Manuscript submitted to:

Volume 2, Issue 2, 37-60.

DOI: 10.3934/matersci.2015.2.37

AIMS Materials Science

Received date 3 March 2015, Accepted date 22 March 2015, Published date 1 April 2015

Review

Optical Properties of Lanthanides in Condensed Phase, Theory and

Applications

In memory of Christian K. Jørgensen

Renata Reisfeld *

Institute of Chemistry, Hebrew University of Jerusalem, Givat-Ram, Jerusalem 91904, Israel

* Correspondence: Email: renata.reisfeld@mail.huji.ac.il.

Abstract: The basic theories of electronic levels and transition probabilities of lanthanides are summarized. Their interpretation allows practical preparation of new materials having application in lighting, solar energy utilization, optoelectronics, biological sensors, active waveguides and highly sensitive bioassays for in vitro detection in medical applications. The ways by which the weak fluorescence arising from electronic transition within the four f-configurations can be intensified will be discussed. This includes the intermixing of the four f-states with ligands of the host matrix, excitation to higher d-electronic states. Additional intensification of luminescence by plasmonic interaction with gold, silver and copper nanoparticles will be discussed. A short history of the time development of the research and the names of the scientists who made the major contribution of our understanding of lanthanides spectroscopy are presented.

Keywords: luminescence increasing; lanthanide; complexes; spectroscopy; energy transfer

1. Introduction

The lanthanides are a fascinating group of elements the optical properties of which arise from the inner f-electrons which are starting with one in Cerium and terminate with thirteen in Ytterbium. The transition probabilities within the for f-orbital are forbidden by Laporte rule and become partially allowed either by mixing of the for f with 5 d-orbital or with a charge transfer states of the neighboring ligands [1,2]. The basic theory of the electronic spectra can be found in references [3,4].

Since the beginning of the twentieth century, the radiative transitions of lanthanide ions have received academic and industrial attention. The study of the photophysics of the lanthanides has given rise of intriguing science. Moreover the technological applications of lanthanide luminescence encompass not only fluorescent tubes and colour televisions, but also immunoassays, optical amplifiers, active vaweguides, luminescent solar concentrators and in the future, perhaps, organic light-emitting diodes.

Lanthanide organic compounds have been widely reported as having the desirable properties of exhibiting intense narrow-band emission via efficient intramolecular energy transfer from the ligand excited state to the central metal ions under UV excitation. The luminescent spectra are intensified greatly by complexation of lanthanide ions with organic ligands. These lanthanide ions form stable crystalline complexes with heterocyclic ligands, such as bipyridyl (bpy) and phenanthroline (phen), which exhibit efficient energy transfer to the chelated lanthanide ions [5,6,7] and cryptates [8]. However, lanthanides complexes with organic ligands for practical uses are limited because of poor thermal stability and mechanical properties, although they also have good phosphor characteristics. This drawback can overcome by protecting them by a glassy surrounding [9].

Recently nanoparticles (NPs) of lanthanides having high luminescence have been shown for numerous applications in medicine and other fields. In order to take the advantage of the properties of the lanthanides additional ways of increasing their fluorescence intensities are studied. This is done by incorporating into the host matrices NPs of silver, gold and copper [10,11,12] in conjunction with the luminescent species.

The characteristic absorption and emission spectra of lanthanide compounds in the visible, near-ultraviolet, and infrared are attributed to transitions between 4f levels due to the fact that they present sharp line with oscillators strengths typically of the order of 10^{-6} . These transitions are electric dipole forbidden but became allowed as forced electric dipole transitions [13–17]. Magnetic dipole f-f transitions are allowed, however they are much weaker.

2. Electronic levels of 4 f-elements

The energy levels of the triply charged ions may be obtained with the highest accuracy from the analysis of the free ion spectra. Another way of obtaining information on the free ion states is to calculate the energy levels theoretically. Such calculations are practically a necessity for guiding the interpretation of the empirical results. Moreover, the calculations furnish the only way to obtain eigenvectors.

The methods for dealing with this problem were developed first by Slater. They were extended and described in considerable detail by Condon and Shortley [3] and later systematized by Racah [4], Judd [18] and Ofelt [19] Wybourne [20] and Dieke [21]. The additional developments can be found in [22,23,24].

The object of the theory is the calculation of the energy levels and the wave functions of atoms even of such complexity as the lanthanides ions. As in all quantum mechanical calculation of complex systems, the theory starts with a system which is sufficiently simplified by the omission of certain interactions for its properties to be obtained without undue complications. This is the so-called zero-order approximation, characterized by the Hamiltonian H^0 with the energies E_n^0 and wavefunctions U_n .

The zero order approximation considers the outer electrons in a central field produced by the nucleus and the 54 electrons in the completed xenon-like shell but disregards the electrostatic repulsion between the outer electrons and any influence of their spins. All outer electrons are, therefore, completely independent of each other and the energy cannot depend on the relative orientations of their orbits.

In this approximation, all states of a configuration have the same energy. The state of an individual single electron is characterized by four quantum numbers n, l, m_l , m_s . A configuration of N electrons is the assembly of states in which the principal quantum number n and the orbital angular momentum l for each electron are given, but m_l and m_s can take all possible values. This can also be expressed by saying that the size and shape of each electron orbit is given but its orientation in space and the spin orientation are arbitrary. For the condensed phase spectra of the lanthanides, the configuration where all outer electrons are in 4f orbits, the 4f^N configuration is of greatest importance.

