Photoluminescence of Europium Complexes

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Introduction

Luminescent europium-based materials have attracted a great deal of attention over the past several decades for their applications ranging from optoelectronic devices and sensors to cellular imaging [1–3]. The excitation (mainly UV) of strongly absorbing organic ligands often results in sensitization of pure red emission from Eu^{3+} complexes, and their spectra due to f-f transitions display large {pseudo}-stokes shifts with long radiative lifetimes [4]. Recent synthetic efforts have also produced visible-light excitable europium complexes which have advantages in biological imaging and for the development of photostable and energy efficient Eu^{3+}-based optoelectronic devices [5,6]. On the other hand, some europium complexes (and doped-nanocrystals) have been shown to display white luminescence due to multiple emissions originating from attached ligands and the Eu^{3+} ion [7–11], which have potential applications in fabrication of single component white organic light emitting diodes (OLEDs) [11]. However, the balance of ligand and metal emission, which determines the emission aggregation. The aggregation of molecular complexes is a self-assembly process, which occurs due to non-covalent interactions and could lead to the formation of larger systems in the range of nano- and micrometres [12]. Since the fabrication of OLEDs involves processing of emitting material from solution to form thin films, which typically are known to form aggregates [13], and considering the above mentioned sensitivity of ligand and metal emission, it is important to understand whether individual molecular species and aggregates of a potentially active Eu^{3+}-based white OLED material emit in the same manner as they do emit in the bulk. However, it is difficult to characterize individual molecular species and aggregates of a luminescent material in solution using photoluminescence (PL) spectroscopy, because ensemble measurements provide an average value rather than the distribution of optical behaviours. On the contrary, single-emitter spectroscopy has been shown to provide novel insights on the heterogeneity of optical properties in a wide variety of luminescent materials [14–17]. Even

sub-ensemble spectroscopic measurements have been useful to understand the diversity of optical behaviours in luminescent materials, especially in the context of aggregates. For instance, a wide variety of optoelectronic behaviours, in terms of both transition energies and radiative lifetimes, have been observed for individual nanoaggregates of conjugated polymers, used as active components of OLEDs [18–20]. There are few reports colour in such complexes, is found to be sensitive to many factors such as solvents, excitation wavelength, temperature and degree of by groups of Lakowicz, Alexandrou and Majima on single molecule/particle imaging of Eu-complexes and Eu-doped semiconductor nanocrystals, which suggest that Eu^{3+} emission can be detected near single-molecule/particle levels [21–23]. The 9-hydroxyphenalenone forms stable complexes with Eu^{3+} ion, which show visible-light sensitized red-europium emission [24–27]. Here, they report near white-light emission from europium complex species with 9-hydroxyphenalenone which have been obtained in methanol and investigated emission characteristics of individual nanoaggregates (NAs) composed of these Eu complex species in the solid state using spectrally resolved PL imaging. Our motivation is to probe whether spatially well separated NAs behave in a similar manner as observed in ensemble and investigate the sensitivity on the balance of metal and ligand emission in individual NAs. Our results show a remarkable heterogeneity in the emission behaviours of complex species at NA levels; not only is the sensitization efficiency enhanced in a majority of sNAs, but also the relative intensities of the $^7F_2$ and $^7F_1$ transitions of Eu^{3+} show considerable variation.

The trivalent europium ion (Eu^{3+}) exhibits an intense red photoluminescence upon irradiation with UV radiation. This photoluminescence is observed not only for Eu^{3+} ions doped into crystalline host matrices or glasses, but also for europium(III) complexes with organic ligands. These ligands can act as an antenna to absorb the excitation light and to transfer the excite energy to the higher energy levels of the Eu^{3+} ion, from which the emitting excited levels can

be populated. The photoluminescence of europium(III) complexes has been studied in solutions [28,29,], polymer matrices [30,31], sol–gel glasses [32,33], functionalized sol–gel glasses [7–11], iono gels [39,40], liquid crystals[41–43], encapsulated into inorganic hosts such as zeolites [44–47]and in metal–organic frameworks (MOFs) [48,49]. The design of europium (III) containing inorganic–organic hybrid materials is a popular research field [50–53]. Europium (III) complexes can be excellent luminescent probes for biochemical or biomedical applications [54–60]. The most important application of europium is the red phosphor Y_2O_3:Eu^{3+}(YOX) in fluorescent lamps [61–63].The red emission of Eu^{3+} can be achieved not only by excitation with UV light, but also by irradiation with an electron beam(cathodoluminescence) [64,65], X-rays, ϒ-rays, α or β particles(radioluminescence) [66–69], strong electric fields (electroluminescence) [70,71], mechanical agitation (triboluminescence or mechanoluminescence) [72–74] or by chemical reactions (chemiluminescence) [75]. A well-known cathodoluminescent phosphoris Y_2O_2S:Eu^{3+}, which is the red phosphor used in the old-fashioned cathode-ray tubes of colour television screens or computer monitors [64,65,76]. This compound replaced the older cathode luminescent europium (III) phosphor YVO_4:Eu^{3+} [77,78]. It is worth mentioning that europium is present in the anti-counterfeiting ink of EURO bank notes [79]. Not only its red luminescence, but also the narrow transitions in the absorption and luminescence spectra are typical features of the Eu^{3+} ion, and these spectroscopic properties have been known from the earliest history of the chemical element europium. The sharp lines in the absorption spectra of Eu^{3+} in solution were first described in 1900 by Demarc̦ay, the discoverer of europium [80], and his observations were confirmed by Prandtl in 1920 [81]. Prandtl was the first to publish a picture of an absorption spectrum of Eu^{3+}[82]. In 1906, Urbain reported on the red luminescence of Eu_2O_3 diluted in lime [83,84]. However, two years earlier in 1904,Urbain had already noticed that crystals of europium(III) sulfateoctahydrate, $Eu_2(SO_4)_3·8H_2O$, had a faint pink colour [85], but he didn't realize that this colour was caused

by the photoluminescence of Eu^{3+} ions excited by the UV part of sunlight [86]. In the absence of this luminescence, europium (III) compounds are colourless. In 1909, Urbain described the cathodoluminescence of Gd_2O_3:Eu^{3+}[87]. The fine structure and the relative intensities of the transitions in the absorption and luminescence spectra of Eu^{3+} can be used to probe the local environment of the Eu^{3+} ion. The spectroscopic data give information on the point group symmetry of the Eu^{3+} site and sometimes also information on the coordination polyhedron. However, a rigorous interpretation of europium(III) spectra can be a daunting task for newcomers in the field of lanthanide coordination chemistry. Chemists who have been trained in the synthesis and characterization of luminescent lanthanide complexes are often lacking a sound theoretical background in lanthanide spectroscopy. The classical books or reviews on spectroscopy of rare earths are often too theoretical or put little emphasis on the relationship between features observed in spectra and structural properties [88–97]. There exist several reviews on the luminescence of lanthanide-based molecular materials or photophysics of lanthanides, but only few of them focus on the Eu^{3+} ion in detail [50,51,54,55,60,91,98–127]. In general, these works do not give a detailed description of the transitions in europium (III) spectra. As a consequence, many authors who describe luminescent europium(III) complexes do not go beyond reporting general statements with little information content, such as mentioning that the transitions observed in the luminescence spectra are the $^5D_0{\rightarrow}^7F_J$ (J = 0–6) transitions or that a very intense hypersensitive transition $^5D_0{\rightarrow}^7F_2$ indicates that the Eu^{3+} is not at a site with a centre of symmetry.

K. Iftikhar *et al.* reported photophysical characteristics of a newly synthesized ternary complexes of Eu with acetylacetone (acac) and a heterocyclic amine, pyrazine (pyz): [Eu(acac)$_3$(pyz)$_2$] in solutions and in the solid state. The primary sensitizer acac was chosen because of its versatile nature and stability under normal conditions. Pyrazine as the ancillary ligand is chosen because it is an efficient chromophore, which has the triplet state at the

optimum energy level. The reaction of [Eu(acac)$_3$(H$_2$O)$_2$] with pyrazine (pyz) gives rise to octa-coordinate square anti-prismatic [Eu(acac)$_3$(pyz)$_2$] complex. The importance of the present investigation is summarized as follows: (i) the complex show excellent photoluminescent properties. The photophysical studies revealed that acac and pyz act as efficient sensitizers. The PL spectra in solutions show remarkable variations in the lanthanide ion-centred luminescence and residual fluorescence, (ii) the complex exhibit phase controlled colour tuning properties exploring their possible use as 'colour indicators'. This facile luminescence variation has a strong advantage of simple procedure to perform, (iii) the theoretical intensity parameters and experimental intensity parameters of the Eu^{3+} complex were calculated and are found to be in good agreement, (iv) the intramolecular energy transfer process predominantly occurs from triplet state $\rightarrow$ ^{5}D$_{0,1}$ and it represents a favourable path. The overall energy transfer takes the path from S$_0$ $\rightarrow$ S$_1$ $\rightarrow$ T$_1$ $\rightarrow$ ^{5}D$_1$ $\rightarrow$ ^{5}D$_0$ $\rightarrow$ ^{7}F$_{0,4}$, and (v) the polyvinyl alcohol (PVA) encapsulated matrices of display superior photostability over the pure complexes with improved photoluminescence. The simple synthesis method, desirable photophysical properties, colour tunability and excellent photostability under normal conditions are promising for use of such materials in device applications and their simplified use as 'colour indicators' [130].

In another work, K. Iftikhar *et al.* reported the synthesis of dinuclear lanthanide β-diketonate complex of general composition [Ln^{1}Ln^2(fod)$_6$(μ-bpm)] (where Ln^1–Ln^2 = Eu–Tb; fod = 6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl- 3,5-octanedionate; bpm = 2,2-bipyrimidine) in which the two lanthanide ions are bridged by a bis-diimine ligand, bpm. The syntheses of the complex were based on the fact that coordinatively unsaturated Ln(β-diketonate)$_3$ chelates rapidly react with diimine ligands such as 1,10-phenanthroline (phen) and 2,2-bipyridyl (bpy) to form coordinatively saturated adducts. The association constant for this process is usually _1 in non-polar solvents. Therefore, it was presumed that a 1:1 reaction of Ln^1(fod)$_3$ and bpm would lead

to the rapid formation of an intermediate adduct, [Ln^1(fod)$_3$(bpm)], with a vacant chelating site on bpm. Dinuclear lanthanide complex of general composition [Ln^{1}Ln^2(fod)$_6$(μ-bpm)] have been synthesized and investigated by f–f absorption and steady-state emission spectroscopy in non-coordinating and coordinating solvents. The complex show good thermal stability up to 200–230ºC, with sharp melting points and do not decompose. The oscillator strengths of the f–f transitions of different lanthanide centres of the complex in comparison with the oscillator strength of their mononuclear and homo dinuclear analogues corroborates well with the stoichiometrically 1:1 hetero dinuclear nature of the complexes. Pyridine (a strong coordinating solvent) brings changes in both the oscillator strength and the band shape of the hypersensitive transitions which is attributed to a change in asymmetry of the field around Ln^{3+} ions due to the coordination of the solvent. However, it is remarkable that a small difference in the size of the lanthanide ions across the series has great impact on the symmetry acquired around the Ln^{3+} ion in the pyridine solution. The steady-state emission spectroscopy proved to be useful technique to study complex–pyridine interactions in solution. The emission spectrum of the complex in pyridine, displayed enhanced intensity of the Eu^{3+} $^5D_0 \rightarrow {}^7F_2$ hypersensitive transition from which the fine structure (stark splitting) have disappeared as compared to the spectrum of the complex in chloroform. Furthermore, ligand fluorescence was also observed in the spectrum of pyridine, which was absent in its spectrum in chloroform. The observation led to the conclusion that the complex dissociates in pyridine and forms two species: [Eu(fod)$_3$(py)$_n$] and [Tb(fod)$_3$(py)$_n$] [131].

