VUV Luminescence Due to $5d - 4f$ Transitions in Gd^{3+} and Lu^{3+} Ions Doped into Fluoride Crystals

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High-resolution ($\Delta\lambda < 1 \text{ \AA}$) VUV emission and excitation spectra as well as luminescence decay kinetics have been studied for several fluoride crystals containing Gd^{3+} and Lu^{3+} ions under excitation by synchrotron radiation. The obtained results evidently show that VUV luminescence ($h\nu \sim 10 \text{ eV}$) observed from these crystals originates from $5d-4f$ transitions in the Gd^{3+} and Lu^{3+} ions. Only fast spin-allowed $5d-4f$ luminescence is observed from Gd compounds, whereas both spin-forbidden and spin-allowed $5d-4f$ luminescence has been detected from Lu compounds, the latter being observed only at high enough ($T > 100 \text{ K}$) temperatures.

Introduction

It is well known that some trivalent rare earth (RE) ions show radiative decay from their mixed $4f^{n-1}5d$ electronic configuration, i.e. such RE ions emit so called $5d-4f$ luminescence (1,2). This luminescence is caused by transitions from the lowest level of $4f^{n-1}5d$ electronic configuration (for the simplicity, we will call this level as the lowest $5d$ level) to the ground state or some excited levels of $4f^n$ electronic configuration of the RE^{3+} ion. Fig. 1 shows a schematic diagram for the energies of zero-phonon transitions from the ground $4f^n$ state to the lowest level of $4f^{n-1}5d$ configuration for RE^{3+} ions doped into $LiYF_4$ crystal. The data for the most of RE^{3+} ions, except for Gd^{3+} and Lu^{3+} , were taken from Refs. (3,4). For the first half of the lanthanide series, transitions from the lowest $5d$ level into the $4f$ levels are spin-allowed (SA) and $5d-4f$ luminescence is fast with typical lifetimes in the nanosecond range. As it is now commonly accepted (2-4), in the second half of series, transitions from the lowest $5d$ state (so-called high-spin (HS) state, with value of spin higher than that in the ground state) are spin-forbidden (SF), and such SF $5d-4f$ luminescence is slow with lifetimes in the μs range. However, depending on the ion, the host, and the temperature, SA luminescence from the higher-lying, so-called low-spin (LS) $5d$ state, with the same value of spin as in the ground state, can coexist with SF luminescence.

For most of the RE^{3+} ions the $4f-5d$ transitions occur in the vacuum ultraviolet (VUV) spectral range and for their experimental studies it is necessary to apply the technique of VUV spectroscopy, preferably in combination with synchrotron radiation, which is the mostly powerful tool for such kind of spectroscopy (5,6).

Up to recently, $5d-4f$ luminescence has been detected only from five RE^{3+} ions: Ce^{3+} , Pr^{3+} , Nd^{3+} , Er^{3+} , and Tm^{3+} . However, our recent studies (7-11) have shown that $5d-4f$ luminescence in deep VUV region (at about 10 eV) is observed also from Gd^{3+} and Lu^{3+} ions if these ions are incorporated into some fluoride host with sufficiently wide band-

gap. This means in particular that data on $5d-4f$ transitions from these two ions can be also used for the analysis of the trends in optical properties of RE^{3+} ions throughout the lanthanide series. In other words, energy values for $4f-5d$ transitions in RE^{3+} ions are now available for all lanthanides, except for radioactive Prometium.

Figure 1. Energies of the lowest $4f^n-5d$ levels for RE^{3+} ions doped into LiYF_4 crystal.

In the present paper, the results of detailed experimental studies of VUV luminescence due to interconfigurational $5d-4f$ transitions in Gd^{3+} and Lu^{3+} ions in several fluorides are presented.

Experimental Details

High-resolution VUV emission and excitation spectra have been measured using the SUPERLUMI set-up operated at the DORIS storage ring of HASYLAB at DESY (12,13). Emission spectra were recorded using an open position sensitive microchannel-plate detector coated with CsI in combination with a 1-meter VUV monochromator, at resolutions up to $0.5 \text{ \AA}$ in second order. The excitation spectra and decay curves of VUV emission were recorded using a Pouey type monochromator (typical spectral bandpass $\Delta\lambda=20 \text{ \AA}$) equipped with a CsI sensitized microsphere plate detector. The excitation spectra were recorded with an instrumental resolution of the primary monochromator as high as $0.7 \text{ \AA}$. The wavelength positions of all features in VUV emission and excitation spectra were determined with accuracy of $\sim 0.5 \text{ \AA}$. By applying deconvolution techniques, a time resolution of the detection system better than 0.1 ns was achieved.