The degeneracy of a configuration in the zero order approximation is given by the product of $2(2l_i + 1)$ for all outer electrons when no equivalent electrons are involved. For the 4f^N configuration which consist entirely of equivalent electrons, the degeneracies are given by the binomial coefficient

 $\binom{14}{N}$ which are 1, 14, 91, 364, 1001, 2002, 3003, 3432 or N = 0 to 7. For the second half of the group,

the degeneracies are the same as in the first half, in the opposite order in accordance with the principle that N 4f electrons are equivalent to 14—N holes in the completed shell and a configuration with a certain number of holes has the same number and kind of states as a configuration with the same number of electrons.

If the interaction between the electrons and between the orbital and spin angular momenta are introduced by appropriate terms H^1 , H^2 , etc. in the Hamiltonian, some of the degeneracy is removed. When the ion is then placed in a condensed matrix field, all of it may be removed so that only non-degenerate states remain. The modification of the state through the influence of the interaction can be calculated from conventional perturbation theory. There are more than 3000 different wavefunctions to deal with in one configuration near the middle of the lanthanides group. This shows that the mere writing down of the wavefunctions and interaction matrices alone would be a nearly impossible task. For this reason, systematic methods have been developed, chiefly by Racah [4], which reduce the labor of computation considerably. In complicated cases, the calculations are still tedious but manageable with some patience. The computation problem is essentially the following.

The chief interactions in the free ion are the electrostatic repulsion between the outer electrons expressed by

$$H^1 \sum_{ij} \frac{e^2}{r_{ij}} \tag{1}$$

Summed over all electron pairs, and the spin-orbit interaction by

$$H^{2} = \sum_{i=1}^{n} \zeta_{i} (l_{1} * s_{i})$$
(2)

where ζ_1 is the spin-orbit interaction constant for the ith electron. For a Coulomb field with an effective nuclear charge Z",

$$\zeta_i = \frac{\alpha^4 R Z''}{r_i^3} \tag{3}$$

with α fine structure constant and R the Rydberg constant. The effective charge Z" is, in general, different from the effective charge Z' occurring in the electrostatic interactions.

In the interaction between the states within one configuration is taken into consideration and, thus interaction between states of different configurations are left out, this is the approximation usually employed. It is reasonably good for the $4f^{N}$ configuration of trivalent lanthanides ions because this configuration is isolated from all others with which it could interact. Because of symmetry considerations (parity), the nearest configuration that can interact with $4f^{N}$ is $4f^{N-1}$ or $4f^{N-1}5d$ or $4f^{N-1}6p$ or $4f^{N-1}6s$ which are of the order of 10^{5} cm⁻¹ above it. Broken shell configurations such as $5p^{5}4f^{N+1}$ can be of importance even though the energy difference is much larger, since the overlap integral may be quite large (Wybourne [20]). According to the radial integral calculations, the contribution from $5p^{5}4f^{N+1}$ is even more important.

When only the influence of the electrostatic interaction is considered, we have the following situation. From the original states in which each electron is characterized by the four quantum numbers: n, l, m_e, m_s, (where only m_e and m_s are of importance for further consideration, as n and l are fixed for the whole configuration), we can by standard methods obtain linear combinations expressing the wave functions of states characterized by the quantum numbers L, S, $L_Z = M_L$, $S_Z = M_S$. L and S correspond as usual to the total orbital and spin angular momenta, respectively, and M_Z and M_S to the projection of these vectors on a fixed axis, usually the Z-axis. The energy does not depend on M_Z and M_S . The energy actually does not depend directly on the numerical value of the total spin S either. In this approximation, S serves merely to identify a symmetry property of the state. Each level characterized by L and S is (2L + 1)(2S + 1)—fold degenerate. Electrostatic interaction (mixing of states) can take place only between two levels with the same L and S. Such interacting levels do not exist for one- and two-electron configurations, but interacting pairs become increasingly common as N increases. The maximum number of interacting levels for a particular value of L and S is given in the second row of Table 1.

In order to obtain energies and eigenvectors, it is necessary to solve secular determinants of order equal to the number of interacting states that that is at most of the order of the number given in Table 1.

N=	1	2	3	4	5	6	7
H^{1}	1	1	2	4	7	9	10
H^1+H^2	1	3	7	19	30	46	50
Total number of levels	2	13	41	107	198	295	327
Multiplets	1	7	17	47	73	119	119

Table 1. Maximum number of interacting levels under electrostatic H^1 and spin orbit H^2 interaction.