In another work, K. Iftikhar *et al.* reported the results of photoluminescence and 4f–4f absorption properties of [Eu(fod)$_3$(bpy)], complex { fod = anion of 6,6,7,7,8,8,8- heptafluoro-2,2-dimethyl-3,5-octanedione; bpy = 2,2′-bipyridyl, phen = 1,10-phenanthroline, bpm = 2, 2′-bipyrimidine; Eu(III) at room temperature in a series of non-aqueous solvents. The effect of changing the environment (ligand/solvent) around the metal ions on the luminescence intensity

and band shape of hypersensitive transition of Eu(III) complex. The photoluminescence properties of eight-coordinate Eu(III) β-diketonate complex with various diimine ligands in solution are sensitive towards; (i) donor solvents due to changes in the inner coordination sphere around Eu(III) ion and (ii) the sensitizing ability of the ancillary ligands. It is also observed that some coordinating solvents (methanol, ethanol and pyridine) have a great impact on the oscillator strength and band shape of the 4f–4f hypersensitive transitions. [132]

In another work, K. Iftikhar *et al.* reported the synthesis, crystal structure and photophysical properties of a novel europium ternary β-diketonate: [Eu(dbm)$_3$(impy)] (dbm is the anion of dibenzoylmethane and impy is the neutral 2-(1Himidazol- 2-yl)pyridine ligand). The reaction of [Eu(dbm)$_3$(H$_2$O)] and impy in ethanol leads to the formation of an octa-coordinated [Eu(dbm)$_3$(impy)] complex. Single crystal X-ray analysis was used to establish the distorted square antiprismatic geometry of the octacoordinate complex. The thermal stability of the complex is good, since it is stable up to 205°C, which makes it suitable for the fabrication of LEDs. The $^5D_0$-$^7F_2$ transition is expected to be forbidden in distorted D$_4$d structures, [57] however, this transition is fairly strong with prominent Stark splitting in the solid complex as well as in the hybrid film. This is due to the mixing of two different states with different J values.[67] The electric-dipole $^5D_0$ - $^7F_0$ transition is sufficiently strong in the solid complex and polymer film. The lifetime of [Eu(dbm)$_3$(impy)] is longer than [Eu(dbm)$_3$(H$_2$O)] in each phase, indicating efficient energy transfer from the triplet state of impy to the emitting level of Eu(III). The decay time of the $^5D_0 \rightarrow ^7F_2$ transition of the hybrid film of the complex is the longest, followed by the solid complex and then the chloroform solution. The CIE chromaticity results show that the solid complex and the hybrid film emit a red colour, whereas the chloroform solution emits a pink colour. The pink colour emission indicates that both red and white light are emitted simultaneously and the mixing of white light dilutes the red, leading to pink. [133]

In another work, K. Iftikhar *et al.* reported the photophysical properties of [Eu(hfaa)$_3$(impy)$_2$] complex (impy is 2-(1H-imidazol-2-yl)pyridine and hfaa is the anion of hexafluoroacetylacetone) . Luminescent Eu(III) complex containing hfaa and impy ligands have been synthesized and characterised. The distorted square antiprismatic geometry is predicted by Sparkle/ RM1 calculations for Eu(III) complex. The complex is thermally stable up to 405 °C. The photoluminescence Eu(III) complex were studied in solid, solution and hybrid films with different concentrations. The complex are highly quantum efficient. emission colour obtained is different in various phases. The change in concentration of the corresponding complex in PMMA substrate results in different emission. The colour change of the emitted light from the thin hybrid films explores their possible use as 'colour indicator diodes'. The PMMA hybrid films of the complex exhibit outstanding photostability over the corresponding bare complex. A good agreement is found between theoretical and experimental JO intensity parameters of Eu(III) complex. The intramolecular energy transfer rates (WET and WBT), in the case of Eu(III) complex, demonstrate that the major energy transfer channels are triplet state $\rightarrow$ $^5D_1$ (it contributes 55.33%) and triplet state $\rightarrow$ $^5D_0$ (it contributes 44.65%). The energy transfer follows the path $S_0 \rightarrow S_1 \rightarrow T_1 \rightarrow {}^5D_1 \rightarrow {}^5D_0 \rightarrow {}^7F_0$, This work not only provides an excellent luminescent and colour tuning features of the synthesized complex, but also provides simple methods for the design of highly photostable luminescent materials.[134]

In another work, K. Iftikhar *et al.* reported the [Eu(hfaa)$_3$phen] complex with Hhfaa and phen and study of their photosensitized luminescence and NM spectra.The results obtained that (i) lanthanide chloride and ammonium hydroxide are much better reagents for obtaining higher yield of the complex investigated, (ii) the complex are thermally very stable and are volatile in nature. Such thermal properties are interesting and important in view of the use of this complex as molecular materials processed by thermal evaporation, (iii) huge upfield and downfield paramagnetic shifts observed for hfaa and phen protons are dipolar in nature. The paramagnetic

shift of the methine protons, in the complex, has their sign opposed to that of paramagnetic shifts of the aromatic protons[135].

In another work, K. Iftikhar *et al.* reported synthesis, structure, thermal behaviour, 4f−4f absorption, and photophysical properties, in the visible and NIR regions, of the [Eu(hfaa)$_3$(pz)$_2$] complex.In an effort to synthesize low-symmetry seven-coordinate lanthanide complexes, the lanthanide chlorides, hfaa and pyrazole, were allowed to react in a 1:3:1 molar ratio in ethanol. However, the reaction did not give the desired product; eight coordinate [Eu(hfaa)$_3$(pz)$_2$] were formed. The complex is highly volatile with low melting points. The presence of electronegative fluorines at the two terminals facilitates the coordination of two pyrazole molecules. The single-crystal X-ray analysis of the Eu complex reveals that the complex crystallize in the monoclinic space group P$_{21}$/c. The lanthanide ion in each of the complex is eight-coordinate with six oxygen atoms from three hfaa and two N-atoms from two pyrazole units and acquires distorted square antiprism structure. The complex is highly luminescent and have volatile nature with low melting point, making them suitable candidates for making luminescent thin film and, consequently, their use in fabricating light-emitting devices operating at lower temperature. The opposite direction shifts of the methine and pyrazole protons, in a given complex, indicate that the induced paramagnetic shifts are predominantly dipolar in nature. The quantum yield and lifetime of Eu(III), in the visible region. The primary ligand, hexaflouroacetylacetone, is a good sensitizer for the complex. The environment around the metal ions is asymmetric, which leads to increased radiative rates and luminescence efficiency [136].

In another work, K. Iftikhar *et al.* reported a modified one step in situ route for the synthesis of [Eu(hfaa)$_3$(bpy)$_2$] complex with hexafluoroacetylacetone (Hhfaa) and 2,2-bipyridine (bpy) in high yields at room temperature (303 K). The reaction of Hhfaa, NH$_4$OH (25% ammonia), bpy and LnCl3.nH$_2$O in a single pot in a 3:3:1:1 or 3:3:2:1 Mratio in ethanol leads to isolation of

air and moisture,stable eight-coordinate complex [Eu (hfaa)$_3$(bpy)] in a high yield. The intermolecular chemical shift ratios of the eight-coordinate complexes are similar in magnitude, indicating that the shifts are predominantly dipolar in nature and the complex are isostructural in solution.[137].

In another work, K. Iftikhar *et al.* reported a method to syntheses [Eu (hfaa)$_3$(indazole)$_n$] complex and hfaa is the anion of hexafluoroacetylacetone n = 3) using indazole ligand, at room temperature. The photophysical properties of indazole and the crystallographically characterized monometallic complex of europium, has been analyzed both as a solid and in solution. The reaction of hydrated Ln(III) chlorides, Hhfaa, and indazole in the presence of ammonium hydroxide in one pot (in situ) gives rise to formation of [Eu(hfaa)$_3$(indazole)$_3$] complex. The Eu in this complex acquired distorted monocapped square antiprismatic structure. The Eu complex is stabilized by the π−π stacking interactions between indazole groups with an interplanar distance of 4.02 and 3.96 Å. The overall stability of the complex is reinforced by the presence of hydrogen bonds between N−H group of indazoles and fluorine atoms of hfaa, N−H⋯F (hfaa−), which facilitates the photoluminescence and electroluminescence properties. The coordination environment, which consists of three hfaa− and indazoles, provides an effective shield around the Eu, that protects the ions from the outer environment (surrounding), and the outcome of this protection is reflected in the form of better luminescence (larger quantum yields) and longer radiative lifetime. Finally, possible use of the compound was explored in fabricating electroluminescent devices by making their emitting layers. The devices having CuPc layers showed better performance as compared to the devices with TDP layers. the best devices were found with the following structure: ITO/CuPc (15 nm)/[Eu complex]:CBP. It was achieved by increasing thicknesses of the layer [138].

Energy level structure of the [Xe]4f^6 configuration

Eu^{3+} has 60 electrons, 54 electrons in the same closed shells as the xenon atom and 6 electrons in the 4f shell. This electronic configuration can be written as [Xe]4f^6, or 4f^6 for short. The 4f shell is well shielded from its environment by the closed 5s^2 and 5p^6 outer shells [139]. The six electrons in the 4f shell can be arranged in 3003 different ways into the seven 4f orbitals, so that the total degeneracy of the [Xe]4f^6 electronic configuration of the trivalent Eu^{3+}ion is 3003. The degeneracy of a 4f^n electronic configuration is given by the binomial coefficient: (1) Here n is the number of 4f electrons (n = 6 for Eu^{3+}). Each different electronic arrangement is called a microstate. The degeneracy of the 4f^6 configuration is partly or totally lifted by several perturbations acting on the Eu^{3+}ion: electron repulsion, spin–orbit coupling, the crystal-field perturbation and eventually the Zeeman effect. The electron repulsion is the electrostatic interaction between the different electrons in the 4f shell. The spin–orbit coupling results from the interaction between the spin magnetic moment of the electron and the magnetic field created by the movement of the electron around the nucleus. The crystal-field effect is caused by the interactions between the 4f electrons and the electrons of the ligands. The Zeeman effect is the splitting of the energy levels by an external magnetic field. After introduction of electron repulsion, the [Xe]4f^6 configuration is characterized by ^{119} $^{2S+1}$L(tau_) terms [140]. The degeneracy of each term is (2S + 1)(2L + 1). S is the total spin quantum number and L is the total

