Vacuum-ultraviolet 5d-4f luminescence of Gd\textsuperscript{3+} and Lu\textsuperscript{3+} ions in fluoride matrices

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The VUV 4f\textsuperscript{n-15}d-4f\textsuperscript{n} luminescence and luminescence excitation spectra of Gd\textsuperscript{3+} (n=7) in LiGdF\textsubscript{4}, GdF\textsubscript{3}, LiYGdF\textsubscript{4}, Gd\textsubscript{3+}, and YF\textsubscript{3}; Gd\textsuperscript{3+}, and of Lu\textsuperscript{3+} (n=14) in LiLuF\textsubscript{4}, LuF\textsubscript{3}, and LiYGdF\textsubscript{4}; Lu\textsuperscript{3+} have been analyzed with high spectral resolution. In systems with intermediate electron-phonon coupling, zero-phonon lines, and phonon sidebands were observed. The excitation spectra of dilit systems exhibit rich fine structure originating from electronic origins of transitions and their phonon replica. Theoretical calculations explicitly taking into account a microscopic model of the crystal field and the crystal lattice vibrational spectra agree well with experimental data and are the basis for a safe analysis of the spectra.

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I. INTRODUCTION

Experiments on interconfigurational 4f\textsuperscript{n-4f\textsuperscript{n-15}d spectra of rare earth (RE) ions in large band gap matrices got started with the pioneering works of Feofilov\cite{feofilov} and Kaplyanskii and Feofilov\cite{kaplyanskii} on the spectra of impurity divalent RE ions in alkaline-earth halides, as well as of Kaplyanskii et al.\cite{kaplyanskii} on the spectra of trivalent cerium in alkaline-earth fluorides. In 1966, 4f\textsuperscript{n-15}d transitions of almost all trivalent RE ions (except Pm\textsuperscript{3+}, Gd\textsuperscript{3+}, and Lu\textsuperscript{3+}) in a CaF\textsubscript{2} matrix were reported by Loh.\cite{loh} Except from Ce\textsuperscript{3+} and Pr\textsuperscript{3+}, the transition energies are in the vacuum ultraviolet (VUV) spectral range where synchrotron radiation (SR) is the most powerful tool for spectroscopic purposes.\textsuperscript{5,6} VUV SR was applied for the first time to the studies of RE\textsuperscript{3+} 4f\textsuperscript{n-4f\textsuperscript{n-15}d excitations by Elias et al.\cite{elias} and Heaps et al.\textsuperscript{8}}

In the pioneering work of Yang and DeLuca,\textsuperscript{9} it was found that Nd\textsuperscript{3+}, Er\textsuperscript{3+}, and Tm\textsuperscript{3+}, doped into fluorides, emit luminescence in the VUV spectral range, originating from 4f\textsuperscript{n-15}d-4f\textsuperscript{n} radiative transitions (so-called 5d-4f luminescence). For the first half of the lanthanide series, transitions from the lowest 4f\textsuperscript{n-15}d level into the 4f\textsuperscript{n} ground state are spin-allowed with short lifetimes (up to \(\tau=50\) ns). In the second half, such transitions are spin-forbidden (lifetimes in the \(\mu s\) range) because the spin of the lowest 4f\textsuperscript{n-15}d state (so-called high-spin state) exceeds the spin of the ground 4f\textsuperscript{n} configuration. However, depending on the ion and the host, spin-allowed emission from the higher-lying low-spin 4f\textsuperscript{n-15}d state (with the same value of spin as in the ground 4f\textsuperscript{n} state) can be also observed.\textsuperscript{10,11}

Up to recently, RE\textsuperscript{3+} luminescence in VUV has been detected only from Nd\textsuperscript{3+}, Er\textsuperscript{3+}, and Tm\textsuperscript{3+}. However, our studies\textsuperscript{12-14} have shown that VUV 5d-4f luminescence (\(h\nu\sim 10\) eV) is also observed from Gd\textsuperscript{3+} and Lu\textsuperscript{3+} ions doped into some fluoride hosts with sufficiently wide energy band gaps. The observation of 5d-4f luminescence from the Gd\textsuperscript{3+} ion is rather unexpected because of the considerable number of closely spaced 4f\textsuperscript{7} levels in the same energy region as the 4f\textsuperscript{6}d\textsuperscript{7} states,\textsuperscript{15} potentially enabling nonradiative relaxation from the lowest Gd\textsuperscript{3+} 4f\textsuperscript{6}d\textsuperscript{7} level to lower-lying 4f\textsuperscript{5}d\textsuperscript{7} levels. However, at low temperatures a rather intense VUV luminescence has been detected from several materials containing Gd\textsuperscript{3+} ions. The situation is different for the Lu\textsuperscript{3+} ion, which has only a single \(1\)\(S_0\) level of the ground 4f\textsuperscript{14} electronic configuration. The reason why Lu\textsuperscript{3+} 5d-4f luminescence has never been detected earlier may arise from the fact that the corresponding photon energy is the highest among all RE\textsuperscript{3+} ions.

In the present paper, the results of a detailed investigation and characterization of VUV luminescence due to interconfigurational 5d-4f transitions in Gd\textsuperscript{3+} and Lu\textsuperscript{3+} ions in several fluorides are presented. In particular, results from stoichiometric Gd\textsuperscript{3+}- and Lu\textsuperscript{3+} fluorides (GdF\textsubscript{3}, LuF\textsubscript{3}, LiGdF\textsubscript{4}, and LiLuF\textsubscript{4}) are compared with results from Gd\textsuperscript{3+} and Lu\textsuperscript{3+} doped fluorides (LiYGdF\textsubscript{4}; Gd\textsuperscript{3+}, YF\textsubscript{3}; Gd\textsuperscript{3+}, LiYGdF\textsubscript{4}; Lu\textsuperscript{3+}). Besides high-resolution luminescence spectra, allowing for an analysis of electron-phonon coupling, high-resolution excitation spectra have been measured as well. For comparison purposes, the Ce\textsuperscript{3+} ion with its simple electronic configuration in the LiYGdF\textsubscript{4} host has been included into our investigation. The phonon sidebands of the Ce\textsuperscript{3+} 5d-4f transitions yield great similarities with those of the Gd\textsuperscript{3+} ion, indicating that the details of the coupling of the 4f\textsuperscript{n-15}d configuration to the matrix mainly depend on the matrix and only to a minor extent to the ion incorporated.

A comparison of experimental spectra with results of simulations performed for LiYGdF\textsubscript{4} doped with Ce\textsuperscript{3+} and Lu\textsuperscript{3+} ions will also be presented. The spectral envelopes were obtained in the framework of the exchange charge model of the ion-lattice interaction by making use of the spectral densities of correlation functions for the relative displacements of the impurity ion and its nearest ligands (eight fluorine ions),
II. EXPERIMENTAL DETAILS

The measurements were performed at the SUPERLUMI station of HASYLAB at DESY, using SR from the DORIS storage ring\textsuperscript{16} for excitation. High-resolution VUV emission spectra were recorded with a 1-meter VUV monochromator and an open position-sensitive microchannel-plate (MCP) detector coated with CsI, at resolution intervals as small as 0.5 Å in second order.\textsuperscript{17} The spectra were not corrected for the spectral response of the detection system. However, taking into account that the measured spectra cover usually a rather narrow spectral region and that the spectral sensitivity is smooth in the spectral range of interest, we believe that such correction will not result in any remarkable changes in the shape of the spectra. The excitation spectra of VUV emission and decay curves were recorded with a Pouey-type monochromator (typical spectral resolution interval $\Delta \lambda = 20$ Å) equipped with a CsI sensitized microsphere-plate detector. By applying deconvolution techniques, a time resolution of the detection system better than 0.1 ns was achieved.

During the present work, the VUV monochromator has been recalibrated by atomic lines. Compared to earlier experiments,\textsuperscript{12,13} the absolute wavelength calibration was improved from ±0.2 Å to ±0.1 Å (corresponding to ±7 cm\textsuperscript{-1} at 82000 cm\textsuperscript{-1}). The relative accuracy of luminescence and excitation spectra is approximately the same because scattered light from the primary monochromator has been used for calibration of the secondary monochromators.

