

RE³⁺ VUV $d \rightarrow f$ luminescence investigated by synchrotron radiation excitation at HASYLAB

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Although known since many years, the vacuum ultraviolet (VUV) $4f^n \leftrightarrow 4f^{n-1}5d$ transitions of heavier trivalent rare earth ions were investigated in detail only during the last decade. An essential prerequisite was synchrotron radiation as a tuneable source of photon excitation in the VUV range. Luminescence spectroscopy under state-selective VUV excitation turned out to be particularly useful to characterize the $4f^n \leftrightarrow 4f^{n-1}5d$ transitions. Most of the progress has been achieved at the Hamburger Synchrotronstrahlungslabor HASYLAB with its unique VUV luminescence facilities. The experiments stimulated calculations for a deep understanding of the transitions. Results of the main groups involved at HASYLAB will be compared. Besides the achievements, limitations and restrictions of the experiments and of the theoretical models get obvious. This may help to stimulate future work.

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1. Introduction

Spectroscopy of $4f^n \leftrightarrow 4f^{n-1}5d$ transitions of trivalent rare earth ions (RE³⁺) in doped insulators is a well established field. The ultraviolet (UV) Ce³⁺ and Pr³⁺ $f \leftrightarrow d$ transitions were investigated since a long time. The vacuum ultraviolet (VUV) $4f^n \leftrightarrow 4f^{n-1}5d$ transitions of the heavier RE³⁺ ions — known at least since 1966 [1] — by far did not attract as much attention as the UV transitions mentioned because VUV spectroscopy was a severe task before synchrotron radiation (SR) came into play, although $4f^n \rightarrow 4f^{n-1}5d$ absorption spectra of RE³⁺ ions in a CaF₂ host showed that high-resolution work was feasible with conventional sources [2].

Already at the beginning of SR spectroscopy, the potential power of SR for luminescence spectroscopy was demonstrated by Yen et al. [3] and applied for the first time to VUV RE³⁺ $4f^n \rightarrow 4f^{n-1}5d$ excitations by Elias et al. [4] and Heaps et al. [5]. The earliest work on $4f^{n-1}5d \rightarrow 4f^n$ VUV RE³⁺ luminescence (Nd³⁺, Er³⁺, Tm³⁺), performed with conventional excitation sources, was published by Yang and DeLuca [6,7]. Nevertheless, the subject was nearly forgotten, because no practical application was within sight at that time.

The situation changed when the aspect of fast scintillators and quantum-cutting phosphors came into play [8–12]. Since then, many groups entered the field, most of them using SR. In particular, luminescence and luminescence excitation spectroscopy with SR turned out to be a powerful method to investigate the so-called „ d -excitations“. The facilities of the Hamburger Synchrotronstrahlungslabor HASYLAB play a key role in this context [13]. In the present paper, the relationship between progress in VUV RE³⁺ $4f^n \leftrightarrow 4f^{n-1}5d$ spectroscopy and the HASYLAB facilities will be demonstrated. The experiments stimulated theoretical work which will be discussed as well. Apart from

a special case, we will not include experiments on Ce³⁺ performed with SR. The main aspect of the present paper is VUV luminescence where at present HASYLAB is perhaps the only laboratory where the presented work was feasible.

2. How it began at HASYLAB

Two groups started independently: the group of Dr. Makhov from the Lebedev Institute (HASYLAB project II-95-59; SUPERLUMI station) and the group of Prof. Meijerink from Utrecht University (HASYLAB project II-96-81 EC; HIGITI station). At that time, two stations were available for VUV luminescence spectroscopy, the HIGITI and the SUPERLUMI station [14]. SR was used for excitation purposes from about 4 to 40 eV. The tunability over a large range was the main aspect why SR was used. Moreover, VUV luminescence could be analysed at both facilities. Another aspect has to be mentioned: SR at HASYLAB consists of short pulses (FWHM below 200 ps) with a comparatively long interpulse period (200 ns to 1 μ s). The time structure was used, e. g., to discriminate between „fast“ (ns-range) and „slow“ (μ s range) luminescence bands.

Due to the fact that there were two stations, the groups had no experimental overlap. Project II-95-59 was devoted to „fast“ scintillators, namely ionic crystals emitting cross luminescence, and ionic crystals with VUV $d \rightarrow f$ type emission. It referred to earlier work with SR at the Lebedev Institute [8]. The first results from the SUPERLUMI experiments were published in the HASYLAB Annual Report 1996 [10] and in Refs. [15,16].

