_4:Ce^{3+}$ at zero temperature is compared with the spectrum measured with high resolution at 10 K in [4]. Note that ZPL 1 is not pronounced well in experiment due to resonant reabsorption [4]. Only peaks identified in measured spectra are marked in Fig. 3 and further figures. Let us consider the band corresponding to transitions $5d \rightarrow 4f$ ($^2F_{5/2}$). As shown in Fig. 3, four peaks in the experimental spectrum are assigned as vibrational maxima 'a1', 'b1', 'm1' and 'c1', while the peak at 514 cm^{-1} , with respect to ZPL 1 energy 33451 cm^{-1} (298.94 nm), cannot be interpreted as a vibrational maximum of any kind and, as it follows from calculations, should be ascribed to ZPL 3.

In the band corresponding to $5d \rightarrow 4f$ ($^2F_{7/2}$) transitions two peaks in the measured spectrum, with the energies 2221 cm^{-1} and 2316 cm^{-1} with respect to ZPL 1 energy, are assigned as ZPL 4 and ZPL 5, respectively (the latter should be distinguished from the 'a4' vibrational peak which has a somewhat smaller energy and is shown in Fig. 3 in parentheses as it is not resolved in the measured spectrum). Four peaks in the measured spectrum are ascribed to vibrational maxima 'a5', 'b4', 'b5' and 'c4'.

Two conclusions can be made on the basis of calculated and measured spectra comparison in Fig. 3.

- 1) Comparison with experiment confirms the calculated energies of main vibrational maxima 'a', 'b' and 'c' (Fig. 1), defining the vibrational structure in $4f-5d$ spectra involving the lowest $5d$ state of the Ce^{3+} ion. This is a success of our microscopic model of electron-phonon interaction, taking into account that no direct fitting of the vibrational structure has been done. It should also be noted that the widths of calculated $5d \rightarrow ^2F_{5/2}$ and $5d \rightarrow ^2F_{7/2}$ bands are also in good agreement with experiment (see Fig. 3). However, peaks in the calculated spectrum are somewhat more pronounced than in the measured one, indicating that we perhaps underestimate inhomogeneous broadening for this spectrum.

2) Microscopic modeling of vibrational structure in the 5d-4f luminescence spectrum in the $\text{LiYF}_4:\text{Ce}^{3+}$ crystal allows to identify peaks in the spectrum measured in [4] and determine energies of the three excited 4f crystal field levels (with respect to the ground 4f level): 514 cm^{-1} (3rd 4f level), 2221 cm^{-1} (4th level) and 2316 cm^{-1} (5th level).

The value 514 cm^{-1} is reported for the first time in literature. The value 2221 cm^{-1} corresponds to the splitting between ${}^2F_{5/2}$ and ${}^2F_{7/2}$ states by spin-orbit interaction and is well-known in literature. The value 2316 cm^{-1} has already been reported in [4]. However, our calculations show that two more 4f crystal field energies 216 cm^{-1} and 2430 cm^{-1} were not determined in [4] correctly. As seen in Fig. 3, corresponding peaks in the measured spectrum should be ascribed to vibrational maxima 'b1' and 'b4', but not to ZPL 2 and ZPL 6. Even if 2nd and 6th 4f crystal field levels coincidentally have energies close to the values given above, it follows from calculations that corresponding transitions from the lowest 5d state of the Ce^{3+} ion have too small relative intensities to be distinguished in the 5d-4f luminescence spectrum in the $\text{LiYF}_4:\text{Ce}^{3+}$ crystal: calculated relative intensities of non-polarized electric dipole $5d \rightarrow 4f$ transitions to the seven 4f levels in the order of energy ascending amount 1, 0.06, 0.39, 0.82, 0.3, 0.02 and 0.035 (in arbitrary units). Note that transition to the 7th 4f level, also having small relative intensity, could in principle be resolved in the 5d-4f luminescence spectrum, as it is separated from other transitions in the $5d \rightarrow {}^2F_{7/2}$ band by a significant energy gap (see the next paragraph). It is also interesting to note that according to calculations electric dipole transitions from the lowest 5d level of the Ce^{3+} ion to the 2nd, 4th and 6th 4f levels with emission of π polarized radiation are symmetry forbidden. Therefore measurements of the 5d-4f luminescence spectrum in $\text{LiYF}_4:\text{Ce}^{3+}$ taking into account polarization of emitted light could be useful to verify interpretation given to the fine structure of this spectrum and could deepen our understanding of its nature.