Single crystals of nominally pure LiGdF\textsubscript{4}, LiGdF\textsubscript{4} doped with 0.05 at. % Ce\textsuperscript{3+}, LiYF\textsubscript{4} doped with 0.5 and 2.0 at. % Gd\textsuperscript{3+}, nominally pure LiLuF\textsubscript{4}, LiYF\textsubscript{4} doped with 0.5, 1.0, and 5.0 at. % Lu\textsuperscript{3+}, LiLuF\textsubscript{4} and LuF\textsubscript{3}, both doped with 0.1 at. % Ce\textsuperscript{3+}, were grown by the Czochralski and Bridge- man methods.\textsuperscript{18,19} Powder samples of LiYF\textsubscript{4} doped with 1.0 and 10.0 at. % Gd\textsuperscript{3+}, and YF\textsubscript{3} doped with 1.0 at. % Gd\textsuperscript{3+}, were obtained by the high temperature diffusion technique. GdF\textsubscript{3} and LuF\textsubscript{3} powder samples were high-purity chemicals with a concentration of unintentional RE and other metals of 0.0005–0.001 %, and an oxygen concentration of 0.02–0.05 %. The crystalline samples were cleaved prior to mounting on the sample holder attached to a flow-type liquid helium cryostat. All measurements have been performed in an UHV environment.

As it was mentioned above, Gd\textsuperscript{3+} 5d–4f luminescence was unexpected due to the fact that the 4f\textsuperscript{2} energy levels are very dense at high energies. Accordingly, it was supposed that radiative 5d–4f transitions in Gd\textsuperscript{3+} would be quenched due to energy transfer from d to f excitations and subsequent nonradiative relaxation into the lower f levels of Gd\textsuperscript{3+} from where emission takes place. Indeed, under VUV excitation, Gd\textsuperscript{3+}–f lines in the UV, visible, and IR are observed in the emission spectra of Gd\textsuperscript{3+}-containing compounds (Fig. 1). In particular, the most intense line near 311 nm is due to transitions from the lowest excited 5d\textsuperscript{3} G\textsubscript{7/2} ground state. The orange (590–640 nm) and IR (720–810 nm) luminescence, which are due to 4f\textsuperscript{2} 6G\textsubscript{7/2}–6P\textsubscript{J} and 6G\textsubscript{7/2}–6I\textsubscript{J} transitions in Gd\textsuperscript{3+}, are also observed under excitation to high energy levels of Gd\textsuperscript{3+}. However, at low temperature, VUV luminescence around 10 eV has been detected as well from several gadolinium fluoride crystals.\textsuperscript{12–14} The energy level scheme and the main radiative and nonradiative transitions for the Gd\textsuperscript{3+} ion in some wide band gap (fluoride) hosts are shown in Fig. 2 (the energies of Gd\textsuperscript{3+} 4f\textsuperscript{2} levels were taken from Ref. 21).

The VUV emission spectrum from the LiGdF\textsubscript{4} crystal (Fig. 3) has a well-resolved fine structure which shows at least seven lines spread over ~500 cm\textsuperscript{-1}, extending into a wide sideband centered at ~78 900 cm\textsuperscript{-1}. The shortest-wavelength line at ~79 385 cm\textsuperscript{-1} has varying intensity for different excitation energies because of reabsorption which changes depending on the penetration depth of the exciting radiation. The spectra are similar for undoped and Ce\textsuperscript{3+}...
doped samples. The VUV emission from crystalline LiYF₄:Gd³⁺/H₂O₈4.90.5%/H₂O₈5.0% has nearly the same shape as that from the LiGdF₄ crystal but is slightly shifted to lower energies (by ~110 cm⁻¹). The spectra from LiYF₄:Gd³⁺ powder samples show only one pronounced line at ~79 220 cm⁻¹ and a wide sideband centered at ~78 900 cm⁻¹. The VUV emission spectra of GdF₃ and YF₃:Gd³⁺ are situated at higher photon energies and show single structureless bands centered at ~80 000 cm⁻¹ and ~79 700 cm⁻¹, respectively. The decay times of VUV luminescence from all Gd³⁺-containing samples are in the nanosecond range. At T =10 K, the following decay times were measured: 2.8 ns for LiGdF₄, 2.5 ns for LiYF₄:Gd³⁺, 0.97 ns for GdF₃, and 1.1 ns for YF₃:Gd³⁺.

VUV luminescence from all Gd³⁺ compounds was observed only at low temperatures. As an example, in Fig. 4 the temperature dependence of the GdF₃ emission is shown. This dependence was approximated by the Mott formula, I(T)/I(0)=[1+A exp(-εₐ/kₐT)]⁻¹ (shown in the inset of Fig. 4). An activation energy εₐ ~400 cm⁻¹ for thermal quenching was obtained from the fit. Around 200 K, the VUV luminescence is quenched completely. For LiYF₄:Gd³⁺, εₐ ~530 cm⁻¹ and 620 cm⁻¹ for 10% and 1% doping concentrations were obtained. The values of εₐ are close to “characteristic” phonon energies of fluoride crystals, showing that the mechanism of thermal quenching can be treated as some kind of phonon-assisted nonradiative relaxation.

![FIG. 2](image-url) Energy level pattern illustrating Gd³⁺ excitation by VUV radiation (bold solid arrow), relaxation (dotted arrows), and observed luminescence (thin solid arrows) in a wide band-gap fluoride matrix. The shaded area covers a range with many closely-spaced f levels, which cannot be distinguished in this scale.

![FIG. 3](image-url) High-resolution VUV emission spectra (Δλ=0.8 Å) of LiGdF₄ and LiYF₄:Gd³⁺(0.5%) single crystals, and of LiYF₄:Gd³⁺(1%), GdF₃ and YF₃:Gd³⁺(1%) powder samples. The excitation energies are given in the figure. T=10 K.

The excitation spectrum of VUV emission from LiGdF₄ single crystal has a well-pronounced onset at 79 000 cm⁻¹, overlapping with the shortest-wavelength line of the emission spectrum (Fig. 5). Hence, VUV luminescence is clearly correlated to the threshold of Gd³⁺ 4f⁻¹ → 4f⁻⁶⁵d excitation. Excitation spectra of UV/visible luminescence from LiGdF₄ have rather rich fine structure. Their onsets are slightly above the onset of the VUV emission (UV/visible luminescence is also observed under direct f⁻f excitation, however, the signal is too weak to be observed with SR.). Excitation spectra of different Gd³⁺ emissions from LiYF₄:Gd³⁺(10%) (powder sample) have no pronounced fine structure but show a distinct threshold. Excitation spectra of all kinds of Gd³⁺ luminescence from LiYF₄ (both powder and crystalline samples) weakly (0.5, 1, 2 %) doped with Gd³⁺ have identical thresholds and the same shape at least in the range 79 000–86 000 cm⁻¹ where the fine structure is clearly observed in all these spectra. The fine structure is most pro-
RE3+ and Ce 3+ ions. The basis of this approximation is the extensively studied in many matrices. According to Ref. 23, KIRM et al. estimate the energy of the lowest 4f transition in the free Ce 3+ ion, equal to 45 800 cm−1 for the compound GdF3 have slightly different thresholds and shapes but all spectra lack fine structure. Excitation spectra of VUV and visible thresholds, whereas the excitation spectrum of UV (311 nm) luminescence from this material shows slightly different shape (Fig. 6).