$$\binom{n}{14} = 14! / n!(14 - n)!$$

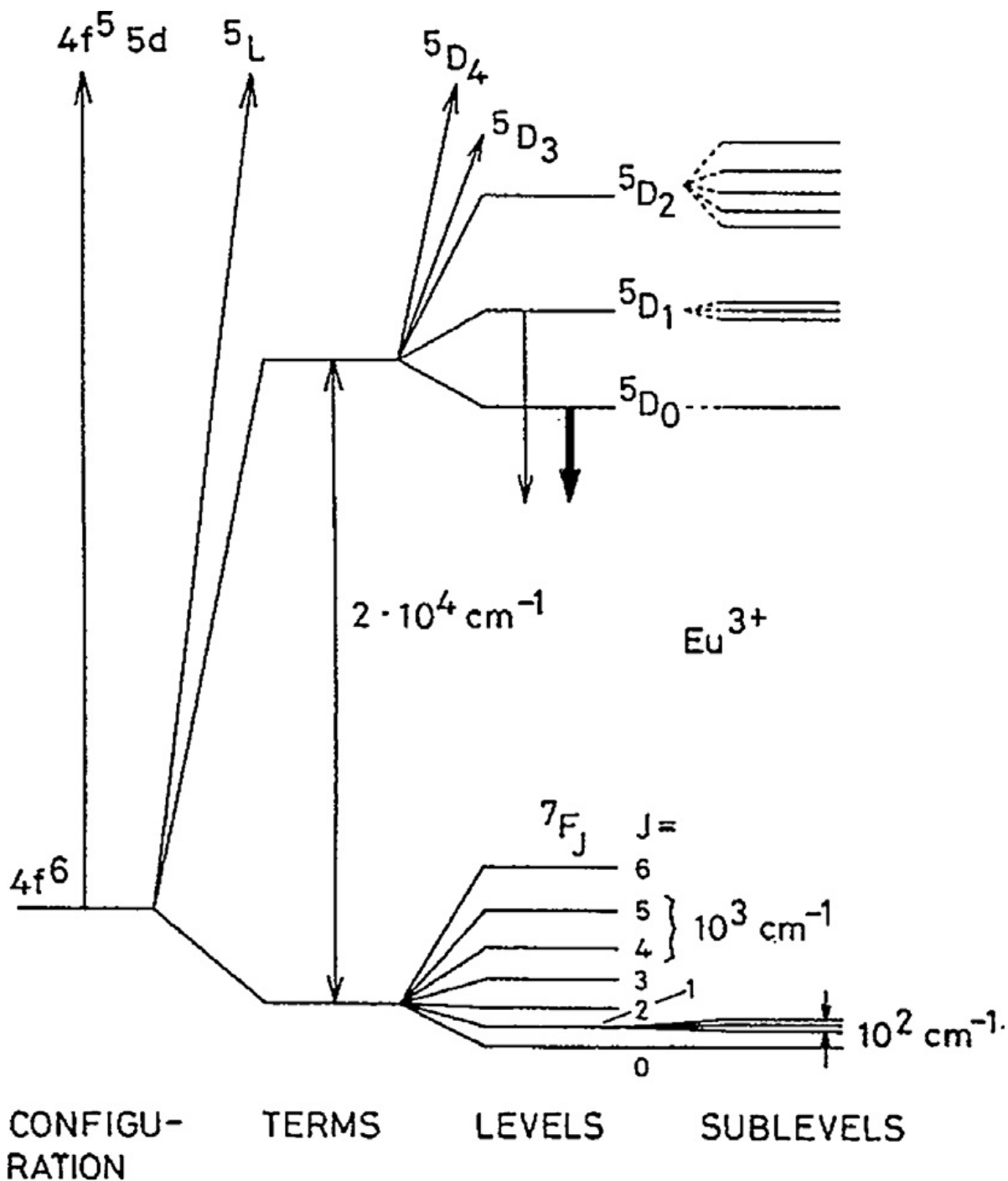**Figure 1.** Partial energy figure of $Eu^{3+}(4f^6)$ showing the relative magnitude of the interelectronic repulsion (terms), spin–orbit coupling (levels) and crystal-field effects (sublevels). The downward arrows indicate the excited states $^5D_0$ and $^5D_1$ from which luminescence occurs.

Luminescence spectra

A luminescence spectrum (or emission spectrum) is recorded by fixing the excitation wavelength, while the detection wavelength of the spectrofluorometer is scanned. The luminescence spectra of europium(III) compounds are more informative than the corresponding absorption spectra. Many europium(III) compounds show an intense photoluminescence, due to the $^5D_0 \rightarrow {}^7F_J$ transitions (J = 0–6) from the   state to the J levels of the ground term ^7F. An overview of the transitions Very often the transitions to the $^7F_5$ and $^7F_6$ levels are not observed, because they are outside the wavelength range of the detectors of spectrofluorometer (vide infra). The luminescence spectrum of the europium β-diketonate complex [Eu(tta)$_{3(}$phen)] is shown (tta = 2-thenoyltrifluoroacetylacetonate, phen = 1,10-phenanthroline). Transitions from higher excited b states ($^5D_1, {}^5D_2, {}^5D_3$) are much less common. An observation that can be made from the inspection of the positions of the different $^5D_0 \rightarrow {}^7F_J$ transitions is that the distance between a J and the J + 1 line increases with increasing J value, i.e. the $^5D_0 \rightarrow {}^7F_1$ transition is very close to the $^5D_0 \rightarrow {}^7F_0$ transition, but the $^5D_0 \rightarrow {}^7F_6$ transition is lying more than 50 nm further to the infrared than the $^5D_0 \rightarrow {}^7F_5$ transition [141]. This behaviour can be explained by the fact that the splitting of the ^7F_J multiplet corresponds quite well to the Landé interval rule: the interval between successive energy levels is proportional to the larger of their total angular momentum values J (i.e. the splitting increases with increasing J values). The majority of the transitions observed in the luminescence spectrum are induced electric dipole transitions (ED transitions). An electric dipole transition is the consequence of the interaction of the lanthanide ion with the electric field vector through an electric dipole. The creation of an electric dipole supposes a linear movement of charge. Such a transition has odd parity. Therefore, the electric dipole operator has odd transformation properties under inversion with respect to an inversion centre. Intra configurational electric dipole transitions (e.g. s–s, p–p, d–d, or f–f transitions) are forbidden by the Laporte selection rule. The Laporte selection

rule strictly applies to a lanthanide ion in the gas phase (i.e., a centrosymmetric environment); however, it is relaxed for lanthanide ions embedded in a medium, since the transitions can be partly allowed by vibronic coupling or via mixing of higher configurations into the 4f wavefunctions by the crystal-field effect. The observed transitions are much weaker than ordinary electric dipole transitions. Therefore, they are often called "induced" electric dipole transitions (or "forced" electric dipole transitions), rather than just electric dipole transitions. The intensities of the ED transitions can be described by the Judd–Ofelt theory [67,142–143]. Some transitions such as the $^5D_0 \rightarrow {}^7F_1$ transition have magnetic dipole character. Magnetic dipole transitions (MD transitions) are allowed by the Laporte selection rule, but their intensities are weak and comparable to those of the induced electric dipole transitions [67]. The intensity of a magnetic dipole transition is largely independent of the environment and can be considered in a first approximation to be constant [144]. For the calculation of the intensities of MD transitions, only the free-ion wave functions are needed, not the crystal-field wave functions. A MD transition is caused by interaction of the lanthanide ion with the magnetic field component of the light via a magnetic dipole. If charge is dis-placed over a curved path during the transition, the transition will possess magnetic dipole character. The curvature of the displacement will only be weakly apparent in a volume as small as the extent of a lanthanide ion, so that magnetic dipole transitions have a weak intensity. Magnetic dipole radiation can also be considered as a rotational displacement of charge. Since the sense of a rotation is not reversed under inversion through an inversion centre, a magnetic dipole transition has even parity. Therefore, a magnetic dipole operator possesses even transformation properties under inversion and allows transitions between states with even parity (i.e. intra-configurational transitions such as 4f–4f transitions). The selection rules for ED and MD transitions. In principle, also electric quadrupole transitions could occur. An electric quadrupole transition arises from a displacement of charge that has quadrupolar character. An electric quadrupole

consists of four points charges with overall zero charge and zero dipole moment. It can be considered as two dipoles arranged in such a way that their dipole moments cancel out. An electric quadrupole has even parity. Electric quadrupole transitions are much weaker than magnetic dipole and induced electric dipole transitions. There is no convincing evidence for electric quadrupole transitions in lanthanide spectra, although hypersensitive induced electric dipole transitions obey the selection rules for electric quadrupole transitions These selection rules on S and L are only strictly valid in the Russell–Saunders coupling scheme. They are relaxed in the intermediate coupling scheme, so S and L are not good quantum numbers in that scheme. Since J remains a good quantum number in the intermediate coupling scheme, the selection rule for J is more rigorous. It can be relaxed only by J-mixing. For these reasons, the $^5D_0 \rightarrow ^7F_J$ (J = 0, 3, 5) transitions have very weak intensities. J-mixing involves the mixing of the wave functions of sublevels of different J levels, when their irreducible representations are the same. Thus, wave functions with the same symmetry can mix under the influence of the crystal field. The degree of J-mixing between two multiplets J and J is inversely proportional to the energy difference between the J and J states, the selection rules for electric quadrupole transitions. The selection rules on S and L are only strictly valid in the Russell–Saunders coupling scheme. They are relaxed in the intermediate coupling scheme, so S and L are not good quantum numbers in that scheme. Since J remains a good quantum number in the intermediate coupling scheme, the selection rule for J is more rigorous. It can be relaxed only by J-mixing. For these reasons, the $^5D_0 \rightarrow ^7F_J$ (J = 0, 3, 5) transitions have very weak intensities. J-mixing involves the mixing of the wave functions of sublevels of different J levels, when their irreducible representations are the same. Thus, wave functions with the same symmetry can mix under the influence of the crystal field. The degree of J-mixing between two multiplets J and J is inversely proportional to the energy difference between the J and J-states.

Transition $^5D_0 \rightarrow {}^7F_2$

The $^5D_0 \rightarrow {}^7F_2$ transition is a so-called "hypersensitive transition", which means that its intensity is much more influenced by the local symmetry of the Eu^{3+}ion and the nature of the ligands than the intensities of the other ED transitions. Hyper-sensitive transitions obey the selection rules $|\Delta S| = 0$, $|\Delta L| \leq 2$ and $|\Delta J| \leq 2$ [67]. These selection rules are the same as the selection rules for a quadrupole transition, but calculations have shown that the intensities of hypersensitive transitions are several orders of magnitude larger than the values expected for quadrupole transitions. Therefore, hypersensitive transitions have been labelled also pseudo-quadrupole transitions [147]. Hypersensitivity is discussed in more details. The intensity of the hypersensitive transition $^5D_0 \rightarrow {}^7F_2$is often used as a measure for the asymmetry of the Eu^{3+}site. Large variations are observed for the intensity of this transition, depending on the type of europium(III)compound. The$^5D_0 \rightarrow {}^7F_2$transition is responsible for the typical red luminescence observed in europium(III) phosphors such asY_2O_3:Eu^{3+}or Y_2O_2S:Eu^{3+}[76,264]. The intensity of the$^5D_0 \rightarrow {}^7F_2$ transition is directly proportional to the value of the Judd–Ofelt intensity parameter. Instead of the absolute intensity of the$^5D_0 \rightarrow {}^7F_2$transition, the ratio R of the intensities of the transitions$^5D_0 \rightarrow {}^7F_2$ and$^5D_0 \rightarrow {}^7F_1$, $I(^5D_0 \rightarrow {}^7F_2)/I(^5D_0 \rightarrow {}^7F_1)$is also often used to compare the intensities of the hypersensitive transition in different europium(III) compounds. Europium(III) β-diketonate complexes, either Lewis base adducts of tris complexes or tetrakis complexes, have typically a very intense hypersensitive$^5D_0 \rightarrow {}^7F_2$transition. It is not un common that the $^5D_0 \rightarrow {}^7F_2$ transition is 10 times more intense than the$^5D_0 \rightarrow {}^7F_1$ transition in this type of complexes [39,40,42,265,266].In the luminescence spectrum of the europium(III) tetrakis β-diketonate complex [C6mim][Eu(tta)$_4$] (where C6mim = 1-hexyl-3-methylimidazolium and tta = 2-thenoyltrifluoracetylacetonate)doped into an iono gel is shown [40]. The$^5D_0 \rightarrow {}^7F_2$ transition dominates the spectrum. The high intensity is often attributed to the low symmetry of the Eu^{3+}, but it is more realistic to con-sider the high polarizability of the chelating β-

diketonate ligands as the intensity enhancing mechanism 217]158]. A dramatic increase in intensity of the hypersensitive transition $^5D_0{\rightarrow}^7F_2$ is observed for the luminescence spectrum of Eu^{3+} in an aqueous solution of K_2CO_3 in comparison with the spectrum of the europium(III) aquo ion [267,268]. This intensity enhancement is due to the formation of the anionic carbonato complex $[Eu(CO_3)_4]^{5-}$ in solution. The intensification finds applications in analytical chemistry: Sinha developed a spectrofluorimetric method to detect Eu^{3+} concen-trations as low as $10{-}7M$ using a 3 M aqueous solution of K_2CO_3 [149]. A sharp decrease in the intensity of the $^5D_0{\rightarrow}^7F_2$ transi-tion was observed when water was added to $Eu(Tf_2N)_3$ dissolvedin the hydrophobic ionic liquids N,N-diethyl-N-methyl-N-(2-methoxyethyl)ammonium bis(trifluoromethylsulfonyl)imide or 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide[150]. Addition of dipicolinate ions to an aqueous solution of Eu^{3+} led to a very strong increase in the intensity of the $^5D_0{\rightarrow}^7F_2$ transition, reaching a maximum when the $[Eu(DPA)_3]^{3-}$ complex was formed [157].