Both single crystals and powder samples of several Gd- or Lu-containing stoichiometric fluoride compounds (LiGdF_4 , GdF_3 , LiLuF_4 , LuF_3) as well as of Gd^{3+} or Lu^{3+} doped fluorides (LiYF_4 , YF_3 , CaF_2) were studied. The crystalline samples were

cleaved prior to the mounting onto a copper sample holder attached to cold finger of a flow-type liquid helium cryostat. All measurements have been performed under UHV conditions.

Results and Discussion

5d – 4f Transitions in Gd³⁺

The observation of 5d-4f luminescence from the Gd³⁺ ions was rather unexpected result. It was generally supposed that such luminescence will be completely quenched due to intersystem crossing from the lowest Gd³⁺ 5d level to many 4f levels located in the same energy region as the 5d state. However the direct 5d-4f nonradiative transitions are heavily spin-forbidden because the spin multiplicity of the lowest 5d level of Gd³⁺ is eight, whereas the 4f levels of Gd³⁺ closest to the 5d level are spin doublets or quartets. Accordingly, at low temperature the radiative decay becomes the dominating decay channel for the lowest 5d state of Gd³⁺.

Figure 2. VUV emission spectra of GdF₃, LiGdF₄ and CaF₂:Gd³⁺(0.1%).

In Fig. 2 three examples of spectra of 5d-4f transitions in the Gd³⁺ ion are shown. The spectra for LiGdF₄ and CaF₂ hosts show fine structure due to zero-phonon line (ZPL) and vibronic replica followed by a broad side band that corresponds to the case of intermediate electron-lattice coupling. This is confirmed by an estimate for the Huang-Rhys parameter $S \sim 1$ from the energy difference between the ZPL and the maximum of the broad side-band, taking into account the phonon spectrum of the host lattices. In contrast to that, the spectrum for Gd trifluoride is smooth with Gaussian shape corresponding to the case of strong electron-lattice coupling (Huang-Rhys parameter is larger than 5 in this case).

Gd³⁺ ions emit fast SA 5d-4f luminescence, as it is typical for RE³⁺ ions from the first half of the lanthanide series. Decay times of Gd³⁺ 5d-4f luminescence vary in different hosts in the range from less than 1 (GdF₃) up to 8.5 ns (CaF₂:Gd³⁺).

VUV luminescence from all Gd^{3+} compounds is observed only at low temperatures. Around 100-150 K (depending on the compound) the Gd^{3+} VUV luminescence is quenched completely. The temperature dependence of the Gd^{3+} VUV luminescence intensity (as well as of the decay time) can be approximated by the well-known formulas for thermal quenching via an activation barrier ε_a :

$$I(T) = [1 + A \cdot \exp(-\varepsilon_a/k_B T)]^{-1} \quad [1]$$

$$\tau(T) = [1/\tau_r + 1/\tau_{nr} \cdot \exp(-\varepsilon_a/k_B T)]^{-1} \quad [2]$$

where k_B is Boltzmann constant, τ_r is radiative decay time and the second term in the second formula describes temperature dependence of nonradiative decay. The activation energies ε_a for thermal quenching obtained from the fit of experimental data with these formulas are of the order of one-two “characteristic” phonon energies of the host crystal (several hundreds cm^{-1} , see e.g. Ref. 10), showing that the mechanism of thermal quenching can be treated as some kind of phonon-assisted nonradiative relaxation from $5d$ to $4f$ levels.

The methodology proposed by P. Dorenbos (14), modified by us using more precise positions of ZPLs instead of maxima of broad bands, allows estimation of the lowest $4f$ - $5d$ transition energy in any RE^{3+} ion doped into a particular host if the value of this energy is known for one of the other RE^{3+} ions, e.g., for Ce^{3+} . The energy for the lowest $4f$ - $5d$ transition in a RE^{3+} ion is given by the formula:

$$E_{ZPL}^{RE} = E_{ZPL}^{Ce} + \Delta E^{RE,Ce} \quad [3]$$

where $\Delta E^{RE,Ce}$ is the energy difference between the first $4f$ - $5d$ transition in some RE^{3+} ion and the Ce^{3+} ion. This energy difference is almost independent from the host and can be regarded as an intrinsic property of the respective ion. For the Gd^{3+} ion this value is $\Delta E^{RE,Ce} = 45800 \text{ cm}^{-1}$ (14). As can be seen in Table I, the estimates agree very well with the experimental values.