Project II-96-81 EC was devoted more generally to VUV spectroscopy of lanthanides. The first publications were focused on VUV levels of RE³⁺ f^n configurations [11] because knowledge about $4f^n$ levels above 50 000 cm⁻¹ was scarce. In particular, the Gd³⁺ levels in LiYF₄ were

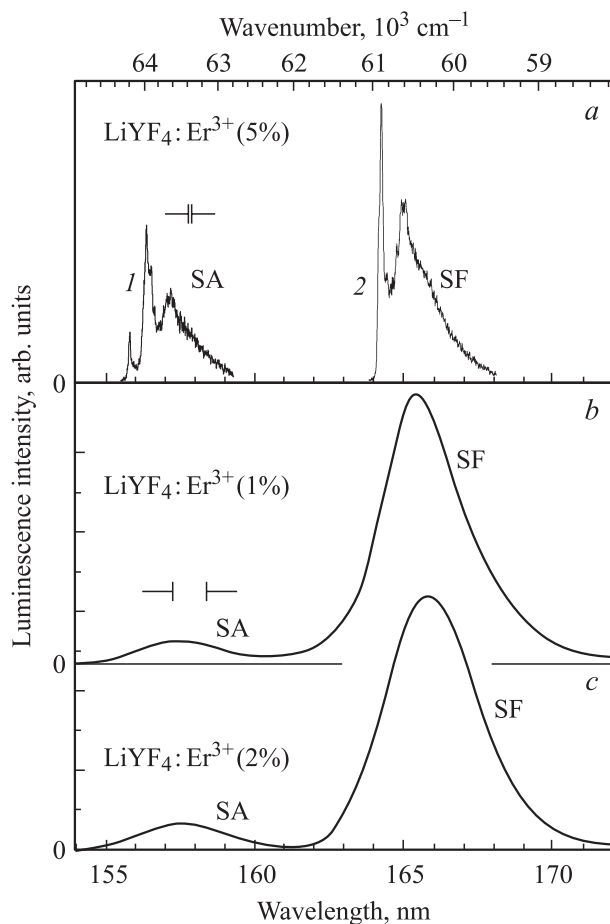


Figure 1. Er³⁺ $4f^{10}5d \rightarrow 4f^{11}$ ($^4I_{15/2}$) SA and SF emission from LiYF₄:Er³⁺ measured. *a* — with $\Delta\lambda = 0.05$ nm (SA and SF intensities not in scale) [20] (Copyright Wiley-VCH Verlag GmbH&Co, KGaA, reproduced with permission); *b* — with $\Delta\lambda \approx 2$ nm [15] (Copyright (1998), with permission from Elsevier); *c* — with $\Delta\lambda \approx 2$ nm [18]. $T = 10$ K.

investigated because Gd³⁺ seemed to be promising for quantum cutting. Several levels between 50 000 cm⁻¹ and 67 000 cm⁻¹ were observed and calculated. Although the f -levels are not in the focus of the present paper, we want to point out that the work mentioned lead to „A complete $4f^n$ energy level diagram for all trivalent lanthanide ions“ [17].

From the point of view of quantum cutting in the visible spectral range, it turned out that a quantum cutter based on Gd³⁺ alone is not possible. However, efficient quantum cutting via cross relaxation in LiGdF₄:Eu³⁺ was observed [12]. In parallel, the group of Prof. Meijerink also investigated the $d \rightarrow f$ type luminescence of LiYF₄ doped with several RE³⁺ ions [18,19]. In Fig. 1, results of both groups are compared. Both groups observed fast and slow bands. At first sight, the Gaussian-type shape seemed to indicate strong electron-phonon coupling.

However, Wegh et al. already indicated that the measured shape was mainly due to poor spectral resolution because zero-phonon lines (ZPLs) were observed in excitation

spectra [18]. Recent high-resolution spectra (Fig. 1) clearly yield intermediate coupling [20] (Sec. 4).

Makhov et al. [10] and Becker et al. [15,16] assigned the fast VUV bands to $d \rightarrow f$ transitions and the slow VUV bands to yet unknown $f \rightarrow f$ transitions. At that time, the spectral resolution of luminescence analysis was so poor that also narrow $f \rightarrow f$ lines showed up as rather broad bands. One example is given in Ref. [11] (Gd³⁺ $^6G_{7/2} \rightarrow ^6P_{7/2}$ emission in LiYF₄). This interpretation turned out to be incorrect. At the 3rd Int. Conf. on f -elements in Paris (1997), Meijerink ascribed in his talk the fast VUV bands to spin-allowed (SA), and the slow bands to spin-forbidden (SF) $d \rightarrow f$ transitions (Er³⁺ and Tm³⁺) [21]. This interpretation was published slightly later [18] and is now generally accepted.

3. Spectroscopy of the $4f^{n-1}5d$ configuration

Apart from the great success concerning quantum cutting, the detailed results of $4f^{n-1}5d$ spectroscopy have to be emphasized, among others, because they stimulated exciting theoretical work. Pieterse et al. measured excitation spectra of $d \rightarrow f$ type luminescence (where it exists) or of characteristic $f \rightarrow f$ luminescence of Tb³⁺, Dy³⁺, Ho³⁺, Er³⁺, Tm³⁺, and Yb³⁺ ions in LiYF₄, CaF₂, and YPO₄ hosts [22,23]. They could not be explained in terms of d -levels which don't interact with the f levels in the (energetic) background. A model was developed to calculate the levels of the $4f^{n-1}5d$ configuration in the respective crystal field in a non-vibrating lattice [24]. In Fig. 2, one example of an excitation spectrum and comparison with theory is shown [23].

