Vacuum ultraviolet 5*d*-4*f* luminescence of Gd³⁺ and Lu³⁺ ions in fluoride matrices

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Research on new optical materials is fundamental for the development of various applications, such as laser systems, plasma TVs, or new detectors for medical diagnosis. Many of these materials make use of ions of rare earth elements (RE), which can absorb and emit light in the ultraviolet and visible wavelength range efficiently. In our work, we have focused on the luminescence and excitation properties of 5d-4f transitions of gadolinium (Gd³⁺) and lutetium (Lu³⁺) ions doped into different fluoride crystals using high-resolution spectroscopy. We could analyze the excitation spectra using model calculations, and assign the fine structure observed in the spectra to different mechanisms. We regarded both pure electronic transitions within the RE ions and phonon-assisted transitions, in which the excited ions interact with the crystal lattice. While the 5d-4f transition energies in Gd³⁺ and Lu³⁺ are too high for current technical applications, our calculations for the 5d absorption bands are applicable to various combinations of host crystals and RE ions. This may be beneficial for the development of new optical materials based on RE³⁺ centres.

Trivalent RE ions play a crucial role in many optical materials, from laser crystals and scintillators to phosphors in fluorescence lamps. Characteristic for the RE³⁺ ions are the numerous *4f* states, which are only weakly coupled to the lattice, as they are shielded by the outer *5s* and *5p* orbitals. In optical spectroscopy, the *4f* states are observed as narrow-line structures. At higher photon energies, *5d* states can be excited, which have stronger coupling to the lattice. The *5d* states are usually characterized by broader bands in the spectra.
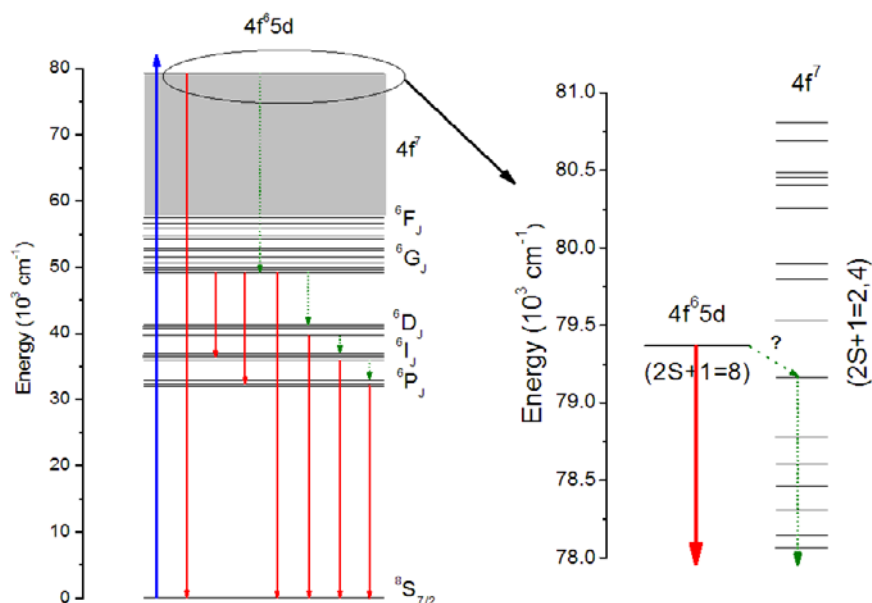
Figure 1: Simplified energy level scheme for the $4f^7$ and the lowest $4f^65d$ states of Gd^{3+} (left side). Blue arrows indicate excitation by VUV radiation, green arrows (non-radiative) relaxation, and red arrows the observed luminescence. The shaded area covers a range with many closely spaced f-levels, which cannot be distinguished in this scale. Right side: $4f^7$ levels in the energy range of the emitting $4f^65d$ state. Non-radiative transitions (intersystem crossing) between $5d$ and $4f$ states are heavily spin-forbidden. Energies according to H. M. Crosswhite et al., J. Chem. Phys. **50**, 5032 (1969).

Until recently, luminescence from trivalent rear earth ions (RE^{3+}) in the vacuum ultraviolet (VUV) has been detected only from Nd^{3+}, Er^{3+}, and Tm^{3+}. However, our studies have shown that VUV $5d$-$4f$ luminescence (hv ~ 10 eV) is also observed from Gd^{3+} and Lu^{3+} ions doped into some fluoride hosts with sufficiently wide energy band gaps [1-4]. The observation of $5d$–$4f$ luminescence from the Gd^{3+} ion is rather unexpected because of the considerable number of closely spaced $4f^7$ levels in the same energy region as the $4f^65d$ states, which should enable relaxation from the lowest Gd^{3+} $4f^65d$ level to lower-lying $4f^7$ levels (Figure 1) [5]. However, at low temperatures, a rather intense VUV luminescence has been detected from several materials containing Gd^{3+} ions. The situation is different for the Lu^{3+} ion, which has only a single ground level of the fully occupied $4f^{14}$ electronic configuration. The reason why Lu^{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^{3+} ions.
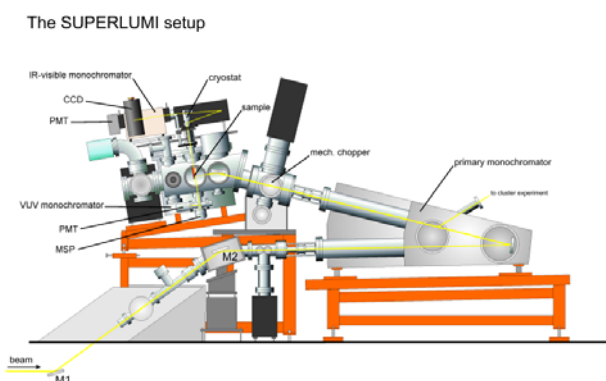