2.1. Matrix Elements of Operators

Calculation of the energy levels of an atom or ion normally processed by first figuring the matrix elements of the electrostatic perturbation potential V, defined as:

$$V = \sum_{i=1}^{N} \left[-\frac{Ze^2}{r_i} - U(r_i) \right] + \sum_{i(4)$$

The first term is purely radial and contributes to energy shifts that are the same for all levels belonging to a given configuration without affecting the energy-level of the configuration. The repulsive Coulomb interaction of the electrons will be different for different states of the same configuration. The summations in Equation (4) are over the coordinates of all the electrons. However, the term energies of a configuration which contains closed shells are the same, apart from a constant energy shift of all the terms, as those of the configuration in which the closed shell have been omitted. Thus in considering the energy-level structure of a configuration, we shall restrict the summation in Equation (4) to those electrons in incomplete shells. Hence in calculation the energy-level structure of a configuration, we must calculate matrix elements of the type

$$\tau SLJM \left| \sum_{i < j} \frac{e^2}{r_{ij}} \right| \tau' S' L' J' M' \tag{5}$$

Since the electrostatic Hamiltonian commutes with the angular momentum operators corresponding to L^2 , S^2 , J^2 and M the matrix elements will be diagonal in L and S (although not it τ) and independent of J and M. Calculation of the matrix elements of Equation (5) commences by first expanding the interaction between each pair of electrons in Legendre polynomials of the cosine of the angle w_{ij} between the vector from the nucleus to two electrons. r < indicates the distance from the nucleus (the point of origin) to the nearer electron and r > indicates distance from the nucleus to the further away electron.

The energies and wavefunctions can be expressed in terms of certain integrals

$$F^{K} \int_{0}^{\infty} \int_{0}^{\infty} \frac{r_{<}^{k}}{r_{>}^{k+1}} R_{i}^{2}(r_{i}) R_{j}^{2}(r_{j}) r_{i}^{2} r_{j}^{2} dr_{i} dr_{j}$$
(6)

where r < is the smaller and r > is the greater of r_i and r_j . The Slater integrals are usually expressed in terms of a subscripted quantity F_k where for f-electrons the relationships are $F_2 = F^2/225$; $F^4 = F^4/1089$; $F_6 = F^6/7361.64$. If the wavefunctions of the central field approximation are known, the integrals F_k can be calculated.

For the 4f^N configuration only the integrals F_0 , F_2 , F_4 , F_6 need be considered. Here, a further simplification can be made which for the 4f^N configuration probably introduced only small errors in comparison to those present because of neglect of the inter-configuration interaction. In the central field is a Coulomb one, it can be characterized by a single constant, the effective nuclear charge Z'. In that case, the F_k must all be functions of Z' or of F_2 one can write $F_4 = 0.145F_2$; $F_6 = 0.0164 F_2$ and (for the triply ionized lanthanides) $F_2 = 12.4Z' = 12.4(Z-34)$ approximately. The parameter F_0 is a common additive constant to all levels and for this reason, is of no importance for the structure of the configuration.

Recent investigations have shown that the wavefunctions, in fact, deviate considerably from being hydrogenic, but in spite of this, and the ratios remain relatively stable. As more experimental details of the crystal and first ion levels become available, these problems will become increasingly important. The simplified theory has nevertheless proved very useful in clarifying the level assignment. Although the theoretical calculations are of limited validity they give a reasonably good account of the observed energies. The calculated levels are, however, good enough for the identification of the empirical levels, at least the lower ones, and ones identified, the latter can, of course, be determined with any desired accuracy. The energies and the assignments of the grand and exited levels can be found in [2] and in Figure 1 where the electronic levels are presented.



Figure 1. Energy level of the trivalent lanthanides.

2.2. Results of theoretical calculations

Most detailed theoretical calculations of energy levels and wavefunctions have been carried out on the $4f^N$ configuration of the trivalent ions and are of direct interest for the crystal spectra. The results may be seen in Figure 1.

The general relations described here are to be found in the book of Wybourne [20]. In all cases the calculations for $4f^{N}$ and ${}^{4fN+1}$ are the same but with a positive ζ for N < 7. Some examples for the simple cases are $4f^{1}$ and $4f^{13}$: This is the case of (Ce³⁺, Yb³⁺). There is no problem here, as there is only one electron. For $4f^{2}$ and $4f^{12}$: Pr³⁺ +, Tm³⁺ here the relatively small number of levels and the fact that nothing more complicated than the solution of a cubic equation makes this a problem suitable even for a desk calculator.

The electrostatic interaction involves no non-diagonal matrix elements, and the positions of the various multiplets can be directly given:

³H: $E_1 = 0$

³F: $E_2 = 15F_2 + 18F_4 - 273F_6 = 13.133F_2$ ¹G: $E_3 = -5F_2 + 148F_4 + 91F_6 = 17.952F_2$ ¹D: $E_4 = 44F_2 - 48F_4 + 728F_6 = 48.979F_2$

³P: $E_5 = 70F_2 + 84F_4 - 127F_6 = 61.286F_2$

¹I: $E_6 = 50F_2 + 60F_4 + 14F_6 = 58.923F_2$

¹S: $E_7 = 85F_2 + 249F_4 + 1729F_6 = 149.461F_2$

The last column gives the results in a Coulomb field.

By diagonalizing the electrostatic and spin orbit matrices, the wave function of the total levels is obtained to a good approximation and their energy calculated [2,3,4,21,22].

3. Transition probabilities of 4 f-elements and the Judd-Ofelt Theory

The optical transitions so typical of the spectra of lanthanides within condensed phase usually correspond to intra- f^N transitions of predominantly electric-dipole character. For a free ion, electric-dipole transitions between states of the same configuration are strictly parity forbidden, and thus any explanation of the observed spectra of glasses must concern itself with non-centro-symmetric interactions that lead to a mixing of states of opposite parity. This mixing may result from several distinct mechanisms. One of the most obvious mechanisms is simply the coupling of states of opposite parity by way of the *odd* terms in the crystal field expansion.