TABLE I. Comparison between calculated and experimental values of the lowest $4f$ - $5d$ excitation energies (zero-phonon lines, cm^{-1}) of the Gd^{3+} ion in LiYF_4 , LiGdF_4 and CaF_2 : Gd^{3+} .

Matrix	LiYF_4	LiGdF_4	CaF_2
Ce^{3+} $4f$ - $5d$ ZPL (experiment)	33450	33615	31930
Gd^{3+} $4f$ - $5d$ ZPL (calculation)	79250	79415	77730
Gd^{3+} $4f$ - $5d$ ZPL (experiment)	79250	79377	77660

This good agreement between estimates and experimental transition energies allowed us to ascribe the observed VUV luminescence to Gd^{3+} transitions from the lowest level of $4f^6 5d$ configuration to the $4f^7$ ground state. This assignment is supported also by the following arguments. The VUV luminescence is observed in stoichiometric and weakly doped compounds, excluding possible excitonic nature of this emission. The decay time of a few nanoseconds is expected for the $5d$ - $4f$ radiative transitions in Gd^{3+} , which are SA because the lowest Gd^{3+} $4f^6 5d$ level has the same spin as the ground state. Only one transition originating from the lowest $5d$ level to the ground state is expected because of the absence of spin-orbit and negligible crystal-field splitting for the 8S ground term of Gd^{3+} ion.

When the RE^{3+} ion is doped into the host like LiYF_4 it substitutes for the Y^{3+} ion almost without distortion of the lattice since the radii of the ions are almost the same. In

this case the vibronic structure in the spectra of different RE^{3+} ions looks very similar and is determined by the phonon spectrum of the host lattice vibrations. In particular, in Fig. 3 it is well seen that the fine vibronic structure of Gd^{3+} $5d-4f$ emission spectrum (which has only one ZPL) practically coincides in shape with that of the Ce^{3+} $4f-5d$ excitation spectrum (which has also only one ZPL) both measured for the $\text{LiGdF}_4:\text{Ce}^{3+}$ crystal. As was shown in Ref. (10), this fine structure coincides also very well with the calculations of Ce^{3+} $4f-5d$ absorption spectrum, which take into account the real phonon spectrum of the host lattice vibrations.

Figure 3. Comparison of Gd^{3+} $5d-4f$ luminescence spectrum (solid curve, lower energy scale) with a Ce^{3+} $4f-5d$ excitation spectrum (dashed curve, upper energy scale) in $\text{LiGdF}_4:\text{Ce}^{3+}(0.05\%)$. Both spectra were measured at $T=10$ K.

On the other hand, if trivalent RE ions are doped into CaF_2 , they substitute for divalent Ca^{2+} ions. Accordingly, the extra positive charge of the RE^{3+} ion relative to Ca^{2+} needs some mechanism of charge compensation. This means that the RE^{3+} ions in CaF_2 crystal always occupy the defect sites and accordingly the vibronic structure in the spectra of $4f-5d$ transitions shows features caused by electron-lattice interaction with local vibrations. It is usually accepted that for small doping concentrations the RE^{3+} ions enter in CaF_2 crystal at so-called tetragonal sites for which charge compensation is achieved by interstitial fluorine ion at the nearest-neighbor position along the $[100]$ direction (15-17). The vibronic structure in the spectra for such sites is dominated by the line at the energy interval $\sim 480 \text{ cm}^{-1}$ from ZPLs. This vibration is usually interpreted as the local breathing mode oscillations of the eight fluorine ions surrounding the RE^{3+} ion. However the vibronic structure is different for the Gd^{3+} ion.

The VUV emission spectrum from the Gd^{3+} doped CaF_2 crystals shows a dominating vibronic line at an energy interval $\sim 370 \text{ cm}^{-1}$, i.e. different value compared to that observed for the tetragonal site (11). The same dominating vibronic line is observed in

the excitation spectrum. This indicates that Gd^{3+} ions reside in CaF_2 in sites of different type than that of tetragonal symmetry. However, the type of this center remains unknown.

5d – 4f Transitions in Lu^{3+}

From several Lu-containing fluoride crystals we detected also VUV luminescence, which is due to interconfigurational 5d-4f transitions in the Lu^{3+} ion. In principle the existence of such luminescence could be expected, because Lu^{3+} ion has no excited levels of the ground $4f^{14}$ electronic configuration and quenching of 5d-4f luminescence due to intersystem crossing, as in the case of the Gd^{3+} ion, cannot be expected at all for Lu^{3+} . 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 4. Lu^{3+} $4f^{13}5d - 4f^{14}$ emission and $4f^{14} - 4f^{13}5d$ excitation spectra taken from LuF_3 , $\text{LiYF}_4:\text{Lu}^{3+}$ (1.0 %) and $\text{CaF}_2:\text{Lu}^{3+}$ (0.04 %). Emission spectra are shown for $T=10$ K (solid curves) and for temperatures in the range between 160 and 200 K for different samples (dotted curves). The relative intensities of emission spectra measured at different temperatures are arbitrary.

