

Vacuum UV excitation of luminescent materials by synchrotron radiation—electronic structure

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Abstract

Excitation spectra of rare earth ions doped into LaF_3 and YF_3 were recorded in the UV and VUV energy range using synchrotron radiation. For Eu^{3+} , Er^{3+} and Dy^{3+} , f-d transitions as well as charge transfer bands were localized. Transitions involving electrons of the host such as the gap energy between the valence and conduction bands were measured.

1. Introduction

The most direct source of information on the electronic energy levels in solids is provided by optical absorption and fluorescence spectra. Synchrotron radiation as a light source is a powerful tool for exploring the vacuum UV energy region. In this region, the optical properties of ionic materials such as rare earth fluorides LaF_3 and YF_3 which are wide gap insulators, are primarily determined by the electronic structure of bands due to anion and cation atomic orbitals. LaF_3 exhibits a hexagonal [1] or more probably trigonal structure [2, 3] and the YF_3 structure is orthorhombic [1]. Both can be easily doped with different lanthanide ions and form to a large extent solid solutions with the different rare earth fluorides. In LaF_3 , the tripositive rare earth ion is surrounded by three different sets consisting of three fluoride ions (site symmetry C_2 [4] but approximately D_{3h} [5]), whereas in YF_3 , the site symmetry is C_{1h} [6].

In doped materials, the excitation spectra of the $4f^n$ impurity luminescence which can be correlated with optical absorption bands, are the result either of transitions from the 4f levels of the lanthanide ion or of transitions from the occupied valence band formed by the p(F-) orbitals in the fluoride host compound. In fact, most of the vacuum UV absorption features in the energy range investigated here arise from transitions where a 4f electron is promoted to a 5d localized band. They are electric dipole Laporte allowed transitions

between two configurations of opposite parity and consequently they give rise to quite strong and broad band spectra. In contrast, the intraconfiguration 4f–4f transitions are Laporte forbidden transitions, forced by the crystal field configuration mixing. They appear, in general, considerably weaker and very sharp. In addition, in the same energy range, fluorescence of high quantum efficiency can also occur as a result of electron transfer originating in the filled molecular orbital delocalized on the ligands and terminating in the partly filled f shell of the rare earth impurity.

In higher energy regions, photon interaction with the solid involves the excitation of valence electrons from a filled valence band to an empty conduction band when photons with energy greater than the gap are absorbed. When excitations of core electrons dominate, broader structures should occur, owing to interband transitions of core electrons belonging to the host lattice. Evidence of core exciton fine structures is not always observed.

The use of tunable synchrotron radiation to excite either a common rare earth impurity in different host lattices or different rare earth impurities in the same solid host allows one to distinguish between the different photon energy absorption mechanisms occurring in the solids. In the experiments to be described, emphasis is placed on those mechanisms that also result in transfer of energy to the f-configuration of the dopant (impurity) rare earth ion, and thus to the observation of fluorescence in the visible range. Mechanisms of host excitation that do not result in energy transfer (or

are of very low quantum yield) are essentially undetected, although by direct absorption measurements they might be observed to give rise to intense absorption bands.

In this work, luminescence excitation spectra excited by VUV and UV photons, recorded on the systems $\text{LaF}_3:\text{RE}^{3+}$ and $\text{YF}_3:\text{RE}^{3+}$ ($\text{RE}^{3+} \equiv \text{Eu}^{3+}(4f^6)$, $\text{Dy}^{3+}(4f^9)$ and $\text{Er}^{3+}(4f^{11})$), are reported and discussed.

2. Experimental procedure

All spectra were obtained using synchrotron radiation from the electron beam storage ring "SUPER-ACO" at the Laboratoire d'Utilisation du Rayonnement Electromagnétique (LURE) at Orsay. The synchrotron beam line provides a photon beam with an effective spectral range of 50–350 nm (approximately 25–3.5 eV) and an average intensity of 10^{11} photons s^{-1} . The light was dispersed through a 3 m computer-driven monochromator maintained at 10^{-9} Torr and equipped with a 300 gr mm^{-1} grating blazed at 63 nm. The dispersion was 1 nm per mm and the beam dimension at the sample approximately 3 mm^2 .

Photoluminescence from the sample was observed at 45° to the VUV incident beam in a horizontal plane. The visible emitted light was collected using a silica rod 10 mm in diameter and guided onto the photomultiplier window through appropriate filters to eliminate direct scattered light and higher order effects. The signal from the photomultiplier tube was transformed by a voltage to frequency converter and stored in the computer memory *vs.* excitation wavelength.