2. Assignment of VUV luminescence to 5d-4f radiative transitions in Gd3+

The methodology proposed by Dorenbos23 allows us to estimate the energy of the lowest 4f-5d transition in the RE3+ ion doped into a particular host if the value of this energy is known for any other RE3+ ion, e.g., for Ce3+, which has been extensively studied in many matrices. According to Ref. 23, the energy for the lowest spin-allowed 4f-5d transition in a RE3+ ion is given by

$$ E_{\text{RE}^{3+}} = 49340 \text{ cm}^{-1} - D(A) + \Delta E_{\text{RE} \text{ Ce}} $$

where 49 340 cm−1 is the energy of the lowest 4f-5d transition in the free Ce3+ ion, D(A) is the crystal field depression energy for the compound A, and $$\Delta E_{\text{RE} \text{ Ce}}$$ is the energy difference between the first spin-allowed 4f-5d transition in the RE3+ and Ce3+ ions. The basis of this approximation is the fact that the crystal field depression is not sensitive to the individual ion, D(A) being an average of the D(RE3+,A) values for different RE3+ ions. In this approximation, the quantity $$\Delta E_{\text{RE} \text{ Ce}}$$ is independent from the host and can be regarded as an intrinsic property of the respective ion, being equal to 45 800 cm−1 for $$\Delta E_{\text{Ce} \text{ Ce}}$$.

The smooth-shaped excitation spectra of VUV luminescence from GdF3 and YF3:Gd3+ have their thresholds near 83 000 cm−1 from GdF3. In the inset, the integrated intensity of the emission is plotted as a function of temperature, together with the simulation curve obtained as the best fit with the Mott formula.

FIG. 4. Temperature dependence of the VUV luminescence from GdF3. In the inset, the integrated intensity of the emission is plotted as a function of temperature, together with the simulation curve obtained as the best fit with the Mott formula.

FIG. 5. High-resolution excitation spectrum (Δλ=0.8 Å) of the Gd3+ 5d-4f emission from LiGdF4 (crystal), measured at 127 nm (78 740 cm−1), together with the respective high-resolution emission spectrum excited by 119 nm photons (upper part of the figure). All other curves are high-resolution excitation spectra of the Gd3+ 6G7/2→6P7/2 emission at 593 nm from LiGdF4 (crystal), from LiYF4:Gd3+(10%) and LiYF4:Gd3+(1%) (powder samples). T=10 K. The energy levels of the Eu3+ $F_{d0}$ multiplet in LiYF4 (Ref. 22) are added for comparison (see text for details).

From the excitation spectrum of LiGdF4 doped with 0.05% Ce3+, the ZPL energy of the lowest Ce3+ 4f-5d transition in LiGdF4 (Fig. 7) was determined (33 615 cm−1). The
estimated energy of the ZPL of the lowest Gd\textsuperscript{3+} 4f\textsuperscript{7-4f}\textsuperscript{6} transition then is 79 415 cm\textsuperscript{-1}, which is close to the threshold of the excitation spectrum of LiGdF\textsubscript{4} VUV emission as well as to the energy of the shortest-wavelength emission line from this crystal /H20849 79 385 cm\textsuperscript{-1}/H20850. Similar estimates for LiYF\textsubscript{4}:Gd\textsuperscript{3+} yield 79 250 cm\textsuperscript{-1} for the ZPL of the lowest Gd\textsuperscript{3+} 4f\textsuperscript{7-4f}\textsuperscript{6} transition, taking 33 450 cm\textsuperscript{-1} for the ZPL of the lowest 4f\textsuperscript{5-5d} transition of Ce\textsuperscript{3+} in LiYF\textsubscript{4}:Ce\textsuperscript{3+}.24 The estimate agrees well with experiment /H20849 79 278 cm\textsuperscript{-1}/H20850.

For GdF\textsubscript{3} and YF\textsubscript{3}:Gd\textsuperscript{3+}, Eq. (1) can be applied directly. The depression energies of GdF\textsubscript{3} and YF\textsubscript{3} are 10 878 cm\textsuperscript{-1} and 9915 cm\textsuperscript{-1}, respectively.23 From Eq. (1), the lowest Gd\textsuperscript{3+} 4f\textsuperscript{5-5d} transition energies are 84 262 cm\textsuperscript{-1} for GdF\textsubscript{3} and 85 225 cm\textsuperscript{-1} for YF\textsubscript{3}:Gd\textsuperscript{3+} result from an overlap of transitions to various sublevels of the first crystal field 5d component, a comparison with the estimates will be misleading. However, the estimates may be better compared with the maxima in the VUV emission spectra, taking into account the Stokes shifts \Delta S for these compounds given in Ref. 23. 5567 cm\textsuperscript{-1} for GdF\textsubscript{3} and 5444 cm\textsuperscript{-1} for YF\textsubscript{3}. The estimated maxima of Gd\textsuperscript{3+} 5d-4f emission in GdF\textsubscript{3} and YF\textsubscript{3}:Gd\textsuperscript{3+} are 78 695 and 79 781 cm\textsuperscript{-1}. For YF\textsubscript{3}:Gd\textsuperscript{3+} the estimate agrees well with the experimental value (79 700 cm\textsuperscript{-1}). For GdF\textsubscript{3}, the experimental value (80 000 cm\textsuperscript{-1}) exceeds the estimate considerably. Note, however, the energy parameters for Gd\textsuperscript{3+} 4f\textsuperscript{5-5d} transitions in GdF\textsubscript{3} given in Ref. 23 were obtained using data from a single paper and may therefore be less accurate than the parameters of YF\textsubscript{3}:Gd\textsuperscript{3+}, resulting in less reliable estimates.

Referring to the good agreement between theoretical estimates and experimental transition energies, the VUV luminescence observed is ascribed to Gd\textsuperscript{3+} transitions from the lowest 4f\textsuperscript{6} 5d level to the 4f\textsuperscript{7} 8S\textsubscript{7/2} ground state. The assignment is supported by the following arguments. The VUV luminescence is observed in stoichiometric and weakly doped compounds, excluding an excitonic nature, which would be an alternative explanation. The decay time of a few nanoseconds is expected for the 4f\textsuperscript{5-5d} radiative transitions in Gd\textsuperscript{3+}, which are spin-allowed because the lowest Gd\textsuperscript{3+} 4f\textsuperscript{5-5d} level has the same spin as the ground state. Only one fast transition originating from the lowest 4f\textsuperscript{5-5d} level to the ground state is observed because of the absence of spin-orbit splitting for the 8S\textsubscript{7/2} ground term of Gd\textsuperscript{3+}. Transitions from the lowest 4f\textsuperscript{5-5d} level to excited 4f\textsuperscript{7} levels are spin- and parity forbidden, i.e., the corresponding luminescence should be extremely weak. The crystal-field splitting of Gd\textsuperscript{3+} 5d level in GdF\textsubscript{3} is expected to be smaller than in LiGdF\textsubscript{4} because of the higher coordination number for Gd\textsuperscript{3+}.

FIG. 6. Excitation spectra (\Delta \lambda =3 Å) of Gd\textsuperscript{3+} 5d-4f, 6p\textsubscript{7/2} - 6S\textsubscript{7/2} and 6G\textsubscript{7/2} - 6P\textsubscript{7/2} emissions from GdF\textsubscript{3} and YF\textsubscript{3}:Gd\textsuperscript{3+}(1%) powder samples. T=10 K.