The systematic theoretical approach explaining the contribution of the next configuration to the f configuration via odd terms in the condensed phase expansion and the energy difference between the two configurations together with the radial integrals can be found in the literature [18,19,23].

Several selection rules follow in application of the triangular conditions to the 3-j and 6-j symbols contained in the theoretical equations. These are:

 $\Delta L = \pm l; \quad \Delta S = 0; \quad \Delta L \le 21; \quad \Delta J \le 21$

The $\Delta L = \pm I$ selection rule means that for f^N configurations the perturbing n figurations may differ only by the single substitution of n'd or n 'g-electrons. Spin-orbit interaction will usually lead to a breakdown of the selection rules on S and L. The selection rule $\Delta J \leq 6$ will be valid as long as J is a "good" quantum number. This selection rule is seen in the usual absence of the transitions ${}^5D_0 \rightarrow$ 7F_3 and 7F_5 in Eu³⁺ spectra. In general, the oscillator strength f or a transition may be expressed as

$$f_e = \frac{8\pi^2 mc}{3he^2} \overline{\overline{v}} \left(A \left| P_\rho^{(1)} \right| B \right)^2 \frac{(n^2 + 2)^2}{9} = \overline{v} \sum_{\lambda, q} \zeta(\lambda, q, \rho) \left(l^N \alpha SLJJ_Z \left| U_{q+\rho}^{(\lambda)} \right| l^N \alpha' S'L'J'J_Z \right)^2$$
(7)

$$\zeta(\lambda, q, \rho) = \frac{8\eta^2 mc}{3he^2} \frac{(n^2 + 2)^2}{9} Y^2(\lambda, q, \rho)$$
(8)

Equation (7) in a simplified form is

$$f_m = \frac{8\pi^2 mc}{3h^2} \bar{v} \left| \frac{-e}{2mc} (\alpha SLJJ_Z | L + g_S S | \alpha SLJJ_Z') \right|^2 n =$$

$$4.028 \times 10^{-11} \bar{v} (\alpha \alpha SLJJ_Z | L + g_S S | \alpha SLJJ_Z')^2 n \tag{9}$$

where \bar{v} is in units of cm⁻¹ and *n* is the refractive index. The matrix of L + g_sS will be given by

$$(\alpha LJJ_Z|L + g_S S|\alpha LJJ_Z) = (-1)^{J-J_Z} \begin{pmatrix} J & 1 & J' \\ -J_Z & \rho & J_Z' \end{pmatrix} \times (\alpha SLJ||L + g_S S||\alpha SLJ')$$
(10)

where $\rho = 0$ gives the z-components of S and L, which will correspond to the absorption or emission of σ -polarized light, and $\rho = \pm 1$ gives the x \pm iy—corresponding to π -polarized light.

The above equations hold for a perturbing configuration of the type $n1^{N-1}n'l'$. Perturbing configurations of the type $n'l'^{4l+1}nl^{N+1}$ will differ in the angular factors by not more than a phase factor. The summation index is limited to even values (that is, 2, 4, and 6 for f-electrons).

The following selection rules may be readily established [3]:

$$\begin{array}{cccc} \Delta l = 0 & \Delta S = 0 & \Delta L = 0 & \Delta J = 0, \pm l & (\text{not } 0 \leftrightarrow 0) \\ \Delta J_Z = 0 & \Delta \mu = 0 & (\sigma\text{-polarization}) \\ \Delta J_Z = \pm l & \Delta \mu = \pm l & (\pi\text{-polarization}) \end{array}$$

In the trivalent lanthanides the transitions of interest take place between states within the $[Xe]4f^{1}5d^{0}6s^{0}$ configuration (with n = 1 for Ce³⁺ to n = 13 for Yb³⁺). As a consequence, they are parity forbidden and consist mainly of weak magnetic dipole (MD) and induced electric dipole (ED) transitions. The intensities of the MD transitions are practically not influenced by the chemical surroundings of the ion, whereas those of the ED transitions are quite sensitive to it. Judd-Ofelt theory has been very successful in understanding and predicting the spectral intensities of the latter, especially for ions in inorganic glasses and crystals. Also, the absorption spectra of lanthanide complexes in solution and molecular crystals have been subjected to analyses on the basis of Judd-Ofelt theory [18,19], but it has rarely been used to predict the emissive properties of lanthanide complexes. A wide variety of lanthanide complexes has been synthesized and studied over the past decades, some of which are highly luminescent. One of the attractions of luminescent lanthanide complexes is that the organic ligand can be endowed with specific physical and chemical properties through chemical design and synthesis.

3.1. Radiative Transitions in Lanthanides

Radiative relaxation from an excited state ψJ of a lanthanide ion usually occurs in various lower lying state $\psi'J'$, giving rise to several lines in the emission spectrum. For example, the red luminescence of Eu³⁺ is a result of transitions from its ⁵D₀ state to all of the lower lying ⁷F_J levels. The spontaneous emission probability, A, of the transition $\psi J \rightarrow \psi'J'$ is related to its dipole strength according to

$$A(\psi J, \psi' J') = \frac{64\pi^4 \upsilon^{-3}}{3h(2J+1)} \left[\frac{n(n^2 - 2)^2}{9} D_{ED} + n^3 D_{MD} \right]$$
(11)