The luminescence intensity of the sample was monitored with the measured excitation spectra of sodium salicylate whose emission is centered at 443 nm. The quantum efficiency of sodium salicylate was assumed to be constant in the energy range investigated [7, 8]. The vacuum UV incident photon beam intensity was determined from the photoelectron current induced on a gold grid at 60 nm (20.7 eV) with a cross-section yield of 0.12.

Powdered samples were obtained by the usual high temperature diffusion technique at 1100 °C under argon atmosphere. Couples of high purity fluorides (matrix + dopant) or fluoride hosts doped with rare earth sesquioxides were ground to achieve intimate mixtures and heated slowly in platinum crucibles. The resulting luminescent powders were pressed into cylindrical depressions in a sample holder using a stainless steel rod to prepare a surface as smooth as possible. The surface is an important parameter for reproducibility of intensity measurements.

Special attention was given to sample intercontamination which was checked by recording sample emis-

sion spectra under mercury line excitation using a Jobin et Yvon HR 1000 monochromator.

3. Results and discussion

An overview of the excitation spectra monitored by the visible fluorescence of Eu^{3+} , Dy^{3+} and Er^{3+} ions in LaF_3 and YF_3 is given in Figs. 1(a) and 1(b) *vs.* incident photon wavelengths ranging from 350 to 50 nm (approximately 3.5–25 eV). The fact that visible fluorescence of the rare earth ions was detected implies that the energies corresponding to the recorded absorption bands were absorbed by the doped solids and transferred to the 4f levels of the impurity ion. The intense red $^5\text{D}_0 \rightarrow ^7\text{F}_j$ multiplet transitions were used as a monitor for Eu^{3+} , the $^4\text{F}_{9/2} \rightarrow ^6\text{H}_j$ transitions for Dy^{3+} and the $^4\text{F}_{7/2} \rightarrow ^4\text{I}_j$ for Er^{3+} . The relative intensities of the recorded bands depend partly on the energy transfer efficiency, and for the borderline case where the transfer is negligible, the absorption is not revealed. For this reason, the classical absorption method or reflectivity measurements are sometimes necessary though much more difficult to achieve.

For the low energy region, from 350 to 250 nm (3.54–4.96 eV), excitation spectra in both matrices exhibit weak absorption features assigned as intraconfiguration 4f–4f transitions.

In the case of Eu^{3+} doped matrices, a weak absorption band appears around 240 nm (5.17 eV). This is due to oxygen content and is attributed to the well known charge transfer band due to electron transfer from the oxygen ligand to the Eu^{3+} central ion [9]. The crossing over of the charge transfer state with the lower $^5\text{D}_j$ states of Eu^{3+} in the normalized configuration coordinate representation provides a very efficient energy transfer towards the radiatively decaying $^5\text{D}_0$ states of the rare earth impurity. This energy relaxation mechanism is widely used in the mercury line excited Eu^{3+} doped phosphors. While the 240 nm band shows oxygen contamination of our samples, its level can be assumed to be quite low since the quantum efficiency of the mechanism involved is very high.

The oxygen electron transfer occurs at higher photon energies for Dy^{3+} and Er^{3+} . It was clearly observed in Er^{3+} doped samples, around 200 nm (6.2 eV) in LaF_3 and 180 nm (6.9 eV) in YF_3 . These values have to be compared with 240 nm recorded for Eu^{3+} in LaF_3 . This energy shift is explained if we consider that one electron is missing from the half-filled stable shell in Eu^{3+} . Then the seventh transferred electron is placed with parallel spin leading to the more stable, $4f^7$, ground configuration of Eu^{2+} (europium is the most oxidizing of the trivalent rare earths with an electron affinity high enough to observe the 2+ state). In reverse, the 10th