If the $^5D_0{\rightarrow}^7F_2$ transition is very weak, the luminescence spectrum is dominated by the $^5D_0{\rightarrow}^7F_1$ transition and an orange luminescence colour is observed [151]. Examples of europium(III) compounds with an orange photoluminescence are $Na_9EuW_{10}O_{36}{\cdot}18H_2O$ (D_4dsymmetry) [152], $YF_3:Eu^{3+}$(D_4d)[272], Gd $B_3O_6:Eu^{3+}$(D_4d), $CeO_2:Eu^{3+}$(O_h) [272], [Eu(4-picoline-N-oxide)_8](PF_6)_3 (D_4d) [274], [Eu(pyridine-N-oxide)_8](ClO_4)_3 (D_4d) [275], $Eu(antipyrene)_6I_3$ (S_6) (antipyrene = 1-phenyl-2,3-dimethyl-5-pyrazolone) [276,277], compounds with the hexakis(nitrito)europate(III) ion $[Eu(NO_2)_6]^{3-}$ (T_h) [278–159], $SnO_2:Eu^{3+}$(D_2h) [280], $Gd_2Sn_2O_7:Eu^{3+}$ (D_3d) [281], $Na_3[Eu(oxydiacetato)_3]{\cdot}2NaClO_4{\cdot}6H_2O$ (D_3) [271,282],[Eu(terpy)_3](ClO_4)_3(D_3) [283], $[Eu(H_2O)_9](BrO_3)_3$(D_3h) [152,153],and $[Eu(H_2O)_9](EtSO_4)_3$(C_3h) [215]. A pink luminescence is observed for $Cs_2NaEuCl_6$ (O_h) at room temperature, but an orange luminescence at 77 K, due to a decrease of the vibrionic intensity of the $^5D_0{\rightarrow}^7F_2$transition [151]. These examples show that correlating the luminescence colour

with a particular symmetry point group is difficult. The list contains compounds with different symmetries, and both centrosymmetric and non-centrosymmetric point groups occur. One could conclude from an orange luminescence that $^5D_0 \rightarrow ^7F$ transition must be weak and much less intense than the $^5D_0 \rightarrow ^7F_1$ transition, but one has to be cautious for compounds that also show emission from higher excited states ($^5D_1$, $^5D_2$, $^5D_3$). Emission from higher excited states can shift the luminescence toward orange and yellow emission colours [154]. The relative contribution of emission from the higher excited states can be tuned by variation of the Eu^{3+} concentration in the host matrix, because higher doping concentrations favour emission from the $^5D_0$ level at the expense of emission from the higher excited states. Not all phosphors show a strong colour shift as a function of Eu^{3+} concentrations. Only phosphors with a large contribution low Eu^{3+} concentrations exhibit strong colour shifts. Examples are the white to orange to red emission with $(Y_{1-x}Eu_x)_2O_2S$ and the yellow to red emission with $(Y_{1-x}Eu_x)_2O_3$ [154]. On the other hand, $(Y_{1-x}Eu_x)VO_4$ shows very little colour change upon variation of the Eu^{3+} concentration. Also compounds with an intense $^5D_0 \rightarrow ^7F_2$ transition shifted to higher energies (shorter wavelengths) can show an orange photoluminescence is expected.

A typical feature of europium(III) complexes with a D_3h symmetry is the narrow ness of the $^5D_0 \rightarrow ^7F_2$ transition, because only one crystal-field line is allowed in this symmetry. This can be seen in the luminescence spectra of tris(hydrotris(1-pyrazolyl)borato)europium(III) [279]. For D_3 symmetry, two components are expected for the $^5D_0 \rightarrow ^7F_2$ transition. This split-ting is sometimes not resolved, as in the case of the europium(III) tris dipicolinate complex $[Eu(DPA)_3]^{3-}$ [157].

Transition $^5D_0 \rightarrow {}^7F_3$

The $^5D_0 \rightarrow {}^7F_3$ transition is in general very weak, because it is forbidden according to the Judd–Ofelt theory, and this transition can only gain intensity via J-mixing [155]. An intense $^5D_0 \rightarrow {}^7F_3$ transition is a sign of strong J-mixing and a strong crystal-field perturbation. This transition is not considered when the Eu^{3+} ion is used as a spectroscopic probe. The β-diketonate complex [Eu(dbm)$_3$(H$_2$O)] is one of the rare examples of an intense $^5D_0 \rightarrow {}^7F_3$ transition [158]. In fact, the $^5D_0 \rightarrow {}^7F_3$ transition of this compound is more intense than $^5D_0 \rightarrow {}^7F_4$ transition. It should be noted that also the $^5D_0 \rightarrow {}^7F_0$ transition and the $^5D_0 \rightarrow {}^7F_2$ hypersensitive transition are very intense in this compound. This observation can be explained by strong crystal-field effects and hence strong J-mixing. On the other hand, the $^5D_0 \rightarrow {}^7F_3$ transition is totally absent in BaEu(CO$_3$)$_2$F and Na$_3$La$_2$(CO$_3$)$_4$F:Eu^{3+}, although these compound give fairly intense luminescence spectra [156]. The absence of this transition was attributed to weak J-mixing, which was also evident from the small values of the second and fourth rank crystal-field parameters (B^2_q and B^4_q). Another remark-able feature in the luminescence spectra of these compounds is the absence of luminescence from excited states higher than $^5D_0$. This is attributed to the high phonon energies of the carbonate groups which efficiently depopulate the excited states. The $^5D_0 \rightarrow {}^7F_3$ transition of the C$_2$v site in BaFCl:Eu^{3+} is more intense than the strongest line of the $^5D_0 \rightarrow {}^7F_4$ transition [148]. This anomalous behaviour was explained by J-mixing induced by the large fourth rank crystal field parameters ($B^4_0 = -1489$ cm^{-1} and $B^4_4 = 1266$ cm^{-1}). The extent of J-mixing was estimated to be about 6.5% (which means that the "$^7F_3$" state has 93.5% $^7F_3$ character and 6.5% $^7F_2$ character). Interestingly, the extent of J-mixing of $^7F_2$ into $^7F_0$ was in this compound only about 2%, due to the small second rank crystal field parameters ($B^2_0 = -72$ cm^{-1} and $B^2_2 = -290$ cm^{-1}). As a result, the $^5D_0 \rightarrow {}^7F_0$ transition has a weak intensity.

In the luminescence spectrum of $Mg_3F_3BO_3:Eu^{3+}$, a very intense transition is observed in the $^5D_0 \rightarrow {}^7F_3$ transition region at 658.3 nm [157]. This transition is much more intense than the $^5D_0 \rightarrow {}^7F_4$ transition. The compound has also other remarkable properties, such as a very intense $^5D_0 \rightarrow {}^7F_0$ transition situated at a very high energy (17,615 cm−1or 567.7 nm) and a very large splitting of the $^7F_1$ level (700 cm−1). This very large splitting causes an overlap between the energy levels of the $^7F_1$ and $^7F_2$ levels. The fact that a very strong crystal-field effect is present inspired the authors to give an alternative explanation for the transition at 658.3 nm instead of attributing this line to the $^5D_0 \rightarrow {}^7F_3$ transition. The authors suggest that the line could also be a crystal-field component of the $^5D_0 \rightarrow {}^7F_2$ transition. In that case, a very large crystal-field splitting of the $^7F_2$ level would occur (1750 cm−1). Further research on this interesting compound is recommended.

Transition $^5D_0 \rightarrow {}^7F_4$

One must be careful with the interpretation of the intensity of the $^5D_0 \rightarrow {}^7F_4$ ED transition. The transition lies in a spectroscopic region in which most photomultiplier tubes have a low sensitivity. Correction of the luminescence spectra is required, because otherwise erroneous conclusions could be drawn. In an uncorrected luminescence spectrum, the intensity of the $^5D_0 \rightarrow {}^7F_4$ transition is too low compared to the other transitions, whereas the intensity of this transition is exaggerated in an over-corrected spectrum. The intensity of the $^5D_0 \rightarrow {}^7F_4$ transition should not be considered in terms of absolute values, but rather compared to the intensity of the $^5D_0 \rightarrow {}^7F_1$ magnetic dipole transition. In many europium luminescence spectra, $^5D_0 \rightarrow {}^7F_4$transition is weaker than the $^5D_0 \rightarrow {}^7F_2$ transition, but several exceptions are known. The luminescence spectra of compounds with D_4d symmetry are often dominated by the $^5D_0 \rightarrow {}^7F_4$tran-sition. In D_4d symmetry, the $^5D_0 \rightarrow {}^7F_2$ transition is forbidden, but the$^5D_0 \rightarrow {}^7F_4$ transition is intense because a centre of symmetry is absent [271,158]. Examples of such compounds are:$Na_9[EuW_{10}O_{36}] \cdot 14H_2O$ (Eu^{3+}decatungstate) [272,159], $YF3:Eu^{3+}$,

GdB$_3$O$_6$:Eu^{3+}[158], [Eu(4-picoline-N-oxide)$_8$](PF$_6$)$_3$ [284] and[Eu(4-picoline-N-oxide)$_8$](ClO$_4$)$_3$ [160]. An undistorted square antiprism has D$_4$dsymmetry, so that for compounds with a lower symmetry than D$_4$d, but with a coordination polyhedron close to a square antiprism, have an intense $^5D_0 \rightarrow {}^7F_4$ transition (and a weak $^5D_0 \rightarrow {}^7F_2$ transition). In the macrocyclic complex [Eu(DOTA)(H$_2$O)]$^-$, the Eu^{3+}is nine-coordinate, with a coordination polyhedron that can be described as a noncapped square antiprism [159,161]. A very intense $^5D_0 \rightarrow {}^7F_4$ transition has been observed for the alkali–metal europium dinitro salicylates (especially for the sodium complex), but the crystal structure of these compounds is not known yet [162]. In these compounds, the $^5D_0 \rightarrow {}^7F_4$ transition is less intense than the $^5D_0 \rightarrow {}^7F_2$ transition $^7F_4$ One must be careful with the interpretation of the intensity of the$^5D_0 \rightarrow {}^7F_4$ ED transition. The transition lies in a spectroscopic region in which most photomultiplier tubes have a low sensitivity. Correction of the luminescence spectra is required, because otherwise erroneous conclusions could be drawn. In an uncorrected luminescence spectrum, the intensity of the $^5D_0 \rightarrow {}^7F_4$ transition is too low compared to the other transitions, whereas the intensity of this transition is exaggerated in an over-corrected spectrum. The intensity of the$^5D_0 \rightarrow {}^7F_4$ transition should not be considered in terms of absolute values, but rather compared to the intensity of the$^5D_0 \rightarrow {}^7F_1$ magnetic dipole transition. In many europium luminescence spectra, the$^5D_0 \rightarrow {}^7F_4$ transition is weaker than the$^5D_0 \rightarrow {}^7F_2$ transition, but several exceptions are known. The luminescence spectra of compounds with D$_4$dsymmetry are often dominated by the$^5D_0 \rightarrow {}^7F_4$ transition. In D$_4$d symmetry, the$^5D_0 \rightarrow {}^7F_2$ transition is forbidden, but the $^5D_0 \rightarrow {}^7F_4$ transition is intense because a centre of symmetry is absent [271,158]. Examples of such compounds area Na$_9$[EuW$_{10}$O$_{36}$]·14H$_2$O (Eu^{3+}decatungstate) [27], YF$_3$:Eu^{3+},GdB$_3$O$_6$:Eu^{3+}[158], [Eu(4-picoline-N-oxide)$_8$](PF$_6$)$_3$ [295] and[Eu(4-picoline-N-oxide)$_8$](ClO$_4$)$_3$ [160]. An undistorted square antiprism has D$_4$d symmetry, so that for compounds with a lower symmetry than D$_4$d, but with a coordination polyhedron close to a