Comparison with experiment is a severe task. In the range of spin-allowed $f \rightarrow d$ excitations, saturation effects distort the relative intensities of the maxima [24]. Saturation effects are obvious from Fig. 2, *a* (single crystal). Although the Er³⁺ concentrations are the same in both parts of the figure, saturation effects are less pronounced in the lower part (powder sample). Moreover, the excitation spectra of different luminescence bands may be different due to branching-ratio effects. The curve shown in Fig. 2, *b* [23] was measured on the Er³⁺ $^4S_{3/2} \rightarrow ^4I_{15/2}$ line. Fig. 2, *a*, however, shows that the excitation spectra of the Er³⁺ SF $d \rightarrow f$ emission in the VUV, the $^4S_{3/2} \rightarrow ^4I_{15/2}$ and the $^2P_{3/2} \rightarrow ^4I_{13/2}$ lines are drastically different [25]. From a rigorous point of view it is therefore not justified to compare calculated spectra with an excitation spectrum of one particular luminescence channel.

The result of theory is a „bar spectrum“. Broadening of the „bars“ by electron-phonon coupling is an essential step towards a realistic absorption spectrum. The authors simulated the vibronic bands by Gaussian curves, displaced from the „bars“ (electronic origins) by energies which were estimated from the phonon spectra of the respective hosts. Calculated oscillator strengths were taken as a measure for

the areas of the Gaussian curves. Superposition of the Gaussians was then compared with experiment. In general, the positions and widths of the excitation bands were reproduced. In some cases, however, deviations between theory and experiment were found.

Recent calculations [26] taking into account interaction with lattice vibrations show that the approach of Reid et al. is justified for many electronic excitations (see below). From a practical point of view, the approach is justified as well because the spectra were measured with a spectral resolution 0.3 nm [22] which is not sufficient to reveal detailed vibronic structures. In spite of the problems mentioned, the work was a breakthrough because for the first time the spectra were compared with the energy levels of the $4f^{n-1}5d$ configuration.

Two ions were missing, Gd^{3+} and Lu^{3+} , although Wegh et al. already observed the onset of $Gd^{3+} 4f^7 \rightarrow 4f^65d$ excitation in an excitation spectrum of the $Gd^{3+} 6P_{7/2} \rightarrow 8S_{7/2}$ emission (Fig. 4 in [11]). However, the steep onset at 127 nm was ascribed to the onset of host-lattice absorption.

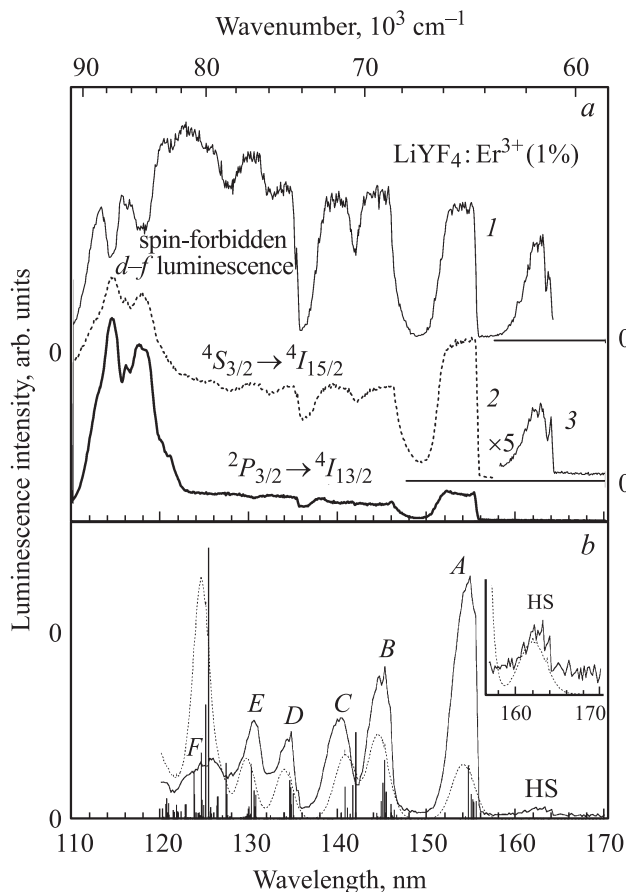


Figure 2. *a)* Excitation spectra of Er^{3+} SF $4f^{10}5d \rightarrow 4f^{11}$ ($4I_{15/2}$) (curve 1), of $Er^{3+} 4S_{3/2} \rightarrow 4I_{15/2}$ (curve 2), and of $Er^{3+} 2P_{3/2} \rightarrow 4I_{13/2}$ emission from $LiYF_4:Er^{3+}$ (1%) single crystal [25]. *b)* Excitation spectra of $Er^{3+} 4S_{3/2} \rightarrow 4I_{15/2}$ emission from $LiYF_4:Er^{3+}$ (1%) powder sample (solid curve) and calculated spectra (bars and dotted curve) [23]. Inset: range of the lowest high-spin state. $T = 10$ K.