here is v is the average transition energy in cm⁻¹, h is Planck's constant $(6.63 \times 10^{-27} \text{ erg s})$, and 2J + 1 is the degeneracy of the initial state (1 for ⁵D₀). D_{ED} and D_{MD} are the electric and magnetic dipole strengths (in esu² cm²) respectively. The factors containing the medium's refractive index, *n*, result from local field corrections that convert the external electromagnetic field into an effective field at the location of the active center in the dielectric medium. The transitions from ⁵D₀ to ⁷F_{0,3,5} (J' = 0, 3, 5) are forbidden both in magnetic and induced electric dipole schemes (*D_{ED}* and *D_{MD}* are zero). The transition in ⁷F₁ (J' = 1) is the only magnetic dipole contribution. Magnetic dipole transitions in lanthanide ions are practically independent of the ion's surroundings and can be well calculated by theory (D_{MD} = 9.6 × 10⁻¹² esu² cm² = 9.6 10⁻⁶ debye²).

The remaining transitions (J = 2, 4, 6) are purely of induced dipole nature.

According to the Judd-Ofelt theory, the strength of all induced dipole transitions (absorption and emission) of a lanthanide ion in a certain matrix can be calculated on the basis of only three parameters Ω_{λ} , using the expression

$$D_{ED} = e^2 \sum_{\lambda=2,4,6} \Omega_{\lambda} |\langle J || U^{(\lambda)} || \rangle J' |^2$$
(12)

The elementary charge e is 4.803×10^{-10} esu. The Ω_{λ} , parameters belong the particular combination of the lanthanides ion and its coordinating environment, end are usually determined experimentally.

 $|\langle J || U^{(\lambda)} || \rangle J'|^2$ are the square reduce dmatrix elements whose values are independent of the chemical environment of the ion. A set of values of all matrix elements for all lanthanide ions is now available in the literature, but smaller sets can be found. The matrix elements that may be used in Equation (12) for Eu³⁺ are tabulated in Tabel 2.

$^{5}D_{0} \rightarrow$	$\left \langle J \ U^{(2)} \ J' \rangle \right ^2$	$\left \langle J \ U^{(4)} \ J' angle ight ^2$	$\left \langle J \big\ U^{(6)} \big\ J' \rangle \right ^2$
${}^{7}F_{2}$	0.0032	0	0
${}^{7}F_{4}$	0	0.0023	0
${}^{7}F_{6}$	0	0	0.0002

Table 2. Squared reduced matrix elements for calculation of the dipole strengths of the allowed induced ED transitions in the emission spectrum of Eu³⁺.

Transitions arising from the ⁵D_o level of the 4f⁶ electronic configuration of Eu³⁺ are intensities between the magnetic dipolar ⁵D₀ --;⁷F₁ (,=, 590 nm) and the electric dipolar ⁵D₀ \rightarrow ⁷F₂ (\approx 610 nm) transitions. The higher this ratio, the closer the local symmetry around Eu³⁻¹⁻ is to an inversion center. A tabulation of most of the transitions can be found in [13]. In the standard theory, the spontaneous emission of a integrated coefficient of the transition between two manifolds *J* and *J'* is given by

$$A_{JJ'} = \frac{4e^2\omega^3}{3\hbar c^3} \left[\frac{n(n^2+2)^2}{9} S_{ed} + n^3 S_{md} \right]$$
(13)

where ω is a angular frequency of the transition, *e* is the electronic charge, *c* is the velocity of light, \hbar is Planck's constant over 2π and *n* is the refractive index of the medium. The electric and magnetic dipole strengths, respectively, S_{ed} and S_{md} (in units of e^2), are given by

$$S_{ed} = \frac{1}{2J+1} \sum_{\lambda=2,4,6} \Omega_{\lambda} \langle \alpha' J \| U^{(\lambda)} \| \alpha J \rangle^2$$
(14)

where the quantities Ω_{λ} are the Judd-Ofelt intensity parameters as described before and *m* is the electron mass.

$$S_{md} = \frac{\hbar^2}{4cm_e c^2} \langle \alpha' J \| L + 2S \| \alpha J \rangle^2 \frac{1}{2J+1}$$
(15)

The reduced matrix elements appearing in Equation (14) are evaluated in the intermediate coupling scheme, and the angular momentum operators L and S are in the units of \hbar . The corresponding expression for the oscillator strength may be obtained from the relation

$$P_{JJ'} = \frac{2J=1}{2J'+1} \frac{mc^2}{2\omega^2 e^2 n^2} A_{JJ'}$$
(16)

The intensity parameters Ω_{λ} depend on both chemical environment and the lanthanide ion. Theoretically, they are given by

$$\Omega_{\lambda} = (2\lambda + 1) \sum_{t,p} \frac{|B_{\lambda tp}|^2}{2t+1}$$
(17)

where $B_{\lambda p}$ depends on the radial wave function, and the odd crystal parameters and energy difference between the 4*f* and next excited configuration of the opposite parity [6].