square antiprism, have an intense $^5D_0 \rightarrow {}^7F_4$ transition (and a weak $^5D_0 \rightarrow {}^7F_2$ transition). In the macrocyclic complex [Eu(DOTA)(H$_2$O)]$^-$, the Eu^{3+} is nine-coordinate, with a coordination polyhedron that can be described as a monocapped square antiprism [159,161]. A very intense $^5D_0 \rightarrow {}^7F_4$ transition has been observed for the alkali–metal europium dinitro salicylates (especially for the sodium complex), but the crystal structure of these compounds is not known yet [162]. In these compounds, the $^5D_0 \rightarrow {}^7F_4$ transition is less intense than the $^5D_0 \rightarrow {}^7F_2$ transition but much more intense than the $^5D_0 \rightarrow {}^7F_1$ magnetic dipole transition. The same remark can be made for LaBO$_3$:Eu^{3+} with an orthorhombic aragonite structure (with Eu^{3+} in an asymmetric site with Symmetry) [146]. The very high intensity of the $^5D_0 \rightarrow {}^7F_4$ transition in Ca$_3$Sc$_2$Si$_3$O$_{12}$:Eu^{3+} was attributed to a distortion of the cubic geometry of the Eu^{3+} site in this garnet host toward the actual D$_2$ symmetry [163]. How-ever, an alternative explanation is a distortion of the cube to a square antiprism. The $^5D_0 \rightarrow {}^7F_4$ transition dominates the spectrum of GdOBr:Eu^{3+}, whereas the $^5D_0 \rightarrow {}^7F_2$ transition is the most intense transition in the isostructural GdOCl:Eu^{3+} compound [172]. This clearly shows that the intensity of the $^5D_0 \rightarrow {}^7F_4$ transition is determined not only by symmetry factors, but also by the chemical composition of the host matrix. Other examples of europium(III)-containing systems with an intense $^5D_0 \rightarrow {}^7F_4$ transition are: Eu(Tp)$_3$(Tp = hydrotris(pyrazol-1-yl)borate) [257],Eu(Tp)$_3$ in PMMA polymer matrix [164] and the two-dimensional frameworks of the formula2∞[Eu$_2$Cl$_6$(4, 4_− bipy)$_3$] · 2(4, 4'−bipy), where 4,4'-bipy = 4,4'-bipyridine [165]. In a recent paper, Skaudzius et al. have made a systematic study of the intensity of the $^5D_0 \rightarrow {}^7F_4$ transition of Eu^{3+} in different orthophosphate and garnet host matrices and investigated the influence of the host material, in particular of the electronegativity, the radius of the rare earth and of other trivalent cations [258]. An increase in the average electronegativity of the trivalent cations, i.e. a decrease of the optical basicity, in the octahedral and tetrahedral sites in the structure of the garnets and orthophosphates led to an increase of the relative intensity of the $^5D_0 \rightarrow {}^7F_4$ transition. In

$Y_3Al_5O_{12}:Eu^{3+}$ (1%), the $^5D_0 \rightarrow {}^7F_4$ transition accounts for 39.5% of the total intensity of the $^5D_0 \rightarrow {}^7F_J$ transitions, whereas this value increases to 49.8% in $LuPO_4:Eu^{3+}$ (1%). The $^5D_0 \rightarrow {}^7F_4$ transition is sometimes considered as a hypersensitive one, but this it is not correct, since it does not obey the selection rules for quadrupole transition.

Transitions $^5D_0 \rightarrow {}^7F_5$ and $^5D_0 \rightarrow {}^7F_6$

In many studies, the $^5D_0 \rightarrow {}^7F_5$ transition (740–770 nm) and the $^5D_0 \rightarrow {}^7F_6$ transition (810–840 nm) are not discussed because they cannot be observed by blue-sensitive PMTs of several commercial Spectro fluorimeters. The classic red-sensitive Hamamatsu R928PMT has a very low sensitivity in the spectral region where these transitions occur. Moreover, the intensities of these transitions are very low. For this reason, many reported europium(III) luminescence spectra show only the $^5D_0 \rightarrow {}^7F_J$ (J = 0–4) transitions or even only the $^5D_0 \rightarrow {}^7F_J$ (J = 0–2) transitions. For $Eu(NO_3)_3 \cdot 6H_2O$, it was reported that the relative intensities for the $^5D_0 \rightarrow {}^7F_J$ (J = 0–6) transitions upon selective excitation in the $^5D_0$ level at 77 K are 0.03, 1.0, 4.9, 0.01, 1.8, 0.05 and 0.4, respectively [166]. The relative luminescence intensities of the $^5D_0 \rightarrow {}^7F_J$ (J = 0–6) transitions in $LaF_3:Eu^{3+}$ at 77 K are: <0.4, 6.45, 5.25, 0.19, 2.80, 0.05 and 0.08 [167]. Whereas the transitions to $^7F_5$ and $^7F_6$ cannot be observed for Eu^{3+} in water, they become visible as weak bands after addition of dipicolinate (DPA) ligands [157]. On the other hand, in the luminescence spectra of hydrated Eu^{3+} in crystalline matrices such as $Eu(BrO_3)_3 \cdot 9H_2O$ [153] or $Na[Yb_{0.95}Eu_{0.05}(dpa)_3] \cdot NaClO_4 \cdot 10H_2O$ [168] weak transitions to $^7F_5$ and $^7F_6$ are present if laser excitation is used. Also luminescence spectra of Eu^{3+} ions in glasses show that these transitions are weak [153,182,169]. On the other hand, the intensity of the $^5D_0 \rightarrow {}^7F_6$ transition is comparable to that of the $^5D_0 \rightarrow {}^7F_4$ transition for the Cs site of $BaFCl:Eu^{3+}$ [148]. This site has also another unusual spectroscopic property: the $^5D_0 \rightarrow {}^7F_0$ transition is the strongest transition in the spectrum

Emission from higher excited states

In some spectra, and especially in those of Eu^{3+} in inorganic host lattices, luminescence can also originate from the $^5D_1, ^5D_2$ and $^5D_3$ levels, even though examples of luminescence from the $^5D_3$ level are very scarce. Crystalline europium(III) compounds with emission from the higher excited states have complicated luminescence spectra with a large number of crystal-field transitions. For instance, more than 120 transitions are observed in the luminescence spectrum of $La_2O_3{:}Eu^{3+}$ recorded at 77 K [168], and more than 100 lines have been reported for the low-temperature luminescence spectra of the Eu^{3+} doped oxychlorides LnOCl (Ln = La,Gd, Y) [170]. In molecular compounds, often only transitions from the $^5D_0$ excited state are observed because of stronger radiation less deactivation. This is especially the case for room-temperature luminescence spectra. In spectra with luminescence from the higher excited states, there can be an overlap between the $^5D_0{\rightarrow}^7F_J$ and the $^5D_{1,2}{\rightarrow}^7F_J$ lines. An overlap has been observed between: $^5D_0{\rightarrow}^7F_0$ and $^5D_2{\rightarrow}^7F_5, ^5D_0{\rightarrow}^7F_2$ and $^5D_1{\rightarrow}^7F_4, ^5D_0{\rightarrow}^7F_3$ and $^5D_1{\rightarrow}^7F_5, ^5D_1{\rightarrow}^7F_0$ and $^5D_2{\rightarrow}^7F_4, ^5D_1{\rightarrow}^7F_1$ and $^5D_2{\rightarrow}^7F_4, ^5D_1{\rightarrow}^7F_2$ and $^5D_2{\rightarrow}^7F_4$, $^5D_0{\rightarrow}^7F_4$ and $^5D_1{\rightarrow}^7F_6$. Discrimination between these is possible by means of time-gated luminescence spectra, because the decay times of the $^5D_1$ and $^5D_2$ states are much shorter than the decay time of the $^5D_0$ state. Time-gated spectra are recorded by a pulsed excitation source. Data collection is started after a given delay time. By a careful choice of the delay time, the measurement of the luminescence of the $^5D_0$ state is started after the $^5D_1$ and higher excited states have already been depopulated. It is possible to selectively excite the $^5D_0$ level by a tenable laser source, avoiding population of higher excited states. The overlap of the lines can also be avoided by working at higher temperatures or at higher Eu^{3+} concentrations, because these conditions favour quenching of the $^5D_1$ and $^5D_2$ excited states. At lower temperature, more transitions starting from the higher excited states are observed. A consequence of the quenching of emission from the $^5D_1, ^5D_2$ and $^5D_3$ excited states is that the emission colour shifts from yellow

to red with increasing Eu^{3+} concentrations or with an increase in temperature [154]. Contrary to what is intuitively expected, deuteration of hydrated europium(III) complexes leads to a decrease of the intensity of the transitions from the $^5D_1$ level compared to those of the $^5D_0$ levels, as shown in a luminescence study of $Eu(NO_3)_3\cdot 6H_2O$ and $Eu(NO_3)_3\cdot 6D_2O$ [166]. This is explained by the fact that deuteration strongly reduces the quenching of the luminescence from the
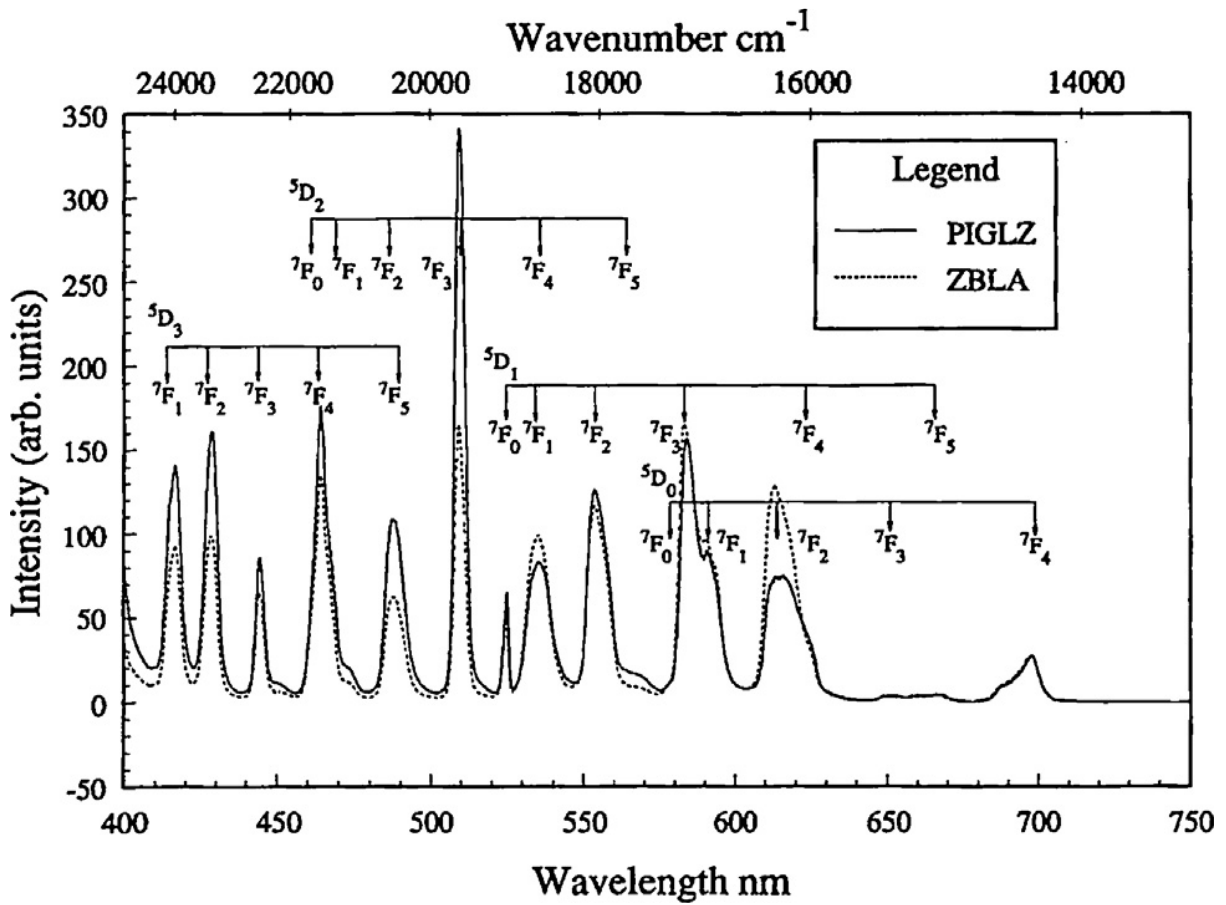