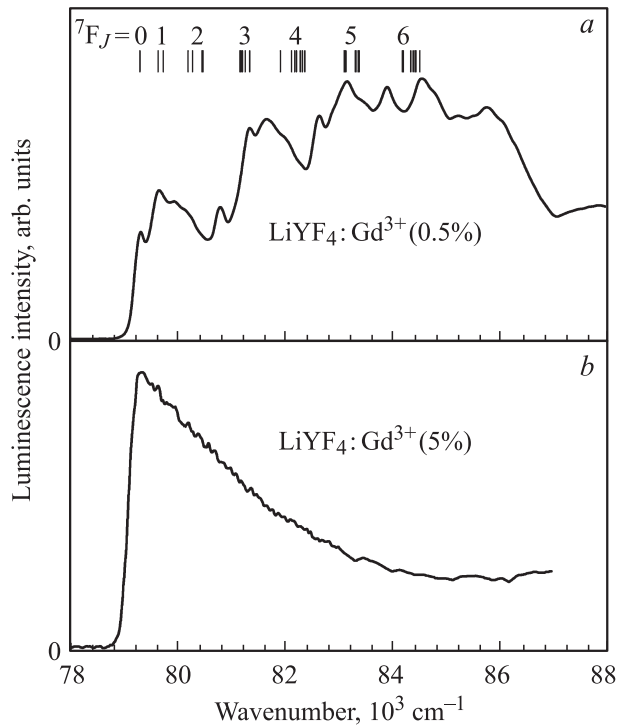


Figure 3. Excitation spectra of $Gd^{3+} 6G_{7/2} \rightarrow 6P_{7/2}$ emission measured with $\Delta\lambda = 0.08$ [26] (a) and 0.3 nm [11] (b) at $T = 10$ K. The $Eu^{3+} 4f^6$ level of $LiYF_4:Eu^{3+}$ [39] are included for comparison. For details see text.

Comparison with measurements by Kirm et al. [26] in Fig. 3 shows that this is not the case. It would have been easy to measure VUV luminescence with an excitation above this onset, and the most exciting RE^{3+} VUV luminescence would have been discovered already at that time.

4. The first high-resolution VUV $RE^{3+} d \rightarrow f$ spectra

In spite of the demand for high-resolution spectra, it took some years until such measurements were performed. This was only feasible at the SUPERLUMI station with its 1 m monochromator for VUV luminescence analysis. This monochromator, however, was lent to the VUV Free-Electron Laser Facility of HASYLAB for some years for spectral characterization of the VUV FEL beam. As soon as the monochromator was back at SUPERLUMI, the first high-resolution spectra were measured [20] (resolution interval 0.05 nm compared to about 2 nm before in luminescence, and 0.08 nm compared to 0.3 nm before in excitation) [13]. Excitation spectra with such a spectral resolution cannot be scanned over a large spectral range (huge amount of beamtime needed!). Moreover, such excitation spectra make sense only on optically „thin“ systems. Therefore, no high-resolution counterpart to the HIGITI data exists till now. Concerning luminescence

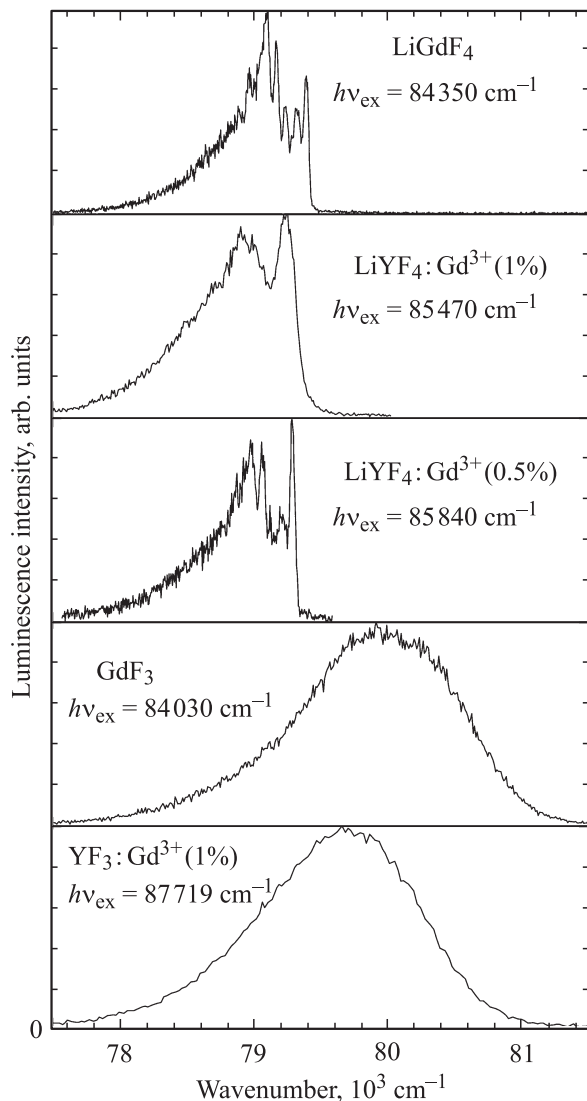


Figure 4. VUV emission ($\Delta\lambda = 0.08$ nm) of LiGdF₄, LiYF₄:Gd³⁺ (0.5%) single crystals, and of LiYF₄:Gd³⁺ (1%), GdF₃ and YF₃:Gd³⁺ (1%) powder samples. The excitation energies are given in the figure. $T = 10$ K. Reprinted figure with permission from Ref. [26]. Copyright (2007) by the American Physical Society.

analysis, position-sensitive detectors make life easier, and many systems have already been investigated.