Recently infrared absorption spectrum of the $\text{LiYF}_4:\text{Ce}^{3+}$ crystal corresponding to ${}^2F_{5/2} \rightarrow {}^2F_{7/2}$ intra-4f transitions have been measured at 10 K [16], providing energies of the four excited 4f (${}^2F_{7/2}$) levels: 2216 , 2313 , 2429 and 3158 cm^{-1} . The first two values are in good agreement with the 4th and 5th 4f levels obtained from analysis of the 5d-4f luminescence spectrum in $\text{LiYF}_4:\text{Ce}^{3+}$ as discussed above. The other two values provide the energies of the 6th and 7th 4f levels. Together with the value 514 cm^{-1} of the 3rd 4f level revealed in the present study, this provides us the knowledge of five out of six excited 4f crystal field levels in the $\text{LiYF}_4:\text{Ce}^{3+}$ crystal, with only the first excited 4f energy level left undetermined yet.

In the present study we established the following 4f crystal field parameters used in the calculation of the $\text{LiYF}_4:\text{Ce}^{3+}$ 5d-4f luminescence spectrum shown in Fig. 3: $B_0^2 = 360\text{ cm}^{-1}$, $B_0^4 = -1390\text{ cm}^{-1}$, $B_4^4 = -1250 + i746\text{ cm}^{-1}$, $B_0^6 = -67.2\text{ cm}^{-1}$, $B_4^6 = -1105 + i458\text{ cm}^{-1}$; spin-orbit coupling constant ζ was established as 624 cm^{-1} , close to values 628 cm^{-1} and 626 cm^{-1} given in [4,16], respectively. These Ce^{3+} ion Hamiltonian parameters give correct energies for ZPL 3, ZPL 4 and ZPL 5, that is necessary for comparison with experiment and interpretation in Fig. 3.

A more thorough determination of 4f crystal field parameters in $\text{LiYF}_4:\text{Ce}^{3+}$ demands fitting the total of five known for the present moment values of the excited 4f crystal field energy levels and also g-factor values for the ground 4f Ce^{3+} state reported in [12]: $g_{\parallel} = 2.765$, $g_{\perp} = 1.473$ ([13] gives close values $g_{\parallel} = 2.737$, $g_{\perp} = 1.475$). In [17] we considered the Zeeman energy $H_{Ze} = \mu_B(2S + L)H$, where H is magnetic field, μ_B is the Bohr magneton, S and L are the spin and angular momentum of the 4f electron, and found that no reasonable set of 4f crystal field parameters can precisely fit the two g-factor values given above. For example, g-factors calculated in the present study with the crystal field parameters set given above amount $g_{\parallel} = 2.829$ and $g_{\perp} = 1.557$, the best fit we could achieve. Calculations show [17] that large

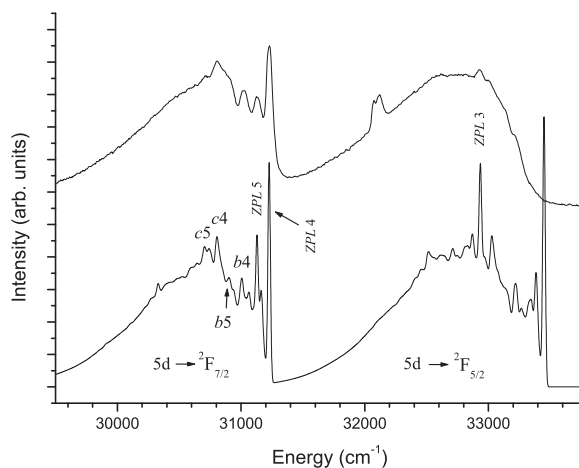


Fig. 4. Calculated for 0 K (lower curve) and measured at 8.5 K [3] (upper curve) 5d-4f luminescence spectra in the $\text{LiYF}_4:\text{Ce}^{3+}$ crystal. For peaks identification notion see text and Fig. 1.