Figure 2. Front view of the SUPERLUMI setup at beamline I of DORIS. The beamline is equipped with a 2-m normal incidence primary monochromator for the VUV range, and three secondary monochromators to detect luminescence from the VUV to IR spectral range. The 1-m high-resolution monochromator used for emission spectra measurements in the VUV is not shown; it is mounted behind the vacuum chambers at a 90°-angle from the exciting beam.
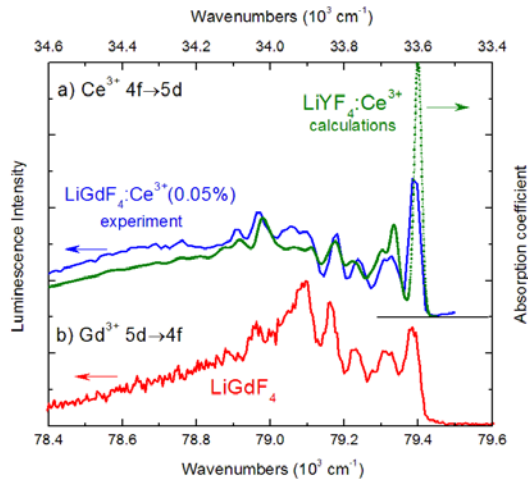
Figure 3. Comparison of phonon structure in the spectra of *5d-4f* transitions of Gd^{3+} and Ce^{3+} in the $LiGdF_4$ matrix. Part (a) shows a high resolution **excitation** spectrum of $LiGdF_4:Ce^{3+}$ (blue, upper wave number scale), and the calculated absorption spectrum for Ce^{3+} *4f-5d* transitions in $LiYF_4$ (green, upper wave number scale). (b) High resolution **emission** spectrum for $LiGdF_4$ (red, lower wave number scale). Both the Ce^{3+} excitation and the Gd^{3+} emission spectra show nearly identical features, indicating that the phonon coupling to the lattice is responsible for the observed fine structure.

The experiments were performed at the SUPERLUMI setup (Beamline I) of the DORIS storage ring (Figure 2) [6]. The 2-m primary monochromator in normal incidence mounting allows excitation in the range 4-40 eV (300-3000 Å) with resolutions up to 0.3 Å [7]. High-resolution luminescence spectra were recorded using a 1-m McPherson normal incidence monochromator with a position sensitive micro-channel plate detector. In second order, a resolution of 0.5 Å was achieved. The samples were mounted on a helium cryostat, covering temperatures in the range 4-400 K. Both single crystals and powder samples of various Gd and Lu containing fluorides were used for the measurements. All experiments were carried out under UHV conditions.
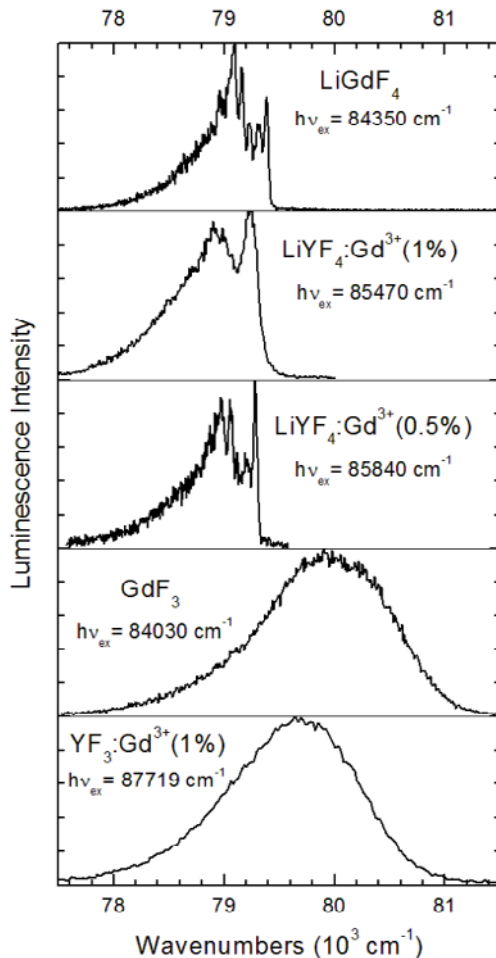

Figure 4. High-resolution VUV emission spectra (0.8 Å resolution) of various Gd^{3+} containing compounds, measured at T = 10 K. The three upper spectra show cases of intermediate coupling of the 5d states with the lattice, zero-phonon lines, and different vibronics can be observed for this case. For GdF_3 and YF_3 doped with Gd^{3+}, the coupling is stronger, resulting in broader and featureless emission bands.