The first examples was LiYF₄:Er³⁺ [20]. The luminescence spectra are shown in Fig. 1. Together with the respective excitation spectra, the results were already presented at the Feofilov Symposium 2004 [27]. SA and SF emission spectra yield fine structure arising from ZPLs terminating at the eight Stark levels of the ⁴I_{15/2} ground state. Comparison of $d \rightarrow f$ emission with high-resolution ⁴S_{3/2} \rightarrow ⁴I_{15/2} $f \rightarrow f$ emission [25,27] allows for discrimination between structures arising from ZPLs and vibronic structures. Concerning the excitation spectra covering a range of about 600 cm⁻¹ above threshold of the respective $f \rightarrow d$ excitation, complete saturation was observed for the

SA excitation. This is due to the rather high concentration of Er³⁺ ions (5%). However, in spite of the high concentration, many structures showed up in the SF spectrum. It turned out that the resolution interval chosen (0.15 nm) was not sufficient for a safe interpretation.

Besides Er³⁺, up to now Tm³⁺ [27–29], Gd³⁺ and Lu³⁺ high-resolution $d \leftrightarrow f$ luminescence and excitation spectra have been investigated. The cases of Gd³⁺ and Lu³⁺ will be discussed separately. The case of Tm³⁺ (matrices: LiSrAlF₆, LiCaAlF₆) turned out to be much more complex than the case of Er³⁺ [29]. Several ZPLs have been established in SA and SF $d \rightarrow f$ emission bands, indicating intermediate coupling. However, comparison with $f \rightarrow f$ emission spectra is by far not as conclusive as in the case of LiYF₄:Er³⁺. Although it is not in the focus of the present paper which concentrates on experiments with SR excitation, we would like to point out that high-resolution VUV $d \rightarrow f$ luminescence of Nd³⁺, Er³⁺, and Tm³⁺ in LiYF₄ and YPO₄ has also been investigated with VUV laser excitation [30].

5. Gd³⁺

Before the experiments to be discussed, RE³⁺ VUV $d \rightarrow f$ luminescence has been observed only from Nd³⁺, Er³⁺, and Tm³⁺. People also looked for VUV $d \rightarrow f$ luminescence from other rare earth ions with an onset of $f \rightarrow d$ excitations in the VUV spectral range, however, without success [8]. Pieterse [31] ascribed the absence of VUV emission to the presence of many $4f$ levels at energies just below the lowest energy $4f^{n-1}5d$ states, causing effective nonradiative decay from the $4f^{n-1}5d$ levels into the $4f^n$ states. The Cd³⁺ ion is the one with the largest number of f levels which are particularly dense around the onset of $f \rightarrow d$ excitations [17]. Therefore, nobody expected Gd³⁺ VUV $d \rightarrow f$ emission.

One of the reasons, why the search was started again was spectrum (b) in Fig. 3. Makhov was convinced that the rise at 127 nm due to the onset of $f \rightarrow d$ excitations [32], and the main goal was the search for detailed structures of $f \rightarrow d$ excitations. The Gd³⁺ emission itself was discovered „by accident“ [33]. The first results have been presented at Feofilov 2004 [27]. In this paper, the progress since then will be discussed.

In Fig. 4 an overview of Gd³⁺ $d \rightarrow f$ luminescence is given [26]. Trifluorides emit broad bands without sharp structures (at the given resolution 0.08 nm). LiYF₄:Gd³⁺ and LiGdF₄ emit spectra with sharp lines and structureless red wings. The trifluorides yield strong electron-phonon coupling with a Huang–Rhys factor of the order of 5 whereas in the other samples, intermediate coupling with a Huang–Rhys factor of the order of 1 is observed. In Ref. [26], many arguments are given in favour of the $d \rightarrow f$ nature of the spectra, although the dense $4f$ level system is in the energetic background. The reason why energy transfer from the lowest d level to the f levels