For GdF\textsubscript{3} and YF\textsubscript{3}:Gd\textsuperscript{3+}, Eq. (1) can be applied directly. The depression energies of GdF\textsubscript{3} and YF\textsubscript{3} are 10 878 cm\textsuperscript{-1} and 9915 cm\textsuperscript{-1}, respectively.23 From Eq. (1), the lowest Gd\textsuperscript{3+} 4f\textsuperscript{5-5d} transition energies are 84 262 cm\textsuperscript{-1} (GdF\textsubscript{3}) and 85 225 cm\textsuperscript{-1} (YF\textsubscript{3}:Gd\textsuperscript{3+}). Since the first broad maxima in the excitation spectra of Gd\textsuperscript{3+} 4f\textsuperscript{5-5d} emission in GdF\textsubscript{3} and YF\textsubscript{3}:Gd\textsuperscript{3+} result from an overlap of transitions to various sublevels of the first crystal field 5d component, a comparison with the estimates will be misleading. However, the estimates may be better compared with the maxima in the VUV emission spectra, taking into account the Stokes shifts \Delta S for these compounds given in Ref. 23. 5567 cm\textsuperscript{-1} for GdF\textsubscript{3} and 5444 cm\textsuperscript{-1} for YF\textsubscript{3}. The estimated maxima of Gd\textsuperscript{3+} 5d-4f emission in GdF\textsubscript{3} and YF\textsubscript{3}:Gd\textsuperscript{3+} are 78 695 and 79 781 cm\textsuperscript{-1}. For YF\textsubscript{3}:Gd\textsuperscript{3+} the estimate agrees well with the experimental value (79 700 cm\textsuperscript{-1}). For GdF\textsubscript{3}, the experimental value (80 000 cm\textsuperscript{-1}) exceeds the estimate considerably. Note, however, the energy parameters for Gd\textsuperscript{3+} 4f\textsuperscript{5-5d} transitions in GdF\textsubscript{3} given in Ref. 23 were obtained using data from a single paper and may therefore be less accurate than the parameters of YF\textsubscript{3}:Gd\textsuperscript{3+}, resulting in less reliable estimates.

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FIG. 7. (a) High-resolution excitation spectrum of LiGdF\textsubscript{4}:Ce\textsuperscript{3+}(0.05%) monitoring Gd\textsuperscript{3+} 6P\textsubscript{7/2} → 8S\textsubscript{7/2} 311 nm emission and calculated Ce\textsuperscript{3+} 4f\textsuperscript{5-5d} absorption spectrum of LiYF\textsubscript{4}:Ce\textsuperscript{3+}(0.05%) (upper wave number scale). (b) High-resolution VUV emission spectrum (\Delta \lambda=0.8 Å) of LiGdF\textsubscript{4} (lower wave number scale). T=10 K.
The dense $4f^7$ level system overlapping with the lowest Gd$^{3+}$ $4f^65d$ level might open an efficient nonradiative relaxation channel, quenching the radiative decay. However, the rather strong emission intensities and the lifetimes in the ns range clearly show that the branching between radiative and nonradiative transitions favors the radiative decay at low temperatures. A selection rule must therefore suppress the nonradiative channel. The spin multiplicity of the lowest $4f^65d$ level of Gd$^{3+}$ is eight, whereas the $4f^7$ levels of Gd$^{3+}$ closest to the $4f^65d$ level are spin doublets or quartets. As a consequence, the nonradiative channel is heavily spin-forbidden.

The crystal-field splitting of the Gd$^{3+}$ ground state is extremely small, i.e., within the spectral resolution interval—only one ZPL is expected in the Gd$^{3+}$ VUV emission, corresponding to the electronic origin of the $4f^7$-$4f^6$ $^5S_{7/2}$ transition. The $5d$-$4f$ luminescence spectra, however, yield several narrow lines, the origin of which is discussed below. For this purpose, the $5d$-$4f$ emission spectrum of LiGdF$_4$ is compared with the excitation spectrum for LiGdF$_4$:Ce(0.05%) at the edge of the Ce$^{3+}$ $f-d$ excitation (Fig. 7). A striking similarity is observed. This is also the case for LiYF$_4$:Gd$^{3+}$. For the Ce$^{3+}$ ion with only one $4f$ electron, a single ZPL is expected for $4f$-$5d$ absorption (excitation) to each crystal-field $5d$ component. All other structures arise from electron-phonon transitions (note the low doping level). The one-to-one correspondence between the Ce$^{3+}$ excitation spectrum and the Gd$^{3+}$ $5d$-$4f$ emission proves that the fine structure in Gd$^{3+}$ $5d$-$4f$ emission is due to one ZPL and its phonon replica. The shape of the spectrum with a ZPL, a few narrow vibronic lines, and a wide lower-energy vibronic side band is typical for intermediate electron-phonon coupling. This is confirmed by an estimate of the Huang-Rhys parameter $S \approx 1$ from the energy difference between the ZPL and the maximum of the wide side band, taking into account the phonon spectrum of LiGdF$_4$. An excellent agreement was obtained also between experimental spectra and calculations of the absorption spectrum for LiYF$_4$:Ce$^{3+}$ (see Fig. 7). This will be discussed in Sec. III C.

The Stokes shift of $\sim 6000$ cm$^{-1}$ observed in GdF$_3$ and YF$_3$:Gd$^{3+}$ for Gd$^{3+}$ $4f^7$-$4f^65d$ transitions is more than 100 times larger than the maximum phonon energy in RE trifluorides, i.e., the Huang-Rhys parameter $S$ exceeds 5 in these matrices, corresponding to strong electron-lattice coupling. This explains the absence of any vibronic fine structure in the emission and excitation spectra.

4. Excitation spectra of Gd$^{3+}$ $5d$-$4f$ luminescence and comparison with the energy level pattern of Eu$^{3+}$

In this section, the excitation spectra presented in Fig. 5 will be discussed. They have a pronounced threshold originating from the onset of $4f$-$5d$ excitations (see Secs. III A 1 and III A 2). They all agree concerning the decrease at high energies. This decrease is due to the onset of host absorption. In between, however, two types of spectra are observed. One type yields a level of emission, which is nearly independent from the excitation energy. This is true for optically dense systems [either LiGdF$_4$ or LiYF$_4$:Gd$^{3+}$ (10%)], and an emission with a fast decay. The other type yields fine structure in an optically dense system (LiGdF$_4$) and a slow emission (593 nm) but also in an optically thin system [LiYF$_4$:Gd$^{3+}$ (1%)] with fast emission.

The first type corresponds to total absorption of the exciting radiation with subsequent relaxation into the emitting level. Provided the quantum efficiency is independent from the penetration depth of the exciting radiation, in this case no distinct fine structure can show up. It is well known, however, that energy transport towards the surface and surface quenching results in a modulation of excitation spectra with a correlation between minima in penetration depths (maxima in absorption) and minima in the excitation spectrum. In the optically dense system LiGdF$_4$, both is observed: on a ns time scale, energy transport to the surface is obviously inefficient (5d-$4f$ emission). On a time scale corresponding to the long lifetime of the 593 nm emission, energy transport to the surface and surface quenching modulates the excitation spectrum. The minima in the excitation spectrum are therefore ascribed to maxima of the absorption coefficient, whatever the nature of these maxima may be. The $5d$-$4f$ excitation spectrum in the optically thin system LiYF$_4$:Gd$^{3+}$ supports this statement. On a ns time scale, in the doped system the energy transport to the surface is even less efficient than in the optically dense system LiGdF$_4$. Therefore, the maxima observed are maxima in absorption. They are clearly correlated to the minima in the excitation spectrum of the 593 nm emission [apart from the small matrix shift of 170 cm$^{-1}$ (Sec. III A 1)]. More details will be given in a forthcoming paper.

The absorption maxima may be of electronic origin, they could originate from vibronic sidebands, or there may be a superposition of both. The splitting between distinct maxima is of the order of 1000 cm$^{-1}$, by far exceeding the splitting of vibronic sidebands as has been observed in the emission spectrum (Sec. III A 3). Therefore, electronic excitations have to be considered. It is certainly too simple to discuss them in terms of the $f^2$ configuration which does not interact with the $5d$ level. On the contrary, the levels of the $4f^65d$ configuration have to be taken into account.

To the best of our knowledge, no calculations of $4f^7$-$4f^65d$ transitions in Gd$^{3+}$ were published in the literature. However, rather extensive studies have been performed for $4f^7$-$4f^65d$ transitions in Eu$^{3+}$, which is isoelectronic to the Gd$^{3+}$ ion. The structure observed for $4f^7$-$4f^65d$ transitions in Eu$^{2+}$ was traced back to the energy level pattern of the $4f^6$ core in the $4f^65d$ state. The levels of the $4f^6$ core were approximated by the well-known $4f^6$ level scheme of Eu$^{2+}$. Rather good agreement between the measured peaks and the Eu$^{2+}$ $4f^6$ levels was obtained.