Here we are discussing only the static model and omitting the vibronic interaction.

$$B_{\lambda tp} = \frac{2}{\Delta E} \langle rt + 1 \rangle \theta(t,\lambda) \gamma_p^t - \left[\frac{(\lambda+1)(2\lambda+3)}{(2\lambda+1)} \right]^{\frac{1}{2}} \langle r^\lambda \rangle (-\sigma_\lambda) \langle 3 \| \mathcal{C}^{(\lambda)} \| 3 \rangle \Gamma_p^t \sigma_{t,\lambda+1}$$
(18)

where ΔE is the energy difference between the barycenters of the excited $4f^{N-1}$ 5d and ground $4f^N$ configurations, $\langle r^{\lambda} \rangle$ is a radial expectation value, $\theta(t, \lambda)$ is a numerical factor, σ_{λ} is a screening factor, $C^{(\lambda)}$ is a Racah tensor operator of rank λ , and $\sigma_{t,\lambda+1}$ is the Kronecker delta function. The first term in the right-hand-side of Equation 18 corresponds to the forced electric dipole mechanism as expressed by the average energy denominator method, and the second term corresponds to the dynamic coupling mechanism within the point dipole isotropic ligand polarizability approximation.

The measured intensity of an absorption band is related to the probability (P) for absorption of radiant energy (oscillator strength) by the expression

$$P = \frac{2303 \ cm^2}{N\pi^2} \int \varepsilon_i(v) dv = 4.318 * 10^9 \int \varepsilon_i(v) dv$$
(18a)

where ε is the molar absorptivity at the energy υ (cm⁻¹) and the other symbols have their usual meanings.

AIMS Materials Science

4. Relaxation process in trivalent lanthanides

The luminescence intensity of emission from a given level depends on the radiative and non-radiative probabilities. The quantum yields is expressed as

$$QY = \frac{\sum Ar}{\sum Ar + Wnr}$$
(19)

where Ar are the radiative transition probabilities and Wnr the non-radiative ones. The several processes can affect the quantum efficiency due to additional non-radiative relaxations. These can arise from multiphonon decay, and concentration quenching, in addition to the energy transfer to neighboring ions. All these processes will lower the quantum efficiency. A multiphonon decay mechanism is responsible for the non-radiative decay in most cases. The results of multiphonon relaxation rates have been summarized for amorphous materials [15,16]. The rates as functions of the energy gaps are straight lines as in figure 2 and 3.



Figure 2. Relative nonradiative relaxation of the highest phonon energy as a function of the host materials: ^{*} GLS, ALS: $3Ga_2S_3*La_2S_3$ (GLS), $3Al_2S_3*La_2S_3$ (ALS) ^{**} ZBLA: 57 % ZrF₄ – 34 % BaF₂ – 4 % AlF₃ – (5-X) % LaF₃ – X % PrF₃ with 0 < X < 5





The *ab initio* calculation of the transition rate between two electronic states with the emission of p phonons involves a very complicated sum over phonon modes and intermediate states. Due to this complexity these sums are extremely difficult to compute: However, it is just this complexity which permits a very simple phenomenological theory to be used. There are an extremely large number of ways in which p phonons can be emitted and the sums over phonon modes and intermediate states are essentially a statistical average of matrix elements. In the phenomenological approach it is assumed that the ration of the p^{th} and $(p-1)^{th}$ processes will be given by a coupling constant characteristic of the matrix in which the lanthanides is situated and not depending on the lanthanides electronic states. For a given lattice at low temperatures the spontaneous relaxation rate is given by:

$$W(0) = Be^{\alpha \Delta E} \tag{20}$$

where B and α are characteristics of the host (a is negative). Thus, a graph of the spontaneous rate versus energy gap will be a straight line in Figure 2, 3 a case when this approach is valid. Experimental data have shown that the approach is very good for a large variety of hosts. In this way all multiphonon rates can be inferred from a few measured rates (see Figures 2, 3).

The dominant emission process is the one which requires the least number of phonons to be emitted. The minimum number of phonon required for a transition between states separated by an energy gap ΔE is

$$p = \frac{\Delta E}{\hbar\omega_{max}} \tag{21}$$

where $\hbar\omega_{max}$ is the maximum energy of optical phonons. With increasing temperature the simulated emission of phonons by termal phonons increases the relaxation rate W according to

$$W(T) = W(0)(1 + \overline{n}(\hbar\omega_{max}))^p$$
⁽²²⁾

where n is the average occupation number of phonons at energy $\hbar\omega_{max}$.

The non-radiative relaxations in the lanthanides ions are related to their excited state populations and are governed by the energy difference between the emitting level and the next lower level, separated by the number of phonons of the host. In the weak-coupling case, for the lanthanides ions, the temperature dependence of the non-radiative rate is given by:

$$W(T) = \beta \exp\left[-(\Delta E - 2h\nu_{max})\alpha\right] \left(\left[\exp\left(\frac{h\nu}{kT}\right) - 1\right]^{-1} + 1\right)^p$$
(23)

where $p = \Delta E/_{hv}$, ΔE is the energy difference between the levels involved, α and β are constants and ν_{max} is the highest available vibrational frequency of the surroundings of the lanthanides ion. For example, Eu³⁺ may not only emit from ⁵D₀, but also from ⁵D₁ and ⁵D₂. The Tb³⁺ ion may not only emit from ⁵D₄ (green), but also from ⁵D₃ (blue). However, this depends critically upon the host lattice.

5. Energy transfer between two lanthanides ions

The above sections summarize the ways in which the electronic f levels of lanthanides ions are populated and depopulated by radiative and non-radiative transitions. As already mentioned the population density of the luminescent levels is generally weak because of the low transition probabilities. However there are other possibilities to increase the luminescence mainly by creating strongly absorbing species that will transfer the energy to the lanthanides ion. The three main ways of such excitation are:

1. Exciting closed shell transition metal complexes such as tungstates, molybdates, vanadates, titanates, etc. This way of excitation and its transfer to the lanthanides has been known since the late 1950s. The method has been applied to phosphors for luminescent lamps and television screens. There is a vast literature and many reports by Phillips, General Electric, Westinghouse, etc. The method is applied to solids melting at high temperature [25].