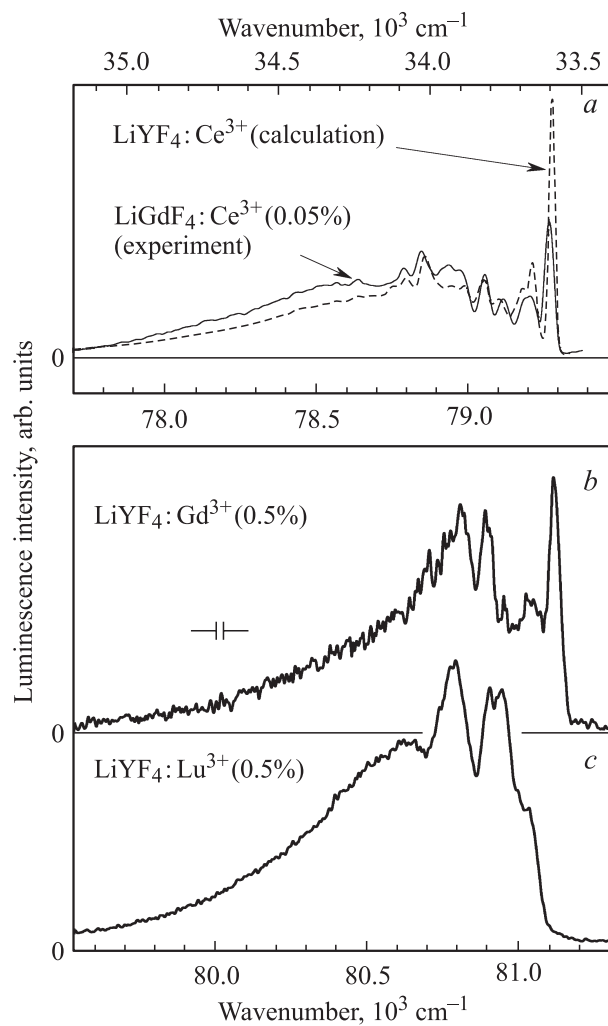


Figure 5. a) LiGdF₄:Ce³⁺ $4f \rightarrow 5d$ excitation spectrum monitored on Gd³⁺ ${}^6P_{7/2} \rightarrow {}^8S_{7/2}$ emission (solid curve), and calculated LiYF₄:Ce³⁺ $4f \rightarrow 5d$ absorption (dashed line). b) Gd³⁺ $4f^65d \rightarrow 4f^7$ emission from LiYF₄:Gd³⁺. c) Lu³⁺ $4f^{13}5d \rightarrow 4f^{14}$ emission from LiYF₄:Lu³⁺. $T = 10\text{ K}$. $\Delta\lambda = 0.08\text{ nm}$ [26].

(although it takes place [26]) does not quench $d \rightarrow f$ luminescence is the following: the spin multiplicity of the lowest d level of Gd³⁺ is eight, whereas the $4f^7$ levels closest to the $4f^65d$ levels are spin doublets or quartets [34]. Therefore, intersystem crossing is heavily spin-forbidden. Around 150 K, the $d \rightarrow f$ luminescence is quenched. An analysis of temperature dependence points towards phonon assisted intersystem crossing to the f levels [26].

The nature of the lines in the spectra with intermediate coupling was already discussed before [27]. Within the spectral resolution, only one ZPL is expected for a given site, due to the simple Gd³⁺ $4f^7$ ground state. On the other hand, different sites could not be ruled out. A key result in this context was an excitation spectrum of Ce³⁺ $5d \rightarrow 4f$ emission in LiGdF₄:Ce³⁺ (0.05%), showing the

same fine structure as Gd³⁺ $d \rightarrow f$ emission in LiGdF₄ (Fig. 5). In the Ce³⁺ case, site effects can be ruled out at the low concentration. Therefore, only one ZPL can show up, and all other structures arise from vibronic sidebands. From the similarity between Gd³⁺ emission and Ce³⁺ excitation it was concluded that the Gd³⁺ spectrum yields only one ZPL. This has been confirmed by calculations of Ce³⁺ excitation spectrum in LiYF₄ matrix [26]. The calculation is included in Fig. 5 (excitation spectrum is „reflected“ at its ZPL and then plotted in a way the the ZPL agrees with the sharp line at the high-energy onset of Gd³⁺ $d \rightarrow f$ emission). Details are discussed in Ref. [26], and a more general comparison of theory with LiYF₄Ce³⁺ experimental spectra [35] is given in Ref. [36]. LiYF₄ has been chosen as a matrix because much data were available for comparison and because a lattice dynamics model [37] was available for the calculation. The new aspect compared to Ref. [24] is the fact that vibrational spectra are explicitly taken into account. On the other hand, the calculations were restricted to ions with a few electrons (Ce³⁺, Pr³⁺, Nd³⁺) and to Lu³⁺. Excellent agreement between the Ce³⁺ spectrum and the calculations is found (Fig. 5). There is also good agreement between experimental and calculated Huang–Rhys factors which are of the order of 1 for the lowest $4f^{n-1}5d$ states. They can be very large for higher $4f^{n-1}5d$ states [26].

In Sec. 3, problems concerning interpretation of high-resolution $f \rightarrow d$ excitation spectra are discussed. There is another source of confusion concerning, in particular, the excitation spectra of the emission with a long lifetime (like SF $d \rightarrow f$ emission or $f \rightarrow f$ emission). Either in the stoichiometric systems or at higher doping levels, energy migration enables surface losses for small penetration depths of the exciting radiation. In this way, maxima in absorption can lead to minima in excitation spectra [38]. The conclusion is: only measurements on doped systems at a very low level of doping will provide us with excitation spectra which can be compared directly with calculated absorption spectra.