Fig.2 Luminescence spectra of Eu^3+doped in the fluoride glasses $ZBLA(57ZrF_4–36BaF_2–4LaF_3–3AlF_3)$ and PIGLZ $(43PbF_2–17InF_3–17GaF_3–4LaF_3–19ZnF_2)$,showing emission from higher excited states.

long lived $^5D_0$ state. The deuterated compound has a similar formula. Emission from the $^5D_2$ level is common for Eu^{3+} in fluoride host matrices, such as $LiYF_4$[171], KY_3F_{10}[172–173], LaF_3 [174]and $NaYF_4$ [175]. Other examples include $LnOF:Eu^{3+}$ (Ln = La, Gd, Y) [176], $Cs_2NaEuCl_6$ [177], $Cs_2AgEuCl_6$[178] and $LaCl_3:Eu^{3+}$[145]. Low temperatures induce

sharpening of the luminescence lines by reducing the lattice thermal agitation. However, lowering the temperature can also induce other changes in the luminescence spectra originating from the higher excited states. The relative populations of the different crystal-field levels of the $^5D_1$ and $^5D_2$ excited states are determined by the Boltzmann distribution. At 4.2 K, only the lower crystal-field levels of the $^5D_1$ and $^5D_2$ states are populated during the radiative decay (luminescence), so that the number offline is reduced in the spectra at 4.2 K compared to the spectra at room temperature or even at 77 K [172]. This considerably simplifies the luminescence spectrum.

Emission from the $^5D_3$ level is observed only for host matrices with very low phonon energies, so that the radiation less decay to the $^5D_2, ^5D_1$ and $^5D_0$ states is very slow. Strong emission from the $^5D_3$ level was observed for the fluorozirconate glass $57ZrF_4–34BaF_2–4AlF_3–3LaF_3–2EuF_3$ [179]. The $^5D_3 \rightarrow ^7F_0$ transition was not observed because it is strictly forbidden, but the $^5D_3 \rightarrow ^7F_J$ (J = 1–4) transitions were observed in the intensity ratios 2:2:1:4, at 417, 43_0, 445 and 465 nm, respectively. The total emission ratios of the transitions from the $^5D_3, ^5D_2, ^5D_1$ and $^5D_0$ state are 1:1:2:6, respectively. The intense emission from the excited states $^5D_3$ and $^5D_2$ makes this glass unique in comparison to other europium(III)-doped host matrices. Even in similar fluorozirconate glasses, such as $64ZrF_4–32BaF_2–2LaF_3–2EuF_3$, the emission from the $^5D_3$ and $^5D_2$ states is much weaker than emission from $^5D_1$ and $^5D_0$ [180], the luminescence spectra of Eu^{3+} in two different fluoride glasses are given, showing very clearly the emission from higher excited states [181].

Occurrence of $^5D_3$ emission in glasses is not restricted to fluoride glasses. It was also observed for Eu^{3+} in tellurite and germanate glasses [182]. In crystalline matrices, $^5D_3$ emis-sion has been reported for $LaF_3:Eu^{3+}$[167], $GdF_3:Eu^{3+}$[183], $LiGdF_4:Eu^{3+}$[249,183], $NaYF_4:Eu^{3+}$[252,175], $NaGdF_4:Eu^{3+}$[250,251,270], $NaGdF_4:(Eu^{3+},Ce^{3+})$ [184], $CsGd_2F_7:Eu^{3+}$[259], $GdOF:Eu^{3+}$[260], $BaY_2ZnO_5:Eu^{3+}$[261], $La_2O_3:Eu^{3+}$[168] and in several europium(III)-doped chloroelpasolites

[185,186].$^5D_3$emission can be observed for Eu^{3+} diluted in Cs_2NaYCl_6, but not for neat $Cs_2NaEuCl_6$due to concentration quenching [187]. Weak emission from the$^5H_3$level of Eu^{3+} has been reported by Kiliaan and Blasse for $NaGdF_4$:(Eu^{3+}, Ce^{3+}) after excitation into the f–d band of Ce^{3+}[184]. The transitions were assigned to the $^5H_3{\rightarrow}^7F_1$ (max= 329 nm),$^5H_3{\rightarrow}^7F_2$ (max = 337 nm) and $^5H_3{\rightarrow}^7F_4$ (max= 358 nm) transitions. The authors assumed that$^5H_3$emission is probably restricted to fluoride matrices, because the charge-transfer band of Eu^{3+} has to be at high enough energy to avoid non-radiative relaxation via the charge-transfer state. How-ever, Tanner and co-workers observed emission from the$^5H_3$level in$Cs_2NaIn_{0.995}Eu_{0.005}Cl_6$upon excitation with synchrotron radiation [185]. Triply doped $NaYF_4$:(Yb^{3+},Er^{3+},Eu^{3+}) nanocrystals showed luminescence of the $^5H_{3-7}{\rightarrow}^7F_{0-3}$ and $^5L_6{\rightarrow}^7F_0$ transitions, as well as emission from the $^5D_3$ and $^5D_2$ levels after infrared excitation at 980 nm [188]. After an upconversion process, the Er^{3+} ion transfers part of its excitation energy to the Eu^{3+} ion.

Polarized emission spectra

The emitted light originating from transitions between crystal-field levels of Eu^{3+} ions embedded in a non-cubic single crystal host matrix is linearly polarized and the polarization directions of the emission lines depend on the selection rules for the symmetry point group of the Eu^{3+} site. The polarization characteristics of the emission lines are useful for the assignment of symmetry labels to the different crystal-field levels [152,189–190]. Emission of linearly polarized light has also been observed for lanthanide complexes embedded in less ordered anisotropic media than on-cubic single crystals. For instance, polarized emission was obtained for europium(III) β-diketonate complexes embedded in stretched polyethylene films [191,189], for an aligned vitrified mesophase of a liquid-crystalline europium(III) complex [190], and for europium(III) complexes dissolved in aligned liquid crystal sol-vents [16]. Polarized luminescence was studied for [Eu(DPA)$_3$]$^{3-}$complexes in a glass obtained by freezing

a water/ethylene glycol(1:2 by volume) [191]. Light polarization can be observed by using linear polarizers. In polarization, the polarizer is parallel to the main crystallographic axis of the host or the alignment/stretching direction. In polarization, the polarizer is perpendicular to this direction.

Sensitized luminescence

Even though light emission by Eu^{3+} can be an efficient process, the weak light absorption is an issue. The $^5L_6 \leftarrow {}^7F_0$ transition at about 395 nm is the most intense transition in the absorption spectra of europium (III) compounds and this transition is often used for direct excitation into the $4f^6$ levels of the Eu^{3+} ion. However, the molar absorptivity ε of this transition is less than 5 $Lmol^{-1}cm^{-1}$, so that only a small part of the excitation light is absorbed. Since the luminescence intensity is proportional to not only the luminescence quantum yield, but also to the amount of light absorbed, weak light absorption results in weak luminescence. Fortunately, the problem of weak light absorption can be overcome by these-called "antenna effect" (or sensitization). Weissman discovered in 1942 that intense metal-centred luminescence is observed for europium(III) complexes of salicylaldehyde, benzoylacetone, dibenzoylmethane and meta-nitrobenzoylacetone upon excitation in an absorption band of the organic ligand [192]. The absorption bands of the organic chromophores are very strong, so that the ligands can absorb much more light than the Eu^{3+} ion itself. After light absorption, the excitation energy is transferred from the organic ligands to the Eu^{3+} ion via intramolecular energy transfer. It took about 20 years before the importance of the seminal work of Weissman was fully appreciated. After the mechanisms of the energy transfer from the organic ligand to the lanthanide ion were
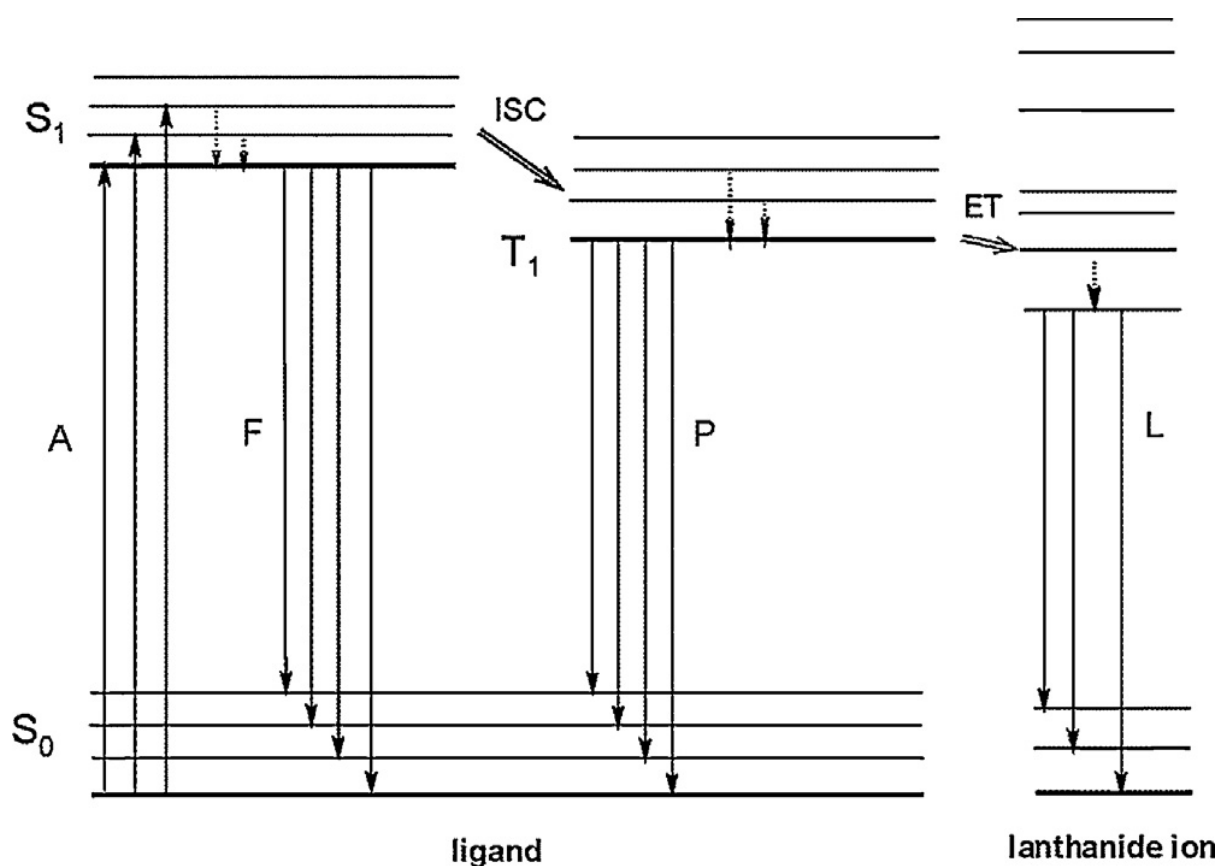
Schematic representation of photophysical processes in lanthanide(III) complexes (antenna effect). Abbreviations: A, absorption; F, fluorescence; P, phosphorescence; L, lanthanide-centred luminescence; ISC, intersystem crossing; ET, energy transfer; S, singlet; T, triplet. Full vertical lines: radiative transitions, dotted vertical lines: non-radiative transitions.

discovered in the early 1960s and after one realized that lanthanide β-diketonate complexes have potential as the active component in chelate lasers, an intense research activity has been going on in the field of luminescent materials based on molecular lanthanide complexes [23]. For a detailed discussion of energy transfer processes in lanthanide complexes, the reader is referred to a recent review by Bünzli and Eliseeva [75].