2. Energy transfer from strongly absorbing lanthanides due to f-d transitions or charge transfer; the literature is very large [24,25,26].

3. Energy transfer between the ligands and the lanthanides ion in complexes [24]. As an example we can take $[Eu(bpy)_3]^{3+}$ studied here [27]. This compound has a macrocyclic ligand containing three 2,2' bipyridine units joined together by two amino groups in the crystal it has three anions to neutralize the charge [27]. The Eu is located in the cage of the cryptate. Intermolecular energy transfer from the ligand to Eu has been recently calculated by the group of Malta [27,28] starting from the classical Fermi's golden rule. According to this rule, within the Born-Oppenheimer approximation, the energy transfer rate, W_{ET}, is given by

$$W_{\rm ET} = \frac{2\pi}{\hbar} |\langle \psi' \phi | H | \psi' \phi \rangle|^2 \cdot F$$
(24)

where ψ and φ' are the initial electronic states of the lanthanide ion and of the ligand, respectively. After energy transfer has taken place, we deal with the electronic states ψ' and φ . The temperature depended factor F contains a sum over Frank-Condon factors and the energy mismatch condition for the transfer for the process. The following expressions for the transfer rate have been obtained [27]:

$$W_{\rm ET} = \frac{2\pi}{\hbar} \frac{e^2 S_{\rm L}}{(2J+1) G R_{\rm L}^6} F \sum_{\lambda} \Omega_{\lambda}^{\rm ed} \langle \alpha' J' \| U^{(\lambda)} \| \alpha J \rangle^2$$
(25)

Corresponding to the dipole-dipole mechanism, also with λ =2, 4 and 6

$$W_{ET} = \frac{8\pi}{3\hbar} \frac{e^2 (1-\sigma_0)^2}{(2J+1)R_L^4} F\langle \alpha' J' \| S \| \alpha J \rangle^2 \sum_m |\langle \phi | \sum_k \mu_z(k) s_m(k) | \phi' \rangle|^2$$
(26)

corresponding to the exchange mechanism. In the above equations J is the total angular momentum quantum number of the lanthanide ion and α specifies the 4f spectroscopic term. G is the multiplicity of the ligand initial state and S_L the dipole strength associated with the transition $\varphi_{is} \rightarrow \varphi'$ in the ligand. U^(λ) is the same unit tensor operator, the reduced matrix elements of which are given in the intermediate coupling scheme, and R_L is the distance from the lanthanide ion to the region of the

ligand molecule in which the ligand donor (acceptor) state is localized. The quantities Ω_{λ}^{ed} are the well-known Judd-Ofelt intensity parameters (for forced electric dipole contribution only).

In Equation (26), S is the total spin operator of the lanthanide ion, μ is the z-component of the electric dipoleoperator, S_m (m = 0, ±1) is a spherical component of the spin operator and the index k runs over the electrons of the ligand. σ_0 represents a screening factor. The matrix element involving the coupled operators m_z and S_m can be treated by a quantum chemical method. The definition of R_L is

$$R_{L} = \frac{\sum_{i} c_{i}^{2} R_{L}(i)}{\sum_{i} c_{i}^{2}}$$
(27)

A complete theoretical model to calculate the luminescent properties of lanthanide coordination compounds is used to analyze the emission quantum yield of the $[Eu(bpy)_3]^{3+}$ and $[Eu(bpy)_3]^{3+}\cdot 2H_2O$ compounds. This theoretical model includes the calculation of the molecular structure, of the ligand-lanthanide energy transfer, of the temporal dependence of the ligand and lanthanide populations, which lead to the emission quantum yield, relative emission intensity and lifetime of the emitting state. This theoretical approach was use to ascertain the presence of the ligand-to-metal-charge-transfer (LMCT) state in these compounds. In addition, this approach has

provided indications of the location of the LMCT stat, as well as of the magnitudes of the energy transfer rates [27–29].

The molecular structure of the $[Eu(bpy)_3]^{3+}$ species has been calculated [27]. The overall structure agrees quite well with similar crystallographic structures presenting a helicoidal C₃ symmetry. The distances between the coordinated nitrogen atoms and the Eu(III) ion are relatively short, namely, an average of 2.53 Å for the bpy·bpy·bpy nitrogen atoms and 2.99 Å amino nitrogen atoms. These short distances favor the shielding of the encapsulated ion from the environment. The energy transfer rates have a strong dependence on the ligand-to-metal distances (R_L). Thus, any small increase in R_L would cause a significant decrease in the energy transfer rates. This is couplet to the fact that the O-H oscillators are important luminescence suppression pathways, making the hydrated compound a poor candidate for an efficient light converter.