In analogy to the procedure of Ryan et al., we included in Fig. 5 the Eu$^{3+}$ $4f^6$ levels of LiYF$_4$:Eu$^{3+}$ taken from Ref.
22 for comparison with the fine structure observed above threshold of Gd$^{3+}$ $4f$-$4f$ excitation. The Eu$^{3+}$ levels were arranged in a way that the Eu$^{3+}$ $4f$ excitation coincides with the Gd$^{3+}$ $4f$-$4f$ $5d$ ZPL. The energy range of the lower $^7F_J$ multiplets of the Eu$^{3+}$ $4f$ configuration matches well the energy spread for the Gd$^{3+}$ electronic transitions under discussion. Therefore, the fine structure is ascribed to electronic levels of the $4f$-$5d$ configuration. A one-to-one correspondence between the maxima and the Eu$^{3+}$ levels, however, cannot be expected in view of the rudeness of the model.

B. $5d$-$4f$ transitions in Lu$^{3+}$

1. Experimental results on LiLuF$_4$, LiYF$_4$:Lu$^{3+}$, and on LuF$_3$ at low temperatures

VUV emission from the LiLuF$_4$ crystal consists of a line at 80 000 cm$^{-1}$ and a wide sideband centered at $\sim$80 180 cm$^{-1}$, whereas the luminescence spectrum from the LiYF$_4$:Lu$^{3+}$ (0.5%) crystal has a steep high-energy onset at $\sim$81 100 cm$^{-1}$ followed by distinct lines and a sideband centered at $\sim$80 630 cm$^{-1}$, i.e. the emission spectrum from LiYF$_4$:Lu$^{3+}$ is narrower than the one from LiLuF$_4$ (Fig. 8). The VUV emission from the LuF$_3$:Ce$^{3+}$ single crystal and from the undoped powder sample of LuF$_3$ consists of a single broad band centered at $\sim$80 500 cm$^{-1}$ (Fig. 9). VUV luminescence from all studied lutetium compounds has a long lifetime beyond the experimental limit (longer than $\sim$1 $\mu$s) and is thermally quenched near 200 K. The VUV luminescence is ascribed to Lu$^{3+}$ $5d$-$4f$ transitions. The long lifetime indicates a spin-forbidden character of $5d$-$4f$ transition. The assignment will be confirmed in Sec. III B 2.

The excitation spectrum of VUV emission from the LiLuF$_4$ crystal has a smooth rise above 81 000 cm$^{-1}$ with some faint structures, and two pronounced peaks at 81 760 and 83 150 cm$^{-1}$ (Fig. 8). In the case of LiYF$_4$:Lu$^{3+}$ (5%), a steep threshold at 81 760 and two lines just above threshold at 81 950 cm$^{-1}$ and 82 240 cm$^{-1}$ are observed. An additional pronounced rise shows up at 83 170 cm$^{-1}$. At the low-energy side of the 81 760 cm$^{-1}$ threshold, weak features are observed in an enlarged scale, corresponding to the faint structures of the rising part of the LiLuF$_4$ spectrum. The excitation spectrum of the LuF$_3$ $5d$-$4f$ luminescence has a threshold near 82 700 cm$^{-1}$ and does not show any fine structure (Fig. 9).

2. Assignment of VUV luminescence to $5d$-$4f$ radiative transitions in Lu$^{3+}$

The energies for the lowest Lu$^{3+}$ $4f$-$5d$ transitions in LiLuF$_4$ and in the LiYF$_4$ matrix are estimated according to

$$E_{ZPL}^{Lu^{3+}} = E_{ZPL}^{Ce^{3+}} + \Delta E_{Lu^{3+},Ce^{3+}}^{Lu^{3+},Ce^{3+}}.$$  

$\Delta E_{Lu^{3+},Ce^{3+}}^{Lu^{3+},Ce^{3+}} = 49 170$ cm$^{-1}$ given in Ref. 23 may be rather uncertain because it is solely based on one paper on gaseous Lu$^{3+}$. The energies of the ZPLs for Ce$^{3+}$ $4f$-$5d$ transitions (33 130 cm$^{-1}$ in LiLuF$_4$:Ce$^{3+}$ and 33 450 cm$^{-1}$ in LiYF$_4$:Ce$^{3+}$) are taken from Ref. 24. Equation (3) then yields the values of the spin allowed Lu$^{3+}$ $4f$-$14f$-$135d$ ZPLs...
in LiLuF₃ and LiYF₄:Lu³⁺, 82 300 and 82 620 cm⁻¹. These values are considerably larger than the energies of the pronounced maxima in the excitation spectra below 82 000 cm⁻¹. In view of the uncertainty of ΔE_{Lu,Ce}^{ZPL}, it is not possible to take the estimates as the basis for an assignment of any structure to a ZPL. However, the estimates clearly prove that the strong signals in the excitation spectra around 82 000 cm⁻¹ arise from spin-allowed transitions in Lu³⁺ from the 4f¹⁴S₀ state to the lowest low-spin (S=0) state of the excited 4f¹⁵5d configuration.

The calculations following the methodology of Dorenbos can be extended to the spin-forbidden 4f-5d transitions since the energy difference, ΔE_{Lu}^{as,sf}, between the spin-allowed and the spin-forbidden 4f-5d excitation energy is merely a property of the respective ion but is nearly independent on the host.

\[ E_{ZPL}^{4f-5d} = E_{ZPL}^{5d} + \Delta E_{Lu,Ce}^{as,sf} - \Delta E_{Lu}^{as,sf}. \] (4)

Unfortunately, the value of ΔE_{Lu}^{as,sf} is not known. However, taking into account the decreasing trend of the energy splitting between spin-allowed and spin-forbidden 4f-5d transitions from Tb³⁺ to Yb³⁺, and that in Yb³⁺ this splitting is of the order 1500 cm⁻¹, we have reasons to argue that ΔE_{Lu}^{as,sf} ≤ 1500 cm⁻¹. The estimates of ZPL energies for spin-forbidden Lu³⁺ 4f-5d transitions in LiLuF₃ and LiYF₄ hosts are >80 800 cm⁻¹ and >81 120 cm⁻¹, respectively. The lower limits of these estimates are close to the weak features observed in the excitation spectra of the respective lattice and the high-energy tails of the respective luminescence curves.

The VUV emission is therefore ascribed to spin-forbidden transitions from the lowest high-spin (S=1) level of the 4f¹⁵5d configuration to the Lu³⁺ 4f¹⁴S₀ ground state.

In contrast to LiGdF₄ and LiYF₄:Gd³⁺ where strong ZPLs at the short wavelength edges of spectra are clearly observed, the 5d-4f spectra from LiLuF₃ and LiYF₄:Lu³⁺ do not show ZPLs (within the experimental sensitivity). The short-wavelength tail of the Lu³⁺ 5d-4f emission overlaps with the long wavelength tail of the weak structure in the excitation spectrum. Obviously, the transition probability for the pure electronic spin-forbidden transition is extremely small, so that only phonon-assisted transitions show up in the spectra. The sharp lines observed in Lu³⁺ 5d-4f luminescence in LiLuF₃ and LiYF₄:Lu³⁺ are therefore ascribed to phonon-assisted transitions, merging into a sideband. The electronic origin may be estimated from the crossing of the emission and excitation spectra (~81 000 cm⁻¹). The absence of the ZPL will be further discussed in Sec. III C.

Concerning LuF₃, the VUV emission is ascribed well to the spin-forbidden Lu³⁺ 5d-4f transitions. Whereas the shape of the emission band corresponds to the strong coupling case, the first excitation band observed in the excitation spectrum is not the counterpart of emission but is mainly due to a convolution of spin-allowed excitations into different crystal field components. Therefore, e.g., the energetic difference between the maxima in emission (80 500 cm⁻¹) and excitation (87 000 cm⁻¹) does not correspond to the Stokes shift. One may speculate that the asymmetric shape of the excitation spectrum around 84 000 cm⁻¹ arises from the spin-forbidden excitation band, indicating a rough estimate of the Stokes shift 4000 cm⁻¹ and an electronic origin at 82 000 cm⁻¹.