The commonly accepted mechanism of energy transfer from the organic ligands to the lanthanide ion is that proposed by Crosby and Whan [262–192]. Upon irradiation with ultraviolet radiation, the organic ligands of the lanthanide complex absorb the ultraviolet radiation and are excited to a vibrational level of the first excited singlet state ($S_1 \leftarrow S_0$). The

molecule undergoes fast internal conversion to lower vibrational levels of the S_1 state, for instance through interactions with solvent molecules. The excited singlet state can be deceived radiatively to the ground state (molecular fluorescence, $S_1 \rightarrow S_0$), or can undergo non-radiative intersystem crossing from the singlet state S_1 to the triplet state T_1. The triplet state T_1 can be deactivated radiatively to the ground state S_0, by the spin-forbidden transition $T_1 \rightarrow S_0$. This results in molecular phosphorescence. Alternatively, the complex may undergo an intramolecular energy transfer from the triplet state to a level of the lanthanide ion. The triplet level is the donor level (energy-transferring level) and the 4f level of the lanthanide ion is the acceptor level (resonance level). By transferring its energy from the triplet level to the lanthanide ion, the organic ligand goes back to its ground state. The energy takes place via an electron-exchange mechanism (Dexter mechanism). This mechanism requires a physical overlap between the orbitals of the donor and the acceptor. Therefore, the energy transfer is strongly distance-dependent and decreases rapidly at distances larger than 0.5 nm. In order to get an efficient energy transfer from the triplet state to the lanthanide, the triplet state should be located at least 1500 cm−1, but preferably 2000 to 3500 cm−1above the emitting level of the lanthanide ion. If the energy difference between the triplet level and the emit-ting level of the lanthanide ion is too small, back transfer can occur and the energy transfer efficiency will drastically decrease. If the energy of the triplet level is below the lowest emitting level of the lanthanide ion, no energy transfer will take place and no lanthanide-centered emission will be observed. The luminescence observed for a specific lanthanide complex is therefore a sensitive function of the lowest triplet level of the complex relative to a resonance level of the lanthanide ion. When speaking about the energy of the triplet state, the energy of the zero-phonon energy of the triplet state is meant. In the case of Eu^{3+}, the $^5D_0$level (at about17, 250 cm^{-1}) is the preferred emitting level, but it is not the best acceptor level. In a systematic study of europium(III) tetrakis β-diketonate complexes, the highest quantum yields are observed for

energy transfer via the $^5D_1$ level, which is about 19,000 cm-1 above the ground state $^7F_0$. The triplet energy for optimal energy transfer is 20,200 cm^{-1} [193]. The preferential energy transfer via the $^5D_1$ level is in accordance with the selection rules for energy transfer via the Dexter mechanism. When the energy of the triplet levels higher than 20,200 cm^{-1}, the quantum yield first decreases, but then increases again when triplet levels becomes resonant with the $^5D_2$ level of Eu^{3+} (located at about 21,500 cm-1). However, energy transfer via the $^5D_1$ level is less efficient than via the $^5D_1$ level. Similar results have been observed for europium(III) polyaminocarboxylate complexes in aqueous solution [194]. As a rule of thumb, the energy gap in between the triplet state and the emitting level $^5D_0$ should be between 1500 and 5000 cm-1 in order to observe efficient luminescence of the europium(III) complex. Since the position of the triplet level depends on the type of ligand, it is therefore possible to control the luminescence intensity of Eu^{3+} by variation of the ligand. The position of the triplet level is temperature dependent, so that the luminescence caused by indirect excitation through the organic ligands is much more temperature sensitive than luminescence caused by direct excitation of the 4f levels. High-pressures have a significant influence on the singlet and triplet levels of the ligands, whereas the 4f levels are much less sensitive to changes in pressure. Therefore, the energy transfer from the triplet state to the 4f levels can be tuned by applying an external pressure on the lanthanide complex [193]. Although Kleinerman proposed mechanism of direct transfer of energy from the excited singlet state S_1 to the energy levels of the lanthanide ion [194], it is not easy to unambiguously prove this mechanism as the main sensitization route due to the very short lifetime of the singlet excited state [75]. When the energy transfer is not very efficient, it is possible to observe some remaining ligand emission together with the lanthanide-centered emission. Molecular oxygen is an external triplet quencher. Quenching of the triplet state by dissolved oxygen in a solution is a competitive process with energy transfer from the triplet state to the lanthanide ion [97]. Therefore, it is recommended to degas solutions

of lanthanide complexes prior to measurement of the luminescence spectra. The position of the lowest triplet state of a lanthanide complex can be determined experimentally by recording the luminescence spectrum (phosphorescence spectrum) of the corresponding gadolinium(III) complex [193,195,196].The energy levels of the Gd^{3+}ion are well above those of the triplet level so that no gadolinium(III)-centered emission is observed. Moreover, the heavy paramagnetic Gd^{3+} ion enhances the inter-system crossing from the singlet to the triplet state, because of mixing of the triplet and singlet states ("heavy atom effect" and "paramagnetic effect") [197–198]. The triplet state acquires partially a singlet character by the spin–orbit coupling interaction, and the selection rules are relaxed. The paramagnetic Gd^{3+} ions low-ers the lifetimes of the triplet states of the organic ligands Muchmore than the diamagnetic La^{3+} and Lu^{3+} ions. Cryogenic temperatures are often necessary to observe phosphorescence, since the triplet state can be deactivated by non-radiative processes. There is also a competition between fluorescence and phosphorescence. At77 K, the solvent quenching of the triplet state is negligible. The triplet levels are always located at a lower energy than the singlet levels. Different theoretical approaches have been developed for a prediction of the position of the singlet and triplet levels of a lanthanide(III) complex. First the geometry of the ground state of the complex is optimized by a Sparkle Model, and then the energies of the singlet and triplet levels are calculated by time-dependent DFT calculations or by a semiempirical INDO/S method [87,199–200].The sensitization of europium(III) luminescence by the antenna effect is not restricted to organic chromophores. Inorganic chromophores can do the job as well. The chromophores can be a constituent of the host matrix or the chromophore can be a co-dopant. Examples of luminescent compounds with chromophores as part of the host matrix are europium(III)-doped vanadate's, molybdates and tungstate's such as $YVO_4:Eu^{3+,}$ $GdVO_4:Eu^{3+}, CaMoO_4:Eu^{3+}$ and $CaWO_4:Eu^{3+}$[50,201–203]. This mechanism is also responsible for the sensitization of the luminescence in europium(III)-doped polyoxometalate

complexes [152,204–269]. In all these chromophores the intense absorption bands are oxygen-to-metal charge-transfer bands. Notice that the Eu^{3+} ion involved in these charge-transfer transitions, in contrast to the ligand to-metal charge transitions discussed further in this section. Although sensitization of lanthanide luminescence via d-block transitions in f–d complexes is an active research field, this approach is mainly used for sensitization of near-infrared-emitting lanthanide ions and not for Eu^{3+} ions [75,205]. Many d-block transition metals quench luminescence of Eu^{3+} since the tails of the d–absorption bands often have a lower energy than the $^5D_0$ excited state of Eu^{3+}. However, one must realize that the energy of the d–d transitions is very strongly influenced by the ligand field and thus by the ligands, so that one given transition metal ion can act either as a sensitizer or quencher of Eu^{3+} luminescence, depend-ing on the ligand environment. An example of a d-block transition metal ion that can act both as a sensitizer or quencher is Cr^{3+}. The transition metals Fe^{3+}, Co^{3+}, Ni^{2+} and Cu^{2+} are known to be efficient quenchers for Eu^{3+} luminescence [75]. The quenching of Eu^{3+} luminescence by even small concentration of these elements has-been used to develop sensitive analytical methods for the determination of trace elements of heavy metal ions in water, mainly for Cu^{2+} [206–207]. The luminescence of Eu^{3+} is completely quenched in the trinuclear trichloroactate complex $CuEu_2(CCl_3COO)_8 \cdot 6H_2O$ [208]. The best known example of sensitization of Eu^{3+} by p-block elements is via the Bi^{3+} ion. Bi^{3+} itself is an efficient activator in luminescent materials, such as $LaPO_4:Bi^{3+}$ [202]. Luminescence of Bi^{3+} originates from the 6s 2shell. Upon cooping of bismuth(III)-containing phosphors with Eu-, the Bi^{3+} luminescence is quenched by energy transfer from Bi^{3+} to Eu^{3+} and intense red Eu^{3+} photoluminescence is observed. This energy transfer has been intensively studied in glasses and in crystalline inorganic compounds [209–212]. Other ions of p-block elements that can sensitize Eu^{3+} luminescence are Pb^{2+} and Sb^{3+} [211,213,214]. The effect of co doping of europium(III)-containing compounds with other trivalent lanthanide ions depends on the nature of the lanthanide ion. A rule of thumb is that

near-infrared emitting lanthanide ions will quench the Eu^{3+} luminescence, because the Eu^{3+} ions will efficiently transfer its excitation energy to the near-infrared emitting lanthanide ion, especially if the other lanthanide ion has energy levels that are resonant with the $^5D_0$ state of Eu^{3+}. This is nicely illustrated by a luminescence study of Y_2O_3:Eu^{3+}(1%) co doped with other trivalent lanthanide ions [215]. Nd^{3+}, Dy^{3+}, Er^{3+}, Tm^{3+} and Yb^{3+} partly quench the Eu^{3+} luminescence. Quenching by Nd^{3+} is very efficient, whereas quenching by Yb^{3+} is not very efficient due to the lack of resonant levels. The results for Sm^{3+} depended on the excitation wavelength; luminescence enhancement was observed after excitation in a Sm^{3+} level (at 407 nm), whereas weak quenching was observed for other excitation wave-lengths. A lanthanide ion that quenches Eu^{3+} luminescence also leads to a decrease of the decay time of the $^5D_0$ state. Ce^{3+}, Pr^{3+} and Tb^{3+} were not included in this study, since it is difficult to keep these ions in the trivalent oxidation state. Reisfeld and Boehm described the energy transfer from Sm^{3+} to Eu^{3+} in phosphate glasses that contain both Eu^{3+} and Sm^{3+}[216]. The energy transfer is not only evident from an increase in the luminescence intensity of Eu^{3+}, but also from the appearance of extra peaks in the excitation spectrum which can be attributed to Sm^{3+}. Energy transfer from Sm^{3+} to Eu^{3+} has been described by several authors for co-doped glasses [217–218] and inorganic phosphors [210,219–220]. Probably the best documented energy transfer of another lanthanide ion to Eu^{3+} is the energy transfer from Tb^{3+} to Eu^{3+}. The emitting level $^5D_4$ of Tb^{3+} is well above the $^5D_0$ emitting level of Eu^{3+}, so that the energy transfer from Tb^{3+} to Eu^{3+} leads to an enhancement of the luminescence intensity of Eu^{3+}. The energy transfer has been studied in glasses [220,221], inorganic compounds [222–223], solid molecular compounds (including metal–organic frameworks) [263,189], and in solution [184–271]. Finally, the uranyl ion (UO_2^{2+}) can sensitize Eu^{3+} luminescence by energy transfer [260–261]. Another possibility to sensitize lanthanide luminescence is via charge-transfer states. This is especially the case for trivalent lanthanide ions which can easily be reduced to the divalent state (redox-sensitive

lanthanide ions) like Sm^{3+}, Yb^{3+} and Eu^{3+}, where light can be absorbed by an intense ligand-to-metal charge trans-fer state (LMCT state) from which the excitation energy can be transferred to the 4f-levels of the lanthanide ion. This process only works well if the energy of the LMCT state is high enough. For instance, for Eu^{3+} sensitization through a LMCT state is efficient if the LMCT is lying above 40,000 cm−1. Low lying LMCT states will partially or totally quench the luminescence [185]. In the case of Eu^{3+}, metal-centered luminescence is totally quenched if the energy of the LMCT is less than 25,000 cm−1. Quenching by low-lying charge-transfer states is the reason for the weak luminescence or the absence of luminescence in europium(III) dithiocarbamatecomplexes [186–188]. In hydrated europium(III) acetylacetonate,Eu(acac)$_3\cdot$3H$_2$O, no luminescence is observed upon excitation in the ligand absorption band, but the compound does show luminescence after excitation in the $^5D_1$, $^5D_2$ or $^5L_6$ levels [264]. The low efficiency of the intramolecular energy transfer is attributed to the presence of low-lying charge-transfer excited states below the ligand singlet levels. Sensitization of Eu^{3+} luminescence via charge-transfer states is much less investigated for molecular europium(III)complexes than for Eu^{3+} in inorganic host matrices [181,265–266].For inorganic compounds, sensitization of Eu^{3+} luminescence via charge-transfer states is a very important mechanism.