In Fig. 4 the examples of Lu^{3+} 5d-4f emission and 4f-5d excitation spectra are shown for several fluoride matrices. Lu^{3+} ions emit at low temperatures only slow SF 5d-4f luminescence. As expected only one emission band is observed in the spectrum because of the absence of spin-orbit and crystal-field splitting of the ground 1S_0 level of Lu^{3+} and the absence of any excited 4f levels. However, an increase of temperature above 100 K

causes appearance of an additional higher-energy emission band due to SA $5d-4f$ transitions. The temperature increase opens another decay channel for the lowest HS $5d$ level of Lu^{3+} , namely thermal population of the higher-lying LS $5d$ state, from which the $5d-4f$ radiative transitions are SA. However, because of indirect excitation of the LS $5d$ state SA luminescence is also slow since it is controlled by the slow decay of SF luminescence.

Again, similar to the case of Gd^{3+} $5d-4f$ luminescence, the spectra for Lu^{3+} doped LiYF_4 and CaF_2 hosts show fine vibronic structure along with a broad side-band that corresponds to the case of intermediate electron-lattice coupling, whereas the spectra of Lu trifluoride are smooth corresponding to the case of strong electron-lattice coupling.

A specific feature of the Lu^{3+} emission spectra in LiYF_4 and CaF_2 matrices at low temperature is that the spectra have no ZPL because of very low probability for pure electronic SF $5d-4f$ transitions, and accordingly only vibronic lines are observable in the spectra. ZPL is well seen at the edge of the excitation spectra corresponding to SA $4f-5d$ transitions in Lu^{3+} . It should be mentioned also that vibronic structure of emission and excitation spectra for Lu^{3+} in CaF_2 definitely differs from that expected for RE^{3+} ions occupying the tetragonal sites, and so, again, further experimental and theoretical studies are needed in order to identify the type of sites in which Lu^{3+} ions reside in CaF_2 crystals.

We applied the methodology of P. Dorenbos also for the estimation of the energy of the lowest $4f-5d$ transition in the Lu^{3+} ion. Unfortunately the agreement between calculations and the experiment for Lu^{3+} is not so good as in the case of the Gd^{3+} ion (see Table II). We explain this fact as being due to low accuracy of the value $\Delta E^{\text{Lu,Ce}} = 49170 \text{ cm}^{-1}$ which was tabulated by P. Dorenbos basing only on a single paper on gaseous Lu^{3+} . Our experimental data allows further significant refinement of this value.

TABLE II. Comparison between calculated and experimental values of the lowest $4f-5d$ excitation energies (zero-phonon lines, cm^{-1}) of the Lu^{3+} ion in $\text{LiYF}_4\text{:Lu}^{3+}$, LiLuF_4 and $\text{CaF}_2\text{:Lu}^{3+}$.

Matrix	LiYF_4	LiGdF_4	CaF_2
Ce^{3+} $4f-5d$ ZPL (experiment)	33450	33615	31930
Lu^{3+} $4f-5d$ ZPL (calculation)	82620	82300	81100
Lu^{3+} $4f-5d$ ZPL (experiment)	81877	81777	82355

Obviously interplay with temperature of SA and SF luminescence depends on the energy separation between LS and HS $5d$ states. The trend of decreasing the energy separation between these states in RE^{3+} ions from Tb^{3+} to Yb^{3+} has been analyzed before in Ref. (18). Our data show that the energy separation for Lu^{3+} follows this trend and is equal to $\sim 800 \text{ cm}^{-1}$, i.e. of the order of only two phonon energies. As a result, the rate of phonon relaxation from the higher-lying LS $5d$ state of Lu^{3+} exceeds the rate of radiative decay at any temperature and accordingly at low temperature only SF $5d-4f$ luminescence from Lu^{3+} is observed. However, because of the same rather small energy separation between LS and HS $5d$ states thermally excited SA luminescence becomes observable at rather low temperatures $T \sim 100 \text{ K}$, resulting in emissions at high energies as shown in Fig. 4

Thermal quenching of Lu^{3+} $5d-4f$ luminescence also occurs at rather low temperatures 150-200 K. The following processes for thermal quenching of RE^{3+} $5d-4f$ luminescence can be considered: (i) nonradiative multi-phonon relaxation from the emitting $5d$ level to lower-lying $4f$ levels; (ii) thermally activated intersystem crossing (via some energy barrier) from $5d$ to $4f$ levels (e.g., as was discussed before for Gd^{3+}); (iii) thermally activated ionization of $5d$ electrons to the conduction band of the host crystal.