$B_{\pm 4}^6$ values ($|B_{\pm 4}^6| \approx 2000\text{ cm}^{-1}$) could solve the problem – by the way, values of this order were used in the fitting in [16], – but such large values are at least one and a half times greater than seem reasonable. We suggested in [17] that it is necessary to consider reduction of the orbital momentum of the 4f electron in the Zeeman energy due to covalency effects, to achieve agreement with experiment. Let us note, as an argument in favor of considering covalency effects, that the effective ionic radius of the Ce^{3+} ion is the largest for trivalent lanthanide ions, it amounts 1.143 \AA and is bigger than the ionic radius of the Y^{3+} ion (1.019 \AA) [18]. A thorough investigation of possible 4f crystal field parameters $\text{LiYF}_4:\text{Ce}^{3+}$ in the context of experimental g-factor values is planned to be published in future.

In Fig. 4 the calculated non-polarized 5d-4f luminescence spectrum in $\text{LiYF}_4:\text{Ce}^{3+}$ at zero temperature is compared with the spectrum measured with high resolution at 8.5 K in [3]. The widths of calculated $5d \rightarrow {}^2F_{5/2}$ and $5d \rightarrow {}^2F_{7/2}$ bands are in good agreement with experiment. Fine structure is not pronounced well in the measured spectrum for the $5d \rightarrow {}^2F_{5/2}$ band, supposedly due to reabsorption of emitting radiation [3]. As follows from calculations, the only well pronounced peak in this band should be ascribed to ZPL 3; weakly pronounced 'b1', 'm1' and 'c1' vibrational maxima can also, in principle, be distinguished in the measured spectrum but were not marked in Fig. 4. The maximum near 32100 cm^{-1} in the experimental spectrum in Fig. 4 is due to emission of spurious traces of Gd^{3+} ions in the crystal [3]. As for the band corresponding to $5d \rightarrow {}^2F_{7/2}$ transitions in the Ce^{3+} ion, the calculated fine structure of the band is in good agreement with the measurements results. Two peaks in the measured spectrum are assigned as ZPL 4 and ZPL 5, and four peaks in the measured spectrum are interpreted as vibrational maxima 'b4', 'b5', 'c4' and 'c5'. For comparison, in [3] the same interpretation was given to ZPL 4 and ZPL 5, but the vibrational maxima 'b4' and 'c4' (see Fig. 4) were interpreted as ZPL 6 and ZPL 7, correspondingly ('b5' and 'c5' maxima were not interpreted in [3]). In sum, comparison of microscopic modeling of vibrational structure with experiment [3] confirms the determination of energies of the three excited 4f crystal field levels 514 cm^{-1} (3rd 4f level), 2221 cm^{-1} (4th level) and 2316 cm^{-1} (5th level) with respect to the ground 4f level.

3.2. Spectra of $\text{LiLuF}_4:\text{Ce}^{3+}$ crystal

In Fig. 5 the simulated non-polarized 5d-4f luminescence spectrum in $\text{LiLuF}_4:\text{Ce}^{3+}$ at zero temperature is compared with the spectrum measured with high resolution at 10.4 K in [3] (let us note that no high resolution measurements of the low-temperature 4f-5d absorption or excitation spectra in the $\text{LiLuF}_4:\text{Ce}^{3+}$ crystal are available in literature, that would resolve the vibrational structure in the band corresponding

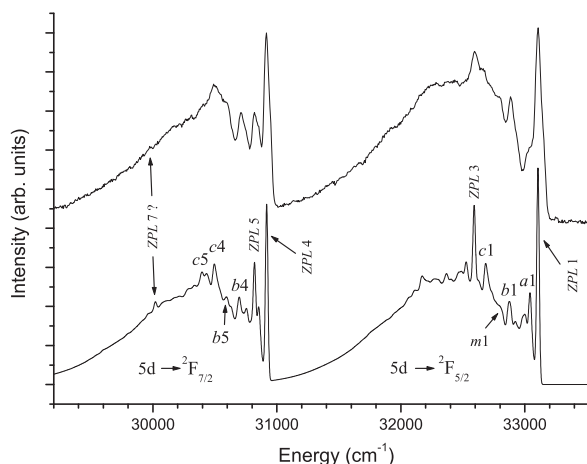


Fig. 5. Calculated for 0 K (lower curve) and measured at 10.4 K [3] (upper curve) 5d-4f luminescence spectra in the LiLuF₄:Ce³⁺ crystal. For peaks identification notion see text and Fig. 1.