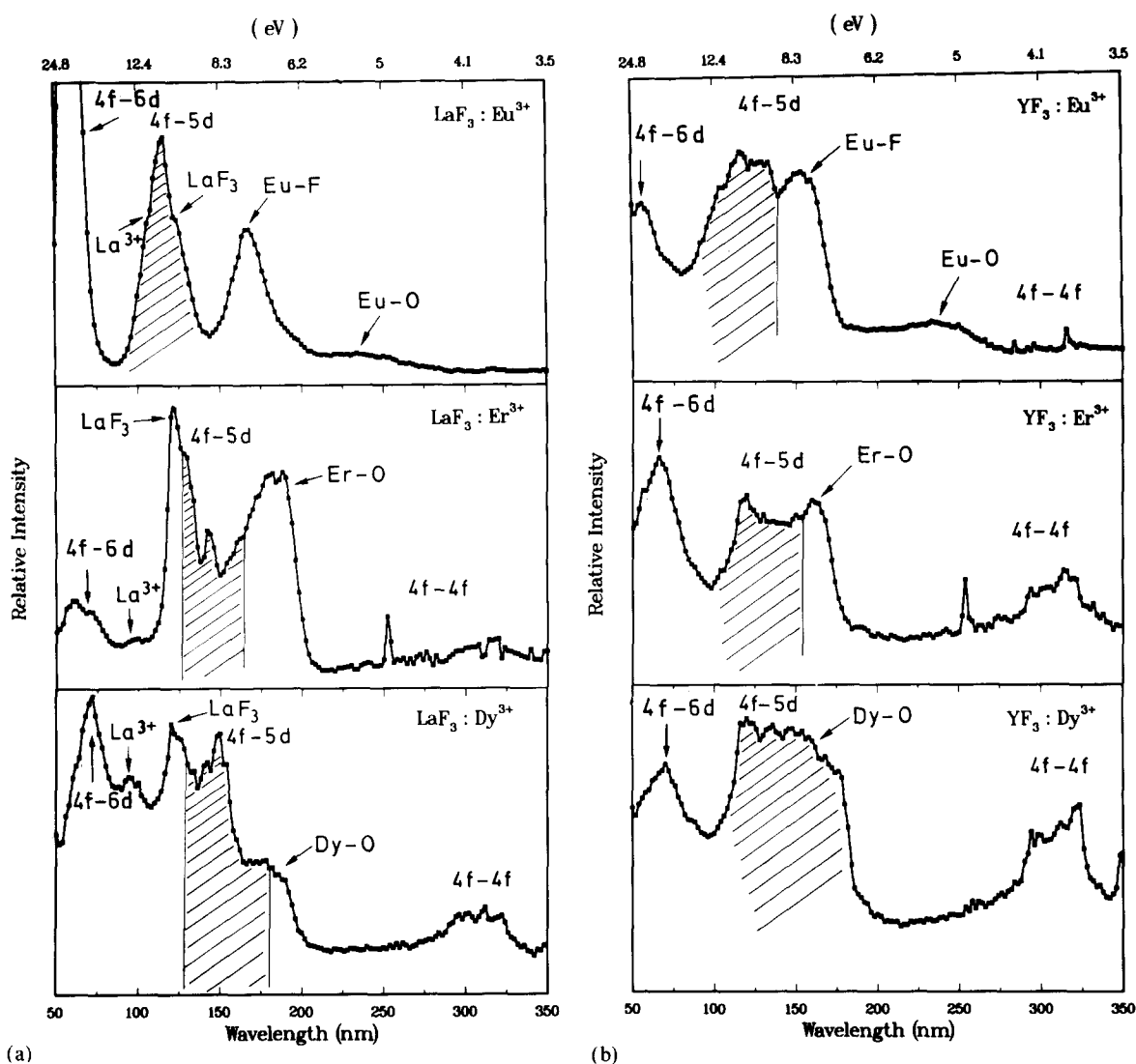


Fig. 1. Excitation spectra of (a) $\text{LaF}_3:\text{RE}^{3+}$ and (b) $\text{YF}_3:\text{RE}^{3+}$ systems ($\text{RE} \equiv \text{Eu, Er, Dy}$). The hatched part corresponds to $f \rightarrow d$ transitions.

and 12th electrons in Dy^{3+} and Er^{3+} must pair up with electrons in orbitals already occupied and consequently lose the stabilization.

It is also for this reason that the electron charge transfer from fluoride ligands to the metallic central ion is only clearly observed in Eu^{3+} doped samples at 180 nm (6.9 eV) in YF_3 and 190 nm (6.5 eV) in LaF_3 . For Dy^{3+} and Er^{3+} , it must occur at much higher energies. The energy shift, measured on Eu^{3+} samples (2.8 eV), from oxygen to fluoride ligands is in full agreement with the large electronegativity of the host fluorine ion.

The next higher energy transitions are the lanthanide impurity $4f^{n-1} \rightarrow 5d^1$ interconfiguration transitions. The general characteristic of these parity allowed transitions, resulting from the promotion of a 4f electron into the 5d level, is a broad bandwidth due to a strong

crystal field interaction. As is well known, for a 5d electron the crystal field perturbation becomes much stronger than the spin-orbit coupling because of the large radial extension of the 5d orbitals. In general, the overlapping between the charge transfer band and the $f \rightarrow d$ transitions makes their identification difficult. However, in some of our doped materials it is possible to distinguish between both interactions. This is the case for the $\text{LaF}_3:\text{Dy}^{3+}$ system where the low-lying level of the d band appears at around 165 nm (7.5 eV) and for $\text{YF}_3:\text{Eu}^{3+}$ where the bottom of the d band is situated at around 140 nm (8.9 eV).

