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Modeling and decoding of fine structure of electron-vibrational 5d – 4f luminescence spectra in $LiRF_4:Ce^{3+}$ (R = Y, Lu) crystals

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ABSTRACT

The 5d-4f luminescence spectra in the $LiYF_4:Ce^{3+}$, $LiLuF_4:Ce^{3+}$ 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 $LiYF_4:Ce^{3+}$ and 514, 2188, 2283 and, possibly, 3134 cm^{-1} for $LiLuF_4:Ce^{3+}$ 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 $LiYF_4:Ce^{3+}$ crystal at low temperatures (and also in the $LiLuF_4:Ce^{3+}$ 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 $Y_3Al_5O_{12}$ [5] and $Na_3LuSi_2O_7$, $NaSr_4(BO_3)_3$ 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 $LiYF_4:Ce^{3+}$ 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 $LiLuF_4:Ce^{3+}$ 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 $LiYF_4:Ce^{3+}$, 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]

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

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 $\boldsymbol{C}^{(p)}$. 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 ζ(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 $LiYF_4:Ce^{3+}$ 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 forth 5d levels: 760 cm^{-1} versus experimentally observed ~1900 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 $LiYF_4:Ce^{3+}$ 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 $LiYF_4:Ce^{3+}$ 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 $LiYF_4:Ce^{3+}$, 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 $LiYF_4:Ce^{3+}$ 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 $LiYF_4:Ce^{3+}$. For details of simulation of the 5d-4f luminescence spectrum in the $LiLuF_4:Ce^{3+}$ crystal – see Section 3.2.

3. Results and discussion

3.1. Spectra of $LiYF_4:Ce^{3+}$ crystal

Let us consider in details the calculated vibrational structure of a band, corresponding to a 4f-5d transition in $LiYF_4:Ce^{3+}$ 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