The only excitation spectrum near to these requirements is shown in Fig. 3, a. The maxima observed may be of electronic origin and/or may originate from vibronic side-bands. The splitting between distinct maxima is of the order of 1000 cm⁻¹, by far exceeding the splitting of vibronic sidebands as observed in luminescence. Therefore, electronic origins have to be considered. To the best of our knowledge, no calculations of Gd³⁺ $4f^7 \rightarrow 4f^65d$ excitations were published. However, extensive studies have been performed on the isoelectronic Eu²⁺ $4f^7 \rightarrow 4f^65d$ excitations [39,40]. The respective Eu²⁺ excitation spectrum [40] is quite similar to the Gd³⁺ excitation spectrum. The structures observed for Eu²⁺ $4f^7 \rightarrow 4f^65d$ transitions were traced back to the energy levels of the $4f^6$ core in the $4f^65d$ state. The levels of the $4f^6$ core were approximated by the Eu³⁺ $4f^6$ levels [39]. The Eu³⁺ $4f^6$ levels of LiYF₄:Eu³⁺ [41] are shown in Fig. 3. They were arranged in a way that the Eu³⁺ $4f^6$ ground state coincides with the Gd³⁺ $4f^7 \rightarrow 4f^65d$ ZPL. The energy range of the lower

7F_j multiplets of the $\text{Eu}^{3+} 4f^6$ configuration approximately matches the energy spread for the Gd^{3+} (as well as for Eu^{2+}) electronic transitions under discussion. Therefore, the fine structure was ascribed to electronic levels of the $4f^6 5d$ configuration [26].

6. Lu^{3+}

The discovery of Lu^{3+} VUV emission [27,33] was a result of a planned search. There was no reason why it should not exist because there are no $\text{Lu}^{3+} 4f$ levels at all in the VUV spectral range. Lu^{3+} emission was measured in $\text{LiYF}_4:\text{Lu}^{3+}$, LiLuF_4 , and in LuF_3 [26]. Like for Gd^{3+} , strong electron-phonon coupling was observed in the

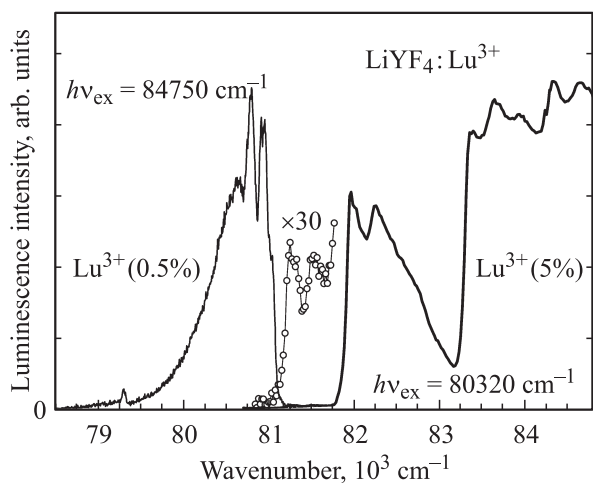


Figure 6. Lu^{3+} SF emission and excitation spectra from $\text{LiYF}_4:\text{Lu}^{3+}$. $\Delta\lambda = 0.08 \text{ nm}$, $T = 10 \text{ K}$. The spectrum in the range of SF $\text{Lu}^{3+} 4f^{14} \rightarrow 4f^{13} 5d$ excitation is given in an enlarged scale [26].

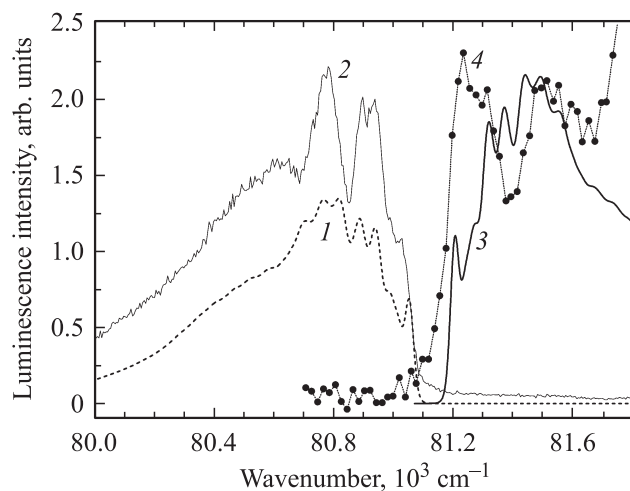


Figure 7. Low temperature simulated (1) and measured (2) emission spectra; simulated (3) and measured (4) excitation spectra in the region of $\text{Lu}^{3+} 4f-5d$ SF transition in $\text{LiYF}_4:\text{Lu}^{3+}$. Reprinted figure with permission from Ref. [26]. Copyright (2007) by the American Physical Society.