 Excitation spectra

Excitation spectra are recorded by monitoring the luminescence intensity as a function of the excitation wavelength: the detection wavelength is fixed and the excitation wavelength is scanned over the spectral region of interest. An excitation spectrum looks similar to an absorption spectrum, but there is no one-to-one relationship. The relative intensities of the transitions can be different and there can be extra peaks present or peaks missing in comparison to the corresponding absorption spectrum. In fact, an excitation spectrum can be considered as being the product of an absorption spectrum and a plot of the quantum yield as a function of

the wavelength. A transition is observed in the excitation spectrum only if this level is efficient in populating the emitting level and thus in generating luminescence. If an energy level is absent in the excitation spectrum it means that this level is not efficient in absorbing the excitation light and/or is not able in populating the emitting level. Another feature of an excitation spectrum is that, in addition to the energy levels of the emitting ion, also energy levels of the sensitizing ion or the antenna ligands are visible. The main application of an excitation spectrum is to determine the optimum excitation wavelength the excitation wavelength for measuring a luminescence spectrum is set at the most intense peak or the maximum of the most intense band in the excitation spectrum. An excitation spectrum does also give access to higher energy levels of a lanthanide ion. Recording an excitation spectrum is the preferred method for determining these energy levels in powder samples or in very diluted crystals or solutions, for which measurement of the absorption spectrum is difficult or even impossible. Measurement of the excitation spectrum is also the preferred method for determination of the energy levels of a lanthanide ion in the vacuum ultraviolet (VUV) region[222 ,239–240]. The main disadvantage of an excitation spectrum is that it cannot be used for studies of intensities of f–f transitions. Whereas Judd–Ofelt intensity parameters Ω_can be derived from absorption spectra, this is not the case for an excitation spectrum. Whereas emission spectra reveal the presence of radiative transitions, excitation spectra can reveal the presence of non-radiative transitions between levels [241]. The presence or absence of levels in the excitation spectra can be used to establish whether decay occurs via a step-by-step process, or whether level-bypassing transitions occur.

Measurement of the excitation spectrum at different emission wavelengths allows detecting different europium(III) species in solution. If only one species is present, the different excitation spectra will look identical. If more than one species is present, differences in peak heights and integrated intensity ratios will be observed in the excitation spectra [161].

Excitation spectroscopy has often been used by Horrocks and co-workers for the study of the binding of the Eu^{3+} ion to specific sites in calcium-binding proteins and other metalloproteins [98,175,242–244] The method consisted of excitation of the $^5D_0$ state by scanning at unable dye laser through the 578–580 nm spectral region, while monitoring the $^5D_0 \rightarrow ^7F_2$ emission at 615 nm. Excitation spectroscopy was also used to study the kinetics of formation of europium(III) complexes and for the determination of complex stability constants [190,243–245]. Measurements of excitation spectra at 5 K of $Eu(ClO_4)_3$dissolved in water revealed the presence of two peaks for the$^5D_0 \leftarrow ^7F_0$ transition at 579.43 nm and 579.17 nm[246]. The transition at 579.43 nm was assigned to the eight-coordinate species $[Eu(H_2O)_8]^{3+}$, while transition at 579.17 nm was assigned to the nine-coordinate complex $[Eu(H_2O)_9]^{3+}$. The two complexes had also two different luminescence decay times:$123 \pm 9s$ for the eight-coordinate complex and 109 ± 8 s for the nine-coordinate complex. In D_2O, the luminescence decay times were much longer: 3.50 ± 0.12 ms for the eight-coordinate complex and 3.70 ± 0.18 ms for the nine-coordinate complex. The eight-coordinate complex forms the minor fraction and the nine-coordinate complex the major fraction. On the other hand, a study using $[Eu(H_2O)_9][(BrO_3)_3]$, $[Eu(H_2O)_9][(C_2H_5SO_4)_3]$ and $[Eu(H_2O)_8]_2[(V_{10}O_{28})] \cdot 8H_2O$ as model compounds for nine- and eight-coordinate Eu^{3+}aquo species in solution concluded on the basis of a comparison of the $^5D_1 \leftarrow ^7F_0$ laser excitation spectra and the $^5D_0 \rightarrow ^7F_{1,2}$ emission spectra of the crystalline model crystal systems with those of 0.1 M aqueous solution of $EuCl_3$ that $[Eu(H_2O)_8]^{3+}$ is the dominating europium(III) species in solution[247]. Excitation spectra have been used to systematically invest-gate vibrionic transitions in the spectra of the Eu^{3+}ion [248]. A vibronic transition involves a simultaneous change in the electronic and vibrational states of the metal ion. Vibrionic transitions in lanthanide spectroscopy have been reviewed by Hüfner [65] and by Blasse [249]. Vibronic transitions are very prominent in the spectra of centrosymmetric lanthanide complexes, because electric dipole transitions can be induced in these systems only

by a vibrionic coupling mechanism between the f electrons and ungeared vibrational modes [159,178,250,251]. However, also non-centrosymmetric lanthanide complexes can show vibrionic transitions, but these are in general less intense than the purely electronic transitions. Blasse and co-workers studied the variation of the electron-phonon coupling strength across the lanthanide series [267,268]. The electron-phonon coupling is strong in the beginning (Pr^{3+}) and at the end of the lanthanide series (Tm^{3+}), but small at the center (Eu^{3+}, Gd^{3+}, Tb^{3+}) [252–253]. Blasse compared the intensity of the vibrionic transitions of the $^5D_0 \rightarrow ^7F_2$ transition in the luminescence spectra with that of the $^5D_0 \rightarrow ^7F_1$ magnetic dipole transition, and the intensity of the $^5D_2 \leftarrow ^7F_0$ transition in the excitation (or absorption) spectra with that of the $^5D_1 \leftarrow ^7F_0$ magnetic dipole transition [248]. He considered the excitation and the absorption spectra of europium(III) compounds to be more suitable for investigation of the vibrionic transitions than the corresponding luminescence spectra, because the crystal field splitting of the $^7F_2$ level is often so large that the vibrionic transitions of the $^5D_0 \rightarrow ^7F_2$ transitions overlap with the electronic lines of $^5D_0 \rightarrow ^7F_2$ transitions and other transitions, e.g. $^5D_0 \rightarrow ^7F_3$. Moreover, the vibrionic transitions are always less intense in the luminescence spectra (emission spectra) than in the excitation spectra. Depending on the host matrix, the vibrionic intensities vary by about two orders of magnitude. Very intense vibrionic transitions are observed for $SrTiO_3:Eu^{3+}$. The intensity of the vibrionic transitions of the $^5D_2 \leftarrow ^7F_0$ transition are ten times more intense as than that of the $^5D_1 \leftarrow ^7F_0$ transition. In the case of $SrTiO_3:Eu^{3+}$, vibrionic transitions accompany even the magnetic dipole transitions, although such vibrionic transitions are forbidden by the selection rules [254]. The intensities of the vibrionic transitions are very weak for $CaSO_4:Eu^{3+}$:the intensity of the vibrionic transitions of the $^5D_2 \leftarrow ^7F_0$ is about1/10thof that of the intensity of the $^5D_1 \leftarrow ^7F_0$ transition [248].Several authors describe vibrionic transitions in excitation and emission spectra of europium(III) compounds with organic ligands[158,255-256].

Conclusions

Europium(III) compounds find widespread applications in lamp phosphors, luminescent markers and in biomedical analyses. In this sense, europium is not a unique lanthanide, since also terbium is used for the same applications. The spectroscopic properties of other lanthanide ions are vaporized in technological applications, e.g. lasers. The Nd-YAG laser is a good example of such an application. However, the Eu^{3+} ion is truly unique as a spectroscopic probe, thanks to its very special electronic configuration. The ground state ($^7F_0$) and the most important emitting excited state ($^5D_0$) are nondegenerate and thus not split by crystal-field effects. The most important transitions in the luminescence spectra are from the $^5D_0$ excited state to the ^7F_J levels with low J values (J = 0, 1, 2) and thus with a limited number of crystal-field levels. The same can be said for the absorption spectra, where the transitions are from the $^7F_0$ ground state to ^5D_J levels (J = 0, 1, 2). The free-ion levels do not overlap and their wave functions can be described well within the Russell–Saunders coupling scheme. J-mixing is limited, so that there are not many violations of the selection rules. The Eu^{3+} ion shows only weak vibronic transitions if the Eu^{3+} ion is not at a centrosymmetric site. It is also convenient that the luminescence is in the visible spectral region (red emission). All these factors make the interpretation of europium(III) spectra much easier compared to that of spectra of other lanthanide(III) ions. By applying the rules of group theory, it is possible to predict the number of crystal-field transitions that can be expected for the absorption and emission spectra of europium(III) compounds. By counting the number of observed crystal-field transitions, the point group symmetry of the Eu^{3+} site can be derived. The transition between the $^5D_0$ and $^7F_0$ state give information on the number of non-equivalent Eu^{3+} sites or on the number of europium(III) complexes that are present in solution. The hypersensitive transitions reflect even very small distortions in the coordination sphere. The Eu^{3+} ion is a probe for the local

symmetry of the lanthanide ion. Therefore, high-resolution spectroscopic studies complement X-ray crystallographic studies on single crystals. Not only the fine structure in the spectra (fingerprinting), but also the observed lifetime of the $^5D_0$ excited states contains valuable information. The best example is the determination of the hydration number of the Eu^{3+} in solution or in hydrated crystals by the Horrocks–Sudnick or a similar formula. This review paper tried to give a realistic overview of the information content that is available in the luminescence, excitation and absorption spectra of europium(III) compounds. The different transitions have been discussed in a systematic way. Europium(III) compounds with special spectroscopic properties have been highlighted. It has been discussed how the Judd–Ofelt theory can be applied to europium(III) spectra and how the intensity parameters are derived. Luminescence lifetimes give insight into the efficiency of conversion of the excitation energy into light. The reader is advised to find a good balance between extracting the correct information from europium(III) spectra and avoiding the pitfall of over-interpretation of the spectra. The Eu^{3+} ion as a spectroscopic probe does not stand on its own. Measurement of spectra of europium(III) compounds has to be complemented by the use of other experimental techniques, which provide complementary information. Only in this way, a correct description of lanthanide containing system can be achieved.

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