to a transition to the lowest 5d state). The simulated spectrum was obtained from the calculated 5d-4f luminescence spectrum in LiYF₄:Ce³⁺ at zero temperature (see Fig. 4) by shifting the onsets of the 5d→²F_{5/2} and 5d→²F_{7/2} bands to energies 33,106 cm⁻¹ and 30,918 cm⁻¹, correspondingly. This means that the gap between the 5d→²F_{5/2} and 5d→²F_{7/2} bands is reduced by 33 cm⁻¹ as compared to LiYF₄:Ce³⁺. As seen in Fig. 5, the calculated electron-vibrational 5d-4f luminescence spectrum is in good agreement with the measurements results. In the 5d→²F_{5/2} band two peaks in the measured spectrum are assigned as ZPL 1 and ZPL 3, while four peaks in the measured spectrum are assigned as vibrational maxima ‘a1’, ‘b1’, ‘m1’ and ‘c1’ (compare with Fig. 3). In [3] the same interpretation was given to the mentioned ZPLs, but the vibrational maximum ‘b1’ was interpreted as ZPL 2 (‘a1’, ‘m1’, ‘c1’ maxima were not interpreted in [3]). In the 5d→²F_{7/2} band in Fig. 5 two peaks in the measured spectrum are assigned as ZPL 4 and ZPL 5 and four peaks in the measured spectrum are interpreted as vibrational maxima ‘b4’, ‘b5’, ‘c4’ and ‘c5’ (compare with Figs. 3 and 4). In [3] the vibrational maxima ‘b4’ and ‘c4’ were interpreted as ZPL 6 and ZPL 7, correspondingly (‘b5’ and ‘c5’ maxima were not interpreted in [3]). The widths of calculated 5d→²F_{5/2} and 5d→²F_{7/2} bands are also in good agreement with experiment.

A weakly pronounced peak at 29972 cm⁻¹ is observed in the measured 5d-4f luminescence spectrum in LiLuF₄:Ce³⁺ [3] - see Fig. 5. Perhaps the measured peak should be ascribed to ZPL 7, thus providing the energy for the 7th 4f crystal field level 3134 cm⁻¹ with respect to the ground 4f level; in the previous section we stressed that despite having small relative intensity transition to this 4f level could in principle be resolved in the 5d-4f luminescence spectrum, as it is resolved in the calculated spectrum as seen in Fig. 5. Another argument for this peak identification as ZPL 7 is that the energy of the 7th 4f crystal field level in LiYF₄:Ce³⁺ measured in [16] equals 3158 cm⁻¹, and decreasing this quantity by 33 cm⁻¹ (the reduction value for the gap between 5d→²F_{5/2} and 5d→²F_{7/2} bands in LiLuF₄:Ce³⁺ as compared to LiYF₄:Ce³⁺) we obtain the energy 3125 cm⁻¹, close to the energy 3134 cm⁻¹, with respect to the ground 4f level, of the measured peak.

The following conclusions can be made on the basis of calculated and measured 5d-4f luminescence spectra comparison in Fig. 5.

1) Fine structure in the 5d-4f luminescence spectra in the LiYF₄:Ce³⁺ and LiLuF₄:Ce³⁺ crystals is almost identical (see also Fig. 3, Fig. 4), indicating that the same vibrational modes are involved in electron-phonon interaction for the lowest 5d state in the Ce³⁺ ion in these crystals (most notably, ‘a’, ‘b’ and ‘c’ modes - see Fig. 1), and that the phonon spectrum is very similar for these host crystal lattices. Though the Lu³⁺ ions are heavier than the Y³⁺ ions, this change of

the ion mass and the corresponding diminishing of the phonon frequencies is thought to be compensated by increase of lattice force constants.