Although no ZPLs are observed, the fine structure of the luminescence spectra of LiLuF₃ and LiYF₄:Lu³⁺ indicates intermediate coupling. Taking into account the estimate of the electronic origin, the effective phonon frequencies (400 cm⁻¹) of the respective lattice and the energetic position of the smooth luminescence sidebands, S ~ 2 is obtained. The Stokes shift between absorption and emission for 4f¹³5d-4f¹⁴ transitions in LuF₃ (~4000 cm⁻¹) is considerably larger than in LuF₄ and LiLuF₃, i.e., Huang-Rhys parameter S > 5 in LuF₃, which is in agreement with strong coupling (absence of any vibronic fine structure).

3. Temperature dependence of Lu³⁺ 5d-4f luminescence

As already mentioned, Lu³⁺ 5d-4f luminescence in the materials studied is thermally quenched at temperatures T > 200 K. However, as a function of temperature, an additional higher-energy emission band appears at temperatures T > 100 K. This band is observed from all studied Lu³⁺-containing compounds independent of the Lu³⁺ concentration, i.e., this is the property of the Lu³⁺ ion but not of the matrix. The results for LiYF₄:Lu³⁺ are shown in Fig. 10. Compared to Fig. 8, the vibronic structures are broader. This is not only due to the larger resolution interval used (2 Å) but also to thermal broadening. The excitation spectrum measured at 8.2 K broadens as well at elevated temperatures. At intermediate temperatures where both bands coexist, the excitation spectra of both bands coincide.

As was discussed above, the transition probability for spin-forbidden 5d-4f radiative transitions from the lowest high-spin (S=1) 4f¹³5d state of Lu³⁺ is very small. However, with increasing temperature, an additional decay channel for the lowest 4f¹³5d level is opened, namely thermal population of the higher-lying low spin (S=0) 4f¹⁵5d state,
from which the 5d-4f radiative transition is spin-allowed. The additional emission band observed is ascribed to the spin-allowed 5d-4f luminescence.

Under thermal equilibrium population of both levels, the intensity ratio for the emission from these levels is determined by the ratio of products of the level population and transition probability from the level. Since the energy separation between high- and low-spin 4f$^{13}$d states in Lu$^{3+}$ is small (as a rough approximation, either the energy separation of the envelopes of both bands or the estimates of electronic origins in Sec. III B 2 may be taken), the emission from the low-spin 4f$^{13}$d state can become intense at rather low temperatures. At $T \sim 150$ K (LiYF$_4$:Lu$^{3+}$), the intensities of both bands are approximately the same. For the level separation of 823 cm$^{-1}$ obtained from calculations (see Sec. III C below), the ratio of transition probabilities for spin-allowed and spin-forbidden 5d-4f transitions is estimated as being $\sim 3 \times 10^3$, which is reasonable. It should be noted that due to the specific mechanism of population of this low-spin 4f$^{13}$d state, the decay kinetics for the high-energy band is controlled by lifetime for spin-forbidden transition and accordingly is slow. A similar effect was observed for Er$^{3+}$ spin-allowed and spin-forbidden 5d-4f luminescence from the LiYF$_4$:Er$^{3+}$ crystal$^{34}$ but at much higher temperatures $\sim 800$ K, since the splitting between high- and low-spin 5d states of the Er$^{3+}$ ion is $\sim 3300$ cm$^{-1}$. $^{33}$

4. Excitation spectra of Lu$^{3+}$ 5d-4f luminescence

In this section, only a few aspects of the excitation spectra (Fig. 8) will be discussed. The excitation spectrum of Lu$^{3+}$ 5d-4f emission in LiYF$_4$:Lu$^{3+}$ (5%) yields pronounced maxima which are ascribed to crystal-field components and phonon sidebands of the 4f$^{13}$d configuration. More details are given in Sec. III C where the spectrum will be compared with calculations.

The most striking features of the LiLuF$_4$ spectrum are the maxima at 81 760 cm$^{-1}$ and 83 150 cm$^{-1}$. In an earlier publication, they were ascribed to ZPLs of spin-forbidden and spin-allowed 5d-4f$^{14}$-4f$^{13}$d transitions.$^{24}$ In view of the new results of the present paper, this interpretation is no longer valid. The pronounced peaks correspond well to the thresholds observed in the excitation spectrum of the dilute system LiYF$_4$:Lu$^{3+}$ (5%) (Fig. 8). Hence, they correspond to excitation with large penetration depths where all kind of surface quenching is of minor importance. Indeed, the general behavior of the LiLuF$_4$ spectrum can be modeled, taking into account diffusive-type energy transfer from the bulk to the surface and surface quenching. The strong peaks arise from excitations in the bulk, which are not affected by surface quenching. More details are given elsewhere.$^{30}$

C. Electron-phonon interaction in the 4f$^{n-1}$5d electronic configurations of RE$^{3+}$ ions and simulations of the 4f$^{n}$-4f$^{n-1}$5d spectra

1. General theory of electron-vibrational 4f$^{n}$-4f$^{n-1}$5d spectra in the adiabatic approximation

To simulate interconfigurational 4f-5d spectral envelopes, we use the approach derived in Ref. 35 and generalized for the spin-forbidden transitions. This approach involves calculations of crystal field parameters for a 5d electron as explicit functions of lattice ion’s coordinates in the framework of the exchange charge model,$^{36}$ numerical diagonalization of the effective impurity ion Hamiltonian containing energies of electrostatic Coulomb and exchange interactions between electrons, spin-orbit interactions and the crystal field interactions for the ground (4f$^n$) and excited (4f$^{n-1}$5d) electronic configurations; calculations of the 5d-electron-phonon coupling constants, and simulations of the band shapes by making use of the realistic phonon spectrum of the host crystal lattice. The crystal field model was improved, in comparison with Ref. 35, by taking into account the extended charge distributions of a 5d electron and ligands’ outer electrons in calculations of the electrostatic component of the ligand field.$^{37}$ An energy gap $\Delta$ between the excited and ground configurations is treated as a fitting parameter. The Hamiltonian of the 5d-electron-phonon interaction, linear in dynamic displacements $u(Ls)$ of the lattice ions

$$H_{cl-ph} = \sum_{L,s,a} V_a(\bar{L}s)[u_a(\bar{L}s) - u_a(00)]$$

[here unit cells and ions in the cell are labeled by $L$ and $s$, respectively, with the impurity ion having the (00) label] is considered within the cluster approximation: modulation of the crystal field by ligand vibrations is considered only. The electronic operators $V_a(\bar{L}s)$ are defined by the coupling constants, which can be obtained by direct differentiation of corresponding crystal field parameters with respect to the lattice ion coordinates. Lattice vibrations are considered in the harmonic approximation.