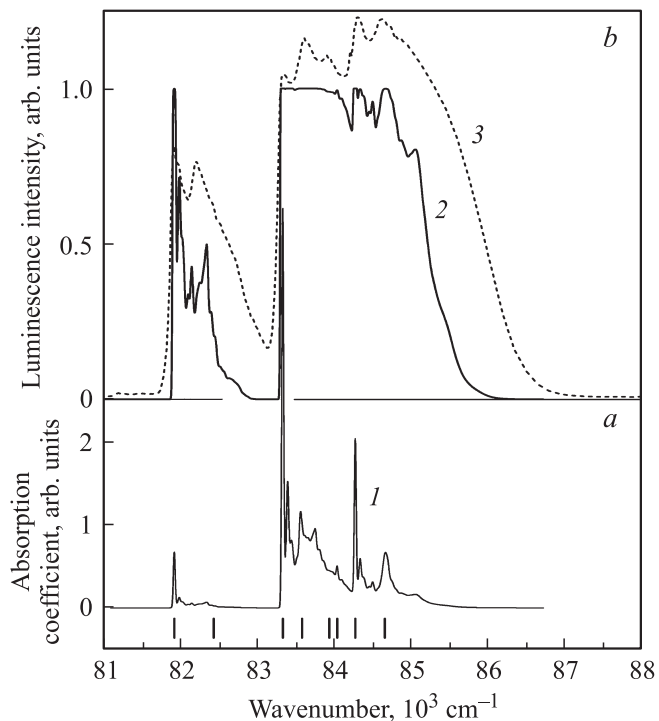


Figure 8. a) Low temperature simulated $\text{Lu}^{3+} 4f-5d$ SA absorption spectrum (thin solid curve 1). b) Modeled (bold solid curve 2) and measured (dashed curve 3) excitation spectra of $\text{LiYF}_4:\text{Lu}^{3+}$ (5%). The bars indicate calculated electronic origins.

trifluoride whereas intermediate coupling shows up in the other systems. At low temperature, only SF-type emission is observed. At elevated temperature, thermal activation leads to SA-type emission at higher energies [26]. In Fig. 6, Lu^{3+} SF $d \rightarrow f$ emission in the range between 80 000 and 81 000 cm^{-1} is shown, together with the respective excitation spectrum. The signal in the excitation spectrum at the onset of SF $f \rightarrow d$ excitation is extremely low.

The emission yields distinct maxima with a smooth side band at lower energies. The high-energy tail is crossing the low-energy tail of the excitation spectrum (SF band) at 81 100 cm^{-1} . The calculations presented in Ref. [26] show that a ZPL is absent. Therefore, the curve crossing is taken as an estimate of the electronic origin. All distinct structures observed in SF luminescence and excitation arise from vibronic sidebands. In Fig. 3, the Lu^{3+} spectrum was plotted with respect on the other spectra in a way that the estimate for the ZPL agrees with the positions of the ZPLs of the other spectra. The agreement concerning vibronic structures of the different spectra underlines the role of Ce^{3+} as a test ion as was proposed in Ref. [27].

In Fig. 7, the SF part of the Lu^{3+} spectra is compared with theory [26]. The calculated emission and excitation spectra, of course, are symmetric with respect to the electronic origin at 81 100 cm^{-1} . The agreement with the experimental emission spectrum is surprisingly good. The agreement in excitation is satisfactory as well, taking into consideration

the rather poor statistics due to the low intensity. The rise observed in the experimental curve around $81\,700\text{ cm}^{-1}$ originated from the onset of SA transitions and is not included in the calculation.

In Fig. 8, excitation spectra are presented for the SA range. Curve 1 was calculated including a convolution with the experimental resolution. At first sight, there seems to be nearly no correspondence to the experimental curve 3 on top of the figure. This is now an example showing that saturation effects have to be taken into consideration. Based on the argument that emission is proportional to what has been absorbed, from the absorption curve the amount of absorbed intensity in a crystal with thickness d was calculated. As the absorption curve was calculated in relative units, the thickness was taken as adjustable parameters. As a criterion of the fit, the relative heights of the two parts of the spectrum were taken. The result is curve 2, showing good agreement with experiment. The electronic origins in the theoretical curve are marked by bars. All other structures arise from vibronic effects.

7. Final remarks

Whereas re-vitalization of $4f^{n-1}5d$ spectroscopy of the heavier RE^{3+} ions was initiated by their potential for scintillators or quantum cutting materials, it turned out that the field is also exciting from a more fundamental point of view. The results clearly showed that it is not allowed to treat the $5d$ excited states independent of the levels of the f^n configuration. Calculations of the energy levels of the $4f^{n-1}5d$ configurations and of oscillator strengths of $4f^n \leftrightarrow 4f^{n-1}5d$ transitions in the respective crystal field are in good agreement with experiments, covering a large of excitation. High-resolution work brings about many details, in particular the interaction of the excitations with the lattice vibrations of the respective host, however, it is restricted to small energy ranges. Theoretical approaches taking into consideration electron-phonon interaction explicitly, are restricted (up to now) to a few „simple“ $4f^{n-1}5d$ configurations, but are very successful.

The experimental progress was only possible because the groups involved had access to the VUV luminescence facilities of HASYLAB. The basis of this success was the use of SR. In the future, the polarisation properties of the source should be used for spectroscopy on oriented crystals. Moreover, in view of the experience gained it would be highly desirable to perform experimental on very diluted systems because parity allowed transitions lead to saturation effects already at a low doping level, in particular if they are also spin allowed. More recently, Gd^{3+} $4f^n$ levels in the VUV have been investigated with laser spectroscopic methods of excited state absorption [42]. The combination of SR-based VUV work and excited state absorption work with laser sources would be a further push for $\text{RE}^{3+}5d$ spectroscopy.

We want to thank our colleagues involved in the SUPERLUMI work, in particular V.N. Makhov who started this research at SUPERLUMI and who pushed it all over the years. Fruitful discussions with A. Meijerink are gratefully acknowledged. Thanks are due to the „crystal growers“ providing us with samples. In particular, we are thankful to B. Malkin who provided us with complementary theoretical work. The continuous support by the technical staff of HASYLAB during many years of exciting research is gratefully acknowledged.

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