2) In analogy with the analysis for the LiYF₄:Ce³⁺ crystal fulfilled in Section 3.1, we can conclude that microscopic modeling of vibrational structure in the 5d-4f luminescence spectrum in the LiLuF₄:Ce³⁺ crystal allows identifying peaks in the spectrum measured in [3] and determining energies of the excited 4f crystal field levels (with respect to the ground 4f level): 514 cm⁻¹ (3rd 4f level), 2188 cm⁻¹ (4th level), 2283 cm⁻¹ (5th level) and, possibly, 3134 cm⁻¹ (7th level). Fitting of 4f crystal field parameters for the Ce³⁺ ion in LiLuF₄ to satisfy the established values of the excited 4f energy levels and g-factor values for the ground 4f Ce³⁺ state in LiLuF₄ reported in [13] remains a task for future investigations.

3.3. Spectra of LiREF₄:Ce³⁺, LiREF₄, LiYF₄:RE³⁺ crystals

We compared the calculated 5d-4f luminescence spectrum in LiYF₄:Ce³⁺ at zero temperature with the 5d-4f luminescence spectrum in Ce³⁺ ions in the LiYbF₄ crystal measured at 4.2 K in [19]. The widths of calculated 5d→²F_{5/2} and 5d→²F_{7/2} bands are in good agreement with experiment; to fulfill the spectra comparison we shifted the calculated spectrum as a whole to lower energies by ~190 cm⁻¹, but the gap between these two bands was not changed. Let us remind that this gap needed to be reduced by 33 cm⁻¹ for the LiLuF₄:Ce³⁺; however, we must mention that spectral resolution in [19] was rather weak, resulting in significant uncertainty in energies (this is the reason why we do not reproduce the figure here). Fine structure is not pronounced well in the measured spectrum for the 5d→²F_{5/2} band due to reabsorption of emitting radiation [19]. However the onset of the spectrum seems to be distinguished and provides the energy of ZPL 1 in this spectrum: 33260 cm⁻¹. As follows from calculations, the only other well pronounced peak in this band should be ascribed to ‘b1’ vibrational maximum. As for the band, corresponding to 5d→²F_{7/2} transitions in the Ce³⁺ ion in LiYbF₄, the calculated fine structure is in good agreement with the measurements results. Two peaks in the measured spectrum are assigned as ZPL 4 and ZPL 5, and three peaks in the measured spectrum are interpreted as vibrational maxima ‘b4’, ‘b5’ and ‘c4’ (compare with Fig. 4). However, no exact 4f crystal field energies for this compound can be figured out for the reasons discussed above.

In [19] a 4f-5d absorption spectrum in the LiYbF₄:Ce³⁺ crystal at 4.2 K was also measured and fine structure was resolved in the band corresponding to transition to the lowest 5d state of the Ce³⁺ ion. We compared it with the calculated vibrational structure of such band in the LiYF₄:Ce³⁺ crystal (see Fig. 1). Three of the maxima in the fine structure of the measured spectrum coincide with the calculated vibrational maxima ‘a’, ‘b’ and ‘c’. Another maximum coincides with the calculated ‘p’ maximum (see Fig. 1), though its intensity in the measured spectrum is significantly higher than in the calculated one. One more maximum - let us denote it as ‘q’ - is observed in experiment, it is shifted from the ZPL 1 by nearly 335 cm⁻¹. No pronounced peak at this energy is found in the calculated spectrum in Fig. 1, so interpretation of ‘q’ peak remains open. If this peak is due to some unaccounted (for example, local) vibrational mode, it should appear in the luminescence spectrum in this compound as well. But simple calculations show that ‘q4’ and ‘q5’ vibrational maxima, that should in this case be present in the 5d→²F_{7/2} band in the 5d-4f luminescence spectrum in LiYbF₄:Ce³⁺, have energies very close to the ‘b5’ and ‘c4’ vibrational maxima mentioned above and therefore cannot be independently observed. On the other hand, superposition of one-phonon peaks ‘q+q’ in the two-phonon envelope in the absorption spectrum could be the reason of experimentally observed high intensity of the closely located ‘p’ maximum discussed earlier.