The shape of the absorption/emission spectrum at low temperatures is easily obtained within the adiabatic and Condon approximations. The electron-phonon interaction is considered as a perturbation in the electron equation of the adiabatic approximation, and zero order electronic functions are exploited in calculations. The absorption coefficient $K_{ab}(\Omega)$ at the radiation frequency $\Omega$ for the electric dipole $a(4f^b) \rightarrow b(4f^{n-1}5d)$ transition, allowed in the Condon approximation, is proportional to the product of the normalized absorption form function$^{38}$

$$F_{ab}(\Omega) = 2\pi e^{-\hbar \sqrt{\hbar}} \sum_{p=0}^{\infty} M_{p,b}(\Omega - \Omega_{ba})$$

and the integral intensity of the transition given by $|\langle b(5d) | d\bar{e} | a(4f)^b \rangle|^2$, where $\bar{e}$ is the polarization vector of radiation, $d$ is the effective electric dipole moment of an ion, $M_{p,b}$ represents a $p$-phonon contribution to the spectrum: $M_{0,b}(\Omega - \Omega_{ba}) = \delta(\Omega - \Omega_{ba})$, and for $p>0$ and any $b_1, b_2, b_3, b_4$ states from the 4f$^{n-1}$5d configuration

$$M_{p,b}(\Omega - \Omega_{ba}) = \frac{1}{(\pi \hbar)^p p!} \int d\omega_1 \ldots d\omega_p D_{bb_{b1}}(\omega_1) \ldots D_{bb_{b4}}(\omega_p)$$

$$\times \delta(\Omega - \Omega_{ba} - \omega_1 - \ldots - \omega_p),$$

$$075111-9$$
from Eq. (H20849) the mirror symmetry between the spin-forbidden states is determined by dynamic admixture of all other 4f \( \rightarrow \) 5d transitions, we consider the electronic wave function of the \( \Omega \) state in the first order in perturbation theory. The corresponding non-Condon form factor is determined by dynamic admixture of all other 4f \( \rightarrow \) 5d states to the \( \Omega \) state, and can be obtained in the following form:

\[
K_{ab}^{(4f)}(\Omega) \sim F_{ab}(\Omega) \left( \varphi(\omega) d\omega \right)^2 + \int F_{ab}(\Omega + \omega) \times \left( f(\omega) + 2Re \left( \varphi(\omega) \int \varphi(\omega') \ast d\omega' \right) \right) d\omega + \int F_{ab}(\Omega + \omega + \omega') \varphi(\omega) \varphi(\omega') \ast d\omega' d\omega',
\]

(9)

where upper and lower signs should be used for the absorption and emission, respectively, and

\[
f(\omega) = \sum_{c' < c+b} \frac{\langle c | d_{c'} | a \rangle \langle c' | d_{c} | a \rangle^* h}{(E_b - E_c)(E_b - E_{c'})} D_{cbc'}(\omega),
\]

(10)

\[
\varphi(\omega) = \sum_{c > b} \frac{\langle a | d_{c} | e \rangle}{E_b - E_c} D_{ebc}(\omega).
\]

(11)

Here the sums are taken over all 4f \( \rightarrow \) 5d states, different from the state \( b \). Unlike the case of the allowed transitions, not only the integral intensities of the forbidden \( a(4f^n) \rightarrow b(4f^{n-1}5d) \) spectral bands depend on the \( a \) state, but also their line shapes, even though we neglect the electron-phonon interaction in the \( a(4f^n) \) state. As it follows from Eq. (9), a possibility to observe directly the form function \( F_{ab}(\Omega) \) and the corresponding ZPL at the frequency \( \Omega_{ba} \) depends on the dimensionless ratio \( |f D_{cbcb}(\omega)|^2/(E_c - E_b) |\) which may be essentially less than unity due to lower values of spectral cross-distributions \( D_{cbcb}(\omega) \) in comparison with the autodistributions \( D_{cbcb}(\omega) \) and \( D_{cbcb}(\omega) \). In a general case, the mirror symmetry between the spin-forbidden absorption and emission spectra is broken due to different signs of the third term at the rhs of Eq. (9).  

2. Simulations of the electron-vibrational spectra in LiYF\(_4\):Ce\(^{3+}\) and LiYF\(_4\):Lu\(^{3+}\)

Following the general approach described above, we have calculated the energy level patterns of the excited configurations and shapes of the electron-vibrational \( f-d \) absorption and emission spectra at low temperatures for the impurity Ce\(^{3+}\) and Lu\(^{3+}\) ions in LiYF\(_4\). 

Trivalent RE ions substitute for Y\(^{3+}\) ions in LiYF\(_4\) crystals in sites with \( S_4 \) point symmetry. The energy level patterns of the excited configurations 5d\(^{1}\) (Ce\(^{3+}\)) and 4f \( ^{13}S_2 \) (Lu\(^{3+}\)) contain five Kramers doublets (in the tetragonal crystal field, the 5d orbital manifold splits into three singlets and a doublet which is split further by the spin-orbit interaction), and 70 singlets and 35 non-Kramers doublets, respectively.

Parameters used in the calculations of the crystal field energies of the excited Ce\(^{3+}\) and Lu\(^{3+}\) configurations are listed in Table I. The spin-orbit coupling constants \( \zeta(4f) \) and \( \zeta(5d) \) were taken from the literature.  

The crystal field parameters were calculated using the analytical radial 5d functions from Refs. 41 and 42 and 2s, 2p functions of the F\(^-\) ion from Ref. 43. Ion charges were fixed as \(-1\) (F\(^-\)), +1 (Li\(^+\)), +3 (Y\(^{3+}\)). Parameters of the exchange charge model \( G_s = 1.69 \) (Ce\(^{3+}\)) and 1.55 (Lu\(^{3+}\)), \( G_p = 2.45 \) and \( G_\varpi = 0.13 \), the overall energy shift of the 5d configuration \( \Delta = 43 827 \) and 104 493 cm\(^{-1}\) for Ce\(^{3+}\) and Lu\(^{3+}\), respectively, and the parameters of the Coulomb [\( F^{(2)}(fd) = 19 727 \) cm\(^{-1}\), \( F^{(4)}(fd) = 10 477 \) cm\(^{-1}\)] and exchange [\( G^{(2)}(fd) = 4662 \) cm\(^{-1}\), \( G^{(3)}(fd) = 5640 \) cm\(^{-1}\), \( G^{(5)}(fd) = 7087 \) cm\(^{-1}\)] interactions between the electrons (for the Lu\(^{3+}\) ion) were obtained from fitting the calculated spectra to the experimental data. Since the shift of a vibronic band maximum from a ZPL roughly compensates for the Jahn-Teller energy, the calculated crystal field energies were fitted to the positions of the corresponding vibronic band maxima. For the impurity Ce\(^{3+}\) centers, a radial local deformation of the crystal lattice was taken into account (the RE ion – ligand distances were enlarged by about 3%).

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Table I. Spin-orbit coupling constants and crystal field parameters in LiYF\(_4\):Ce\(^{3+}\) and LiYF\(_4\):Lu\(^{3+}\) (in cm\(^{-1}\)).

<table>
<thead>
<tr>
<th></th>
<th>Ce(^{3+})</th>
<th>Lu(^{3+})</th>
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<tr>
<td>( \zeta(4f) )</td>
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<td>3406</td>
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<td>-413+254i</td>
</tr>
<tr>
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<td>1939</td>
</tr>
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The correlation functions for relative displacements of the impurity RE$^{3+}$ ion and its nearest neighbors were computed in the framework of the lattice dynamics model of the LiYF$_4$ crystal derived in Ref. 27. To compare the simulated spectral envelopes with the measured spectra, form-functions (7) were convoluted with a Gaussian to take into account the inhomogeneous broadening ($\sim 25$ cm$^{-1}$) induced by random lattice strains and with a Lorentz distribution to account for the relaxation broadening. The relaxation broadening was described with a Lorentz distribution to account for the inhomogeneous broadening in LiGdF$_4$:Ce$^{3+}$. The calculated Huang-Rhys parameters for the 5$^d$ states are described in Table II. The simulated line shape for the 4$^f$ transition with the Huang-Rhys parameter $\sigma(\epsilon\|\Delta)$, the ZPL frequency, the Huang-Rhys parameters and the relative intensity $\alpha(\epsilon\|\pi)$ are compared with the experimental data.

The observed excitation spectrum (see Fig. 8) corresponds to the first group of the 4$^f$ states. In Table II we present calculated characteristics for the states from this group, which have nonzero absorption intensity: the number of a state, the crystal field energy $E_{CF}$, the Jahn-Teller energy $E_{JT}$, the ZPL frequency, the Huang-Rhys parameter, and the relative integral intensities of the $\sigma$ and $\pi$ polarized electric-dipole transitions [the squared matrix elements of the first rank spherical operators between the $1S_0(4f^{14})$ ground state and the corresponding 4$^f$ state].