For higher energy photons, we assign the excitation bands of the visible fluorescence to band to band transition or core excitations of the host lattice. The band to band transition in LaF_3 (Fig. 2), occurs between

TABLE 1. Resonant absorption energies in $\text{LaF}_3:\text{RE}^{3+}$ and $\text{YF}_3:\text{RE}^{3+}$ systems ($\text{RE} \equiv \text{Eu}, \text{Er}, \text{Dy}$)

Host	Band to band transition	Lowest level 4f-5d configuration	Charge transfer band
LaF_3	120 nm (10.3 eV)	Eu^{3+} , 125 nm (9.9 eV)	Eu-O, 250 nm (5.0 eV)
		Er^{3+} , 165 nm (7.5 eV)	Eu-F, 190 nm (6.5 eV)
		Dy^{3+} , 175 nm (7.0 eV)	Er-O, 200 nm (6.2 eV)
YF_3	115 nm? (10.8 eV)	Eu^{3+} , 140 nm (8.8 eV)	Dy-O, 200 nm (6.2 eV)
		Er^{3+} , 155 nm (8.0 eV)	Eu-O, 240 nm (5.2 eV)
		Dy^{3+} , 187 nm (6.6 eV)	Eu-F, 180 nm (6.9 eV)
			Er-O, 180 nm (6.9 eV)
			Dy-O, 180 nm (6.9 eV)

the occupied 2p (F^-) orbitals forming the valence band, and the conduction band which originates from 5d and 6s unoccupied orbitals of La^{3+} , probably partially overlapped with 3s orbitals of F^- ions. This absorption band is clearly observed at 120 nm (10.3 eV) in $\text{LaF}_3:\text{Er}^{3+}$, consistent with data reported in the literature [10, 11]. From 100 nm (12.4 eV), towards the lowest wavelengths, the strong features are attributed to 4f-6d transitions in the rare earth ions overlapped with excitation of core levels of the lattice ions. In the last case the absorptions arise from the deeper 5p orbitals in La^{3+} towards the excited 5d and 6s orbitals. Promotion of valence band electrons into parts of the conduction band have also to be considered. All these host levels are assumed to be more or less strongly coupled with the excited levels of the impurity, depending upon whether they produce more or less luminescence of the 4f system. For the YF_3 samples, the spectra are less clear. The large peak centered at around 60 nm (20 eV) seems to be due to transitions localized on the impurity

and could be assigned as 4f \rightarrow 6d interconfiguration transitions.

All the results are regrouped in Table 1.

4. Conclusion

The excitation spectra of rare earth impurity luminescence in fluoride hosts allow one to distinguish, in the UV and vacuum UV energy range, different mechanisms of interaction between photons and solids. Conclusions can be drawn from the different spectra of different activators in the same host lattice or the same activator in different lattices. By exciting the lanthanide samples, it is quite easy to distinguish between intraconfiguration or interconfiguration transitions but the distinction between interconfiguration transitions and charge transfer bands can only be achieved by selecting the host-impurity couple. In the energy range investigated, we expect a structureless band for the electron transfer and broad structured features due to a large crystal field splitting of the d levels. The shift between the lowest levels of the d band for a common 4fⁿ ion in the two hosts, LaF_3 and YF_3 , is partly dependent upon the host crystal field effect. For higher energy photons broad structures arise from interband transitions of core electrons of the host overlapped with interconfiguration transitions.

The main interest of the present investigation is focused on the localization in energy of the different charge transfer bands involving in our case oxygen and fluorine anions and determination of the energy gap in ionic compounds. These values can be compared with those calculated using different theoretical models in order to check the model validity.

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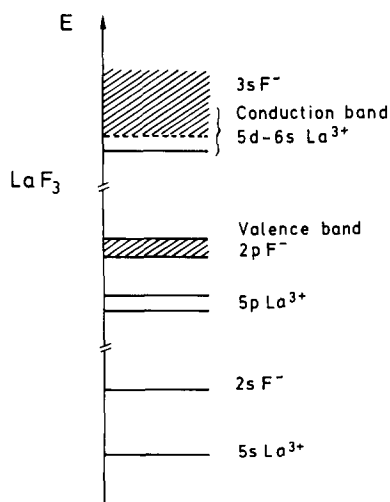


Fig. 2. Energy level diagram for LaF_3 .

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