We also made an attempt to compare the calculated vibrational structure of a band, corresponding to a 4f-5d transition involving the lowest 5d state of the Ce³⁺ ion in the LiYF₄ crystal (see Fig. 1), with

experimental results for some other double fluorides crystals with sheelite structure, for which either only data on absorption (excitation) spectrum is available or $4f^n - 4f^{n-1}5d$ transitions take place in a RE ion other than Ce^{3+} .

The $4f^6 5d-4f^7$ emission spectra in the $LiYF_4:Gd^{3+}$ and $LiGdF_4$ crystals were measured in [15] at 10 K; they have the onsets at 79280 cm^{-1} and 79380 cm^{-1} , correspondingly. Similar fine structure is observed in these spectra. Three of the maxima in this fine structure are shifted from the onset by energies close to the calculated energies of 'a', 'b' and 'c' vibrational maxima in Fig. 1. Two more maxima in this fine structure are shifted from the onset by energies of nearly 160 cm^{-1} and 310 cm^{-1} , the latter maximum having the biggest intensity in the whole emission band. To interpret these two peaks correctly one needs to fulfill the modeling of low-temperature emission spectra corresponding to $4f^6 5d-4f^7$ transitions in the Gd^{3+} ions in these compounds.

We compared the $4f-5d$ excitation spectrum in the $LiGdF_4:Ce^{3+}$ crystal corresponding to a transition involving the lowest $5d$ state of the Ce^{3+} ion, that was measured with high resolution at 10 K in [15], with the calculated vibrational structure of a band, corresponding to a $4f-5d$ transition involving the lowest $5d$ state of the Ce^{3+} ion in the $LiYF_4$ crystal (see Fig. 1). Much similarity was revealed again in vibrational structure of the calculated and measured bands. Six peaks in the measured spectrum coincide with the calculated vibrational maxima 'a', 'b', 'm', 'c', 'n' and 'p' (see Fig. 1). One more maximum observed in experiment is shifted from the spectrum onset (a ZPL) by nearly 330 cm^{-1} and is very similar to the 'q' maximum found in the $4f-5d$ absorption spectrum in the $LiYbF_4:Ce^{3+}$ crystal measured in [19] (see above).

Overall, we may conclude that electron-vibrational spectra of RE ions in double fluorides crystals with sheelite structure, corresponding to interconfigurational $4f^n - 4f^{n-1}5d$ transitions involving the lowest state of the excited configuration of the RE ion, have similar vibrational structure, with the most common features defining spectral lineshapes being the vibrational maxima that we denoted as 'a', 'b' and 'c' in Fig. 1. However, appearance of a vibrational maximum irreproducible by calculations (a maximum denoted as 'q', with the energy of nearly 330 cm^{-1} with respect to corresponding ZPL) in experimental spectra in several crystals with heavy RE ions in host lattice remains a problem for further analysis.

4. Conclusions

Microscopic modeling of electron-vibrational interconfigurational $4f^n - 4f^{n-1}5d$ spectra in dielectric crystals doped with RE ions proved to be an effective tool for spectra analysis and interpretation that is necessary for prediction of characteristics of crystals used in contemporary quantum technologies. In the present theoretical study good agreement between the calculated low-temperature $5d-4f$ luminescence spectra in the $LiYF_4:Ce^{3+}$ and $LiLuF_4:Ce^{3+}$ crystals and experimental results available in literature was achieved, supporting the developed model of electron-phonon interaction based on the exchange charge model of crystal field. Calculations showed that three vibrational peaks with the energies 65 cm^{-1} , 223 cm^{-1} and 420 cm^{-1} with respect to zero-phonon transition energy dominate in the vibrational structure in these luminescence spectra. Comparison of simulation results with the experimentally observed spectral envelopes allowed distinguishing

zero-phonon lines from vibrational maxima in the latter and, consequently, determining several of the $4f$ electron energy levels for the impurity Ce^{3+} ion. Thereby, a new method of determination of crystal field energy values for the $4f$ electron in Ce^{3+} ion in $LiYF_4$ and in $LiReF_4$ crystals, which are not available otherwise, was proposed. Comparison with experimental data for several other double fluorides crystals with sheelite structure revealed general similarity in electron-phonon interaction for the lowest state of the excited configuration of the RE ion in these crystals.

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