The calculated Huang-Rhys parameters for the 5$^d$ crystal field states of Ce$^{3+}$ ion in LiYF$_4$ equal 2.9, 17.4, 6.0, 6.0, 16.4, with the smallest value for the lowest 5$^d$ state, thus explaining why the ZPL is observed only in the transitions which involve this state, while all other 4$^f$-5$^d$ bands can be approximated well by smooth Gauss distributions with different widths. The simulated line shape for the 4$^f$-5$^d$ absorption to the lowest 5$^d$ state in LiYF$_4$:Ce$^{3+}$ with the well pronounced fine structure is in a good agreement with the measured shape of the excitation spectrum of Ce$^{3+}$ luminescence in LiGdF$_4$:Ce$^{3+}$ (Fig. 7) as well.

The calculated crystal field energies of the Lu$^{3+}$ 4$^f$ configuration spread over the range 81 000 cm$^{-1}$ –113 000 cm$^{-1}$, with nearly 90% of absorption intensity being in the second half of the spectrum. The structure of the spectrum follows general regularities found in the spectra of RE-doped LiYF$_4$ crystals. Three groups of states can be distinguished: 16 states from 81 000 to 84 700 cm$^{-1}$, weakly coupled to phonons (with the Huang-Rhys parameters from 0.7 to 1.6); 16 states from 87 400 to 90 700 cm$^{-1}$, strongly coupled to phonons (with the Huang-Rhys parameters from 4.5 to 7.6); the continuum of mixed electron-phonon states distributed in the range of energies from 93 000 to 113 000 cm$^{-1}$, with the Huang-Rhys parameters varying from 0.4 to 7 (these levels interact strongly with the nonadiabatic phonons).
At first sight, there seems to be a significant discrepancy in calculated and experimental transition intensities. However, we have to take into consideration that LiYF₄:Lu³⁺(5%) reaches optical saturation at least in the peaks of the spin- and parity-allowed 4f-5d transitions. Therefore, from the theoretical absorption curve $K(\Omega)$, the actual excitation spectrum has been estimated by $\{1 - \exp[-K(\Omega)d]\}$, where $d$ is the crystal thickness (curve 2 in Fig. 11). As the absorption curve was calculated in arbitrary units, $d$ was treated as a parameter. It was adjusted in a way that the relative height of the main maxima is reproduced. The overall agreement is satisfactory, though it is clear that the simulated ZPLs are more pronounced than the measured ones; the reason for the discrepancy may be that we have not taken into account interactions of crystal field doublets with nonadiabatic phonons.

The low energy intensive band in the excitation spectrum of LiYF₄:Lu³⁺(5%), with a narrow line at 81 950 cm⁻¹, is ascribed to the spin-allowed transitions to the lowest (3,4) doublet. The energy gap $\Delta$ was chosen so that the corresponding ZPL coincides with the observed narrow line. The maximum of the simulated vibronic band is at 82 327 cm⁻¹, greater than the experimental value by about 100 cm⁻¹. The next intensive band in the excitation spectrum has 5 pronounced maxima. We list their energies with the assignment greater than the experimental value by about 100 cm⁻¹. The peaks of the spin- and parity-allowed $4f$ transitions.

FIG. 12. The low temperature simulated (1, dashed curve) and measured (2, thin solid curve) emission spectra; simulated (3, bold solid curve) and measured (4, dotted curve) excitation spectra in the region of Lu³⁺ 4f-5d spin-forbidden transitions in LiYF₄:Lu³⁺,

The overall agreement is satisfactory, though it is clear that the simulated ZPLs are more pronounced than the measured ones; the reason for the discrepancy may be that we have not taken into account interactions of crystal field doublets with nonadiabatic phonons.

The low energy intensive band in the excitation spectrum of LiYF₄:Lu³⁺(5%), with a narrow line at 81 950 cm⁻¹, is ascribed to the spin-allowed transitions to the lowest (3,4) doublet. The energy gap $\Delta$ was chosen so that the corresponding ZPL coincides with the observed narrow line. The maximum of the simulated vibronic band is at 82 327 cm⁻¹, greater than the experimental value by about 100 cm⁻¹. The next intensive band in the excitation spectrum has 5 pronounced maxima. We list their energies with the assignment greater than the experimental value by about 100 cm⁻¹. The peaks of the spin- and parity-allowed $4f$ transitions.

The intensities of transitions from the ground state $^1S_0(4f^{14})$ to the lowest quasidoublet (1,2) in the 4f $^{13}5d$ configuration equal zero (in Condon approximation), however the corresponding ZPL energies are at the threshold of the weak feature in the observed excitation spectrum (see Fig. 8). Besides, the first state is positioned in the middle between the first feature in the emission spectrum (81 035 cm⁻¹) and the first maximum of the weak feature in the excitation spectrum (81 240 cm⁻¹). This supports the hypothesis of Sec. III B 2, that the phonon-assisted spin-forbidden 4f $^{14}4f$ $^{13}5d$ transitions are observed in these spectra.

We simulated the absorption and emission spectra for the forbidden transitions utilizing Eqs. (9)–(11). The results of calculations are compared with the weak feature observed in LiYF₄:Lu³⁺(5%) excitation spectrum and with the LiYF₄:Lu³⁺(0.5%) emission spectrum in Fig. 12. The agreement is satisfactory, especially for the emission spectrum (no additional fitting has been done). Only the term $\int f_{ab}(\Omega - \omega)f(\omega)d\omega$ brings about significant contribution to the form function $K_{ab}(\Omega)$ [see Eq. (9)] for the forbidden transitions under investigation. This explains the absence of the ZPLs in experimental emission and excitation spectra corresponding to the spin-forbidden transitions in LiYF₄:Lu³⁺, and leads to symmetric calculated spin-forbidden absorption and emission spectra. The fine structure in the calculated spectra comes from a convolution of the ZPL in $F_{ab}(\Omega)$ with $f(\omega)$ and reproduces the spectral distributions of the electron-phonon coupling between the lowest quasidoublet and other

IV. CONCLUSIONS

The VUV $4f^{n-15d}-4f^n$ luminescence and luminescence excitation spectra of various Gd³⁺ and Lu³⁺ containing fluorides have been analyzed with high spectral resolution. Gd³⁺ ions emit only fast (nanosecond) spin-allowed 5d-4f luminescence as it is typical for RE³⁺ ions from the first half of the lanthanide series. At low temperatures, Lu³⁺ ions emit exclusively slow spin-forbidden 5d-4f luminescence. With increasing temperature, however, an admixture of spin-allowed 5d-4f emission shows up. Strong electron-phonon coupling has been observed from REF₄-type systems, whereas the spectra of the more complex LiREF₄ systems exhibit intermediate coupling with zero-phonon lines (Gd³⁺) and phonon sidebands.

Spectral envelopes of some of the spectra have been simulated as well. Contrary to earlier attempts to calculate VUV 5d-4f luminescence and luminescence excitation spectra where electron-phonon interaction was simulated with Gaussian broadening of electronic excitations and Gaussian sidebands in luminescence, the present theoretical results originate from a microscopic semiphenomenological model of the crystal field and the crystal lattice vibrational spectrum. The simulations were restricted to the Ce³⁺ and Lu³⁺ ions with simple $4f^55d$ and $4f^{13}5d$ electronic configura-
tions, respectively. Good agreement between experiment and theory was achieved. The absence of a ZPL in the Lu$^{3+}$ spectra with intermediate electron-phonon coupling was also obtained from the simulation of the spin-forbidden spectrum. Concerning the more complicated case of Gd$^{3+}$ with its 4f$^6$5d electronic configuration, the luminescence spectra were calculated in an indirect way. Based on the observation that the Gd$^{3+}$ 5d-4f luminescence spectrum in LiYF$_4$ is very similar to the excitation spectrum of the Ce$^{3+}$ 5d-4f emission in the same host, the spectra were calculated for the Ce$^{3+}$ ion. In this way, it was possible to identify the phonon structures in the Gd$^{3+}$ luminescence spectra. It is the combination of the high-resolution spectra with their theoretical treatment that brought about an understanding of Gd$^{3+}$ and Lu$^{3+}$ 5d-4f luminescence and luminescence excitation in various fluoride-type hosts.

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