The Lu^{3+} ion has no excited $4f$ levels and therefore thermal quenching of Lu^{3+} $5d$ - $4f$ luminescence should be attributed to thermally activated ionization of $5d$ electrons to the conduction band. The same mechanism should be responsible for thermal quenching of Tm^{3+} $5d$ - $4f$ luminescence. For Tm^{3+} the energy gap between the highest-energy excited $4f$ 3P_2 level and the lowest $5d$ level exceeds more than 40 times the highest phonon energy of the crystal host, making improbable the mechanisms of thermal quenching for Tm^{3+} $5d$ - $4f$ luminescence due to both kinds of nonradiative relaxation to $4f$ levels. Among all three ions in the second half of lanthanide series, which show $5d$ - $4f$ luminescence, only Er^{3+} ion has some $4f$ levels with energies close to the emitting $5d$ levels, and relaxation via $4f$ levels can contribute to thermal quenching of Er^{3+} $5d$ - $4f$ luminescence.

Obviously, the temperature of thermal quenching via thermally activated ionization mechanism depends on the energy separation between the lowest $5d$ level and the bottom of the conduction band. By taking into account the decreasing trend of this energy separation towards heavier REs, which was analyzed in Ref. (19), one can expect that $5d$ - $4f$ luminescence will be quenched at lower temperatures for heavier RE^{3+} ions. Indeed, the thermal quenching of Er^{3+} $5d$ - $4f$ luminescence occurs at $T > 500$ K, whereas analogous process for Tm^{3+} $5d$ - $4f$ emission starts already at ~ 450 K. Thermal quenching of Lu^{3+} $5d$ - $4f$ luminescence occurs at much lower temperature than that of Er^{3+} and Tm^{3+} as expected, since the lowest HS $5d$ level of Lu^{3+} is situated ~ 2100 cm^{-1} closer to the conduction band than the lowest HS $5d$ level of Er^{3+} (19).

Figure 5. Trends in $5d$ levels position with respect to the conduction band for RE^{3+} ions (in LiYF_4) in the second half of lanthanide series.

If one combines data on the energy separation between HS and LS $5d$ states with data on the energy distance between the lowest $5d$ level and the bottom of the conduction band, the energy diagram shown in Fig. 5 can be obtained. The reference point in this diagram is the energy position of the lowest HS $5d$ level of Lu^{3+} (in LiYF_4), which was chosen as equal to activation energy ($\varepsilon_a = 0.22$ eV) of thermal quenching for SF Lu^{3+} $5d$ - $4f$ luminescence in this crystal obtained by fitting the experimental data with standard formula for thermal quenching (20). It can be seen from the Figure that the energy distance between the conduction band and the lowest LS $5d$ level (from which SA $5d$ - $4f$

transitions take place) is rather small and is similar for the ions from Ho^{3+} to Lu^{3+} . This consideration explains in principle why in all RE^{3+} ions from the second half of lanthanide series which show $5d-4f$ luminescence the reappearance of SA luminescence under heating is observed roughly at the same temperature range as thermal quenching of total $5d-4f$ luminescence takes place.

Conclusions

High-resolution ($\Delta\lambda < 1 \text{ \AA}$) VUV emission and excitation spectra as well as decay kinetics of VUV luminescence were obtained using synchrotron radiation for several Gd^{3+} and Lu^{3+} doped fluorides as well as for some Gd- and Lu-containing stoichiometric crystals. It was evidently shown that VUV luminescence observed in these compounds originates from $4f^65d - 4f^7$ transitions in case of the Gd^{3+} ion, and from $4f^{13}5d - 4f^{14}$ transitions in case of the Lu^{3+} ion. At first sight, the crystals with VUV emission due to $5d-4f$ transitions in the Gd^{3+} and Lu^{3+} ions look like rather exotic light emitters. However, taking into account the possibility of upconversion excitation of Gd^{3+} (via intermediate levels) to the $4f^65d$ electronic configuration by KrF excimer laser, as was shown in Ref. (21), such deep VUV emitters can play a role in future applications, e.g., in deep UV photo-lithography or in photochemistry.

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