In our publication, we present the results of a detailed investigation and characterization of VUV luminescence due to *5d–4f* transitions in Gd^{3+} and Lu^{3+} ions in several fluorides. In addition to high-resolution luminescence spectra, high-resolution excitation spectra have been measured as well, allowing the detailed analysis of the electron-phonon coupling. For comparison purposes, the Ce^{3+} ion with its simple electronic configuration, doped into the $LiGdF_4$ host, has been included into our investigation (Figure 3).

High-resolution emission spectra for Gd^{3+} *5d-4f* transitions in $LiGdF_4$ are displayed in Figure 3 (b), together with *4f-5d* excitation spectra of Ce^{3+} doped into $LiGdF_4$ (a), which was shifted and inverted on the energy scale. The presence of narrow zero-phonon lines and vibronics in combination with broad side-bands indicates that for this matrix the electron-phonon coupling for the lowest *5d* state is of intermediate strength (Huang-Rhys factor S ~ 1). The fine structure in both spectra matches astonishingly well. In addition, a calculated absorption curve for $LiYF_4$ doped with Ce^{3+} is given [8]. Again, all major peaks of the spectra are reproduced, confirming our assignment of the fine structure to phonon-assisted transitions.

Figure 4 shows high-resolution emission spectra due to the Gd^{3+} *5d-4f* transition in various Gd^{3+} containing matrices, measured at T = 10 K. In all cases, luminescence is thermally quenched at temperatures above 200 K. While the upper spectra of $LiGdF_4$ and $LiYF_4$:Gd^{3+} are richly structured with a series of distinct lines, the spectra of GdF_3 and YF_3:Gd^{3+} show nearly featureless emission bands. For the last two compounds, a strong coupling of Gd^{3+} ion and the lattice exists (expressed by a Huang-Rhys factor S > 5), which leads to the absence of fine structure in the spectra.
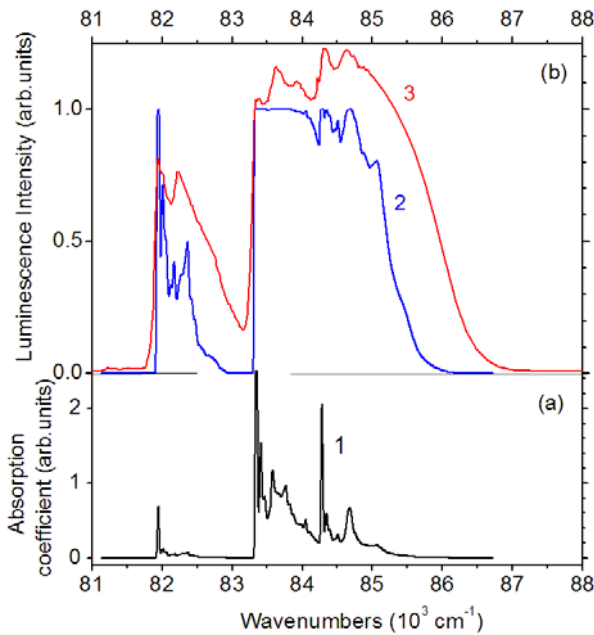

Figure 5. (a) Calculated Lu^{3+} *4f – 5d* spin-allowed absorption spectrum (1, black curve). (b) Model curve for the excitation spectrum (2, blue line) created from the calculated absorption, and measured low temperature excitation spectrum (3, red curve) for $LiYF_4$:Lu^{3+} (5%).

A comparison of calculated and measured spectra of Lu^{3+} doped into $LiYF_4$ is shown in Figure 5. A direct comparison of the absorption spectrum obtained from theoretical calculations (1) with the measured excitation spectrum (3) does not yield satisfactory results. Only after modelling the excitation spectrum (2) from absorption curve $K(\Omega)$ by approximating $1-\exp[-K(\Omega)\ d]$ (*d:* thickness of the sample), the experimental curve can be approximated. There are still various discrepancies, especially on the high-energy side of the excitation bands, but the fine structure for the *4f-5d* transitions is well reproduced within the limits of the current model.

In conclusion, we have shown that *5d-4f* emission from Gd^{3+} and Lu^{3+} incorporated into some fluoride crystals can be observed at low temperatures. Both emission and excitation spectra show a rich fine structure, which can be described in a framework of electron-phonon coupling for the *5d* states. The combination of high-resolution VUV spectroscopy and theoretical modelling using the real vibrational spectrum of the crystal lattice allows a detailed analysis of Gd^{3+} and Lu^{3+} *5d* excitations in various fluoride-type hosts. With our theoretical model, the *5d* absorption band structure can be determined for various combinations of RE ions for a given host material without need for additional experimental data. We hope therefore that calculations based on our model will be useful in the development on new optical materials based on RE^{3+} transitions.

Acknowledgements

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