The calculations on the singlet and triplet states of both the $[Eu(bpy)_3]^{3+}$ and $[Eu(bpy)_3]^{3+}\cdot 2H_2O$ species agree quite well which the experimental data. Namely, the calculated singlet state is about 30100 cm⁻¹ compared to the experimental value of 31800 cm⁻¹; the triplet state is calculated to 19500 cm⁻¹ and the experimental value is about 20300 cm⁻¹. It should be noted that the experimental value for the singlet state was obtained from the absorption spectrum of the $[Eu(bpy)_3]^{3+}$ compound, and the triplet state from the emission spectrum of the $[Eu(bpy)_3]^{3+}$ compound. From these calculated energy levels it has been possible to establish the most important states involved in the energy transfer process.

There are five 4f levels of these Eu compounds that are in quasi-resonance conditions with the ligand excited states. These states are then used to calculate the energy transfer rates using the theoretical model. In order to obtain transfer rates several parameters are needed, which have been obtained from the structure and spectroscopic calculations. For the [Eulbpy·bpy]³⁺ compound the following data were used to obtain the energy transfer rates: $R_L = 3.5$ Å, triplet = 4100 cm⁻¹, $A_{rad} = 1000 \text{ s}^{-1}$, which is the sum of the spontaneous emission coefficients of the transitions ${}^5D_o \rightarrow {}^7F_{0,1,2,4}$ and the theoretical value of the z-component of the electric dipole matrix element is $1.02 \times 10^{-36} \text{esu}^2 \text{ cm}^2$.

In addition, the value of 1053 s⁻¹ has been assumed for the inverse of the lifetime of the emitting state (⁵D₀). The dipole-dipole contribution for the transfer rates was calculated by using the following theoretical values for Ω_{λ} (in units of 10–20 cm²): $\Omega_2 = 0.16$, $\Omega_4 = 0.50$ and $\Omega_6 = 0.4$.

A value of 10^{-1} s⁻¹ was assumed for the non-radiative decay rates between the 4f-4f transition. Some of the most important energy transfer rates are larger for the ⁵D₀ and ⁵D₁ states, where the exchange interaction dominates, than for the higher excited 4f states, where the multipolar interactions are the most important ones.

This process is observed when there are two different ions in the matrix. We may excite one ion, the donor, and observe fluorescence from another ion, the acceptor.

Lanthanides ions are especially suitable for energy transfer studies due to their well-defined and narrow electronic levels, to which absorption occurs and from which fluorescence is observed. Symbolically, energy transfer can be written as

$$2(D) \rightarrow 1(D) \rightarrow 1(A) \rightarrow 2(A) \text{ or } D^* + A \rightarrow D + A^*$$
(28)

The donor system returns from the excited state 2(D) to the ground state 1(D) and the energy releases is used to bring the activator system from the ground state 1(A) to its exited state 2(A). In the case of the lanthanides, the transfer is a non-radiative one, i.e. no photon will appear in the system

during transfer. Förster predicted that for the organic system, the rate of energy is proportional to the overlap of the donor emission and the acceptor absorption spectra and to R^{-6} , where R is the distance between the donor and the acceptor. The discussion of Förster was extended by Dexter for ions in inorganic crystals, for detailed descriptions see [2,15,25]. The probability of energy transfer by dipole-dipole (dd) interaction in a simple case where the Born-Oppenheimer approximation holds is given in reference [15] as

$$P_{da(dd)} = \left(\frac{3h^4c^4Q_a}{4\pi R^6 n^4\tau_d}\right) \left(\frac{\varepsilon}{k^{1/2}\varepsilon_c}\right)^4 x \int \left[\frac{f_d(E)f_a(E)}{E^4}\right] dE$$
(29)

where R is the separation of nuclei of donors and acceptors, ε_c is the electric field within the crystal, ε is the electric field in vacuum and $f_d(E)$ is the observed shape of the emission band normalized to unity;

$$\int f_{\rm d}({\rm E}){\rm d}{\rm E}=1.$$

E is the energy; the subscripts d and a refer to donors and acceptors, respectively; $f_a(E) = \sigma(E)$ is the normalized function of the acceptor absorption

$$Q_a = \int \sigma(E) dE$$
,

The measured area under the absorption band, and

$$\int F_a(E)dE = 1.$$

 τ_d is the decay constant of the pure donor; and σ is the absorption cross section. The equation may also be written as follows:

$$P_{da(dd)} = \frac{3hc^2 Q_a Q_d g_d}{4\pi^3 nR^6 g_{d\prime}} \left(\frac{\varepsilon}{k^{1/2} \varepsilon_c}\right)^4 \frac{f_d(E) F_a(E)}{E^2} dE$$
(30)

where g are the degeneracies of the initial an excited state of the donor and Q are the areas of the acceptor and donor absorption curves.

In addition to dipole-dipole energy transfer we may observe energy transfer due to exchange interaction. The probability p(exc) of these can be written according to [15], as

$$p(exc) = \frac{2\pi}{h} Z^2 f_d(E) F_a(E) dE$$
(31)

In this formula, Z is not accessible to direct optical measurement and Z^2 varies with distance R as exp(-R/L), where L is an effective average Bohr radius of donor and acceptor ions in excited and unexcited states.

While the former two interactions are electrostatic in origin, the exchange interaction arises from the antisymmetry requirements of the electronic wavefunction for a system consisting of a donor and an acceptor.

6. Spectroscopy of lanthanides complexes

Another possibility to increase the luminescence of the lanthanides as mentioned above is using lanthanides complexes which can be excited in their charge transfer state or using the f-d

transitions [8,30].

The dramatic increase of the luminescence of lanthanides in the complex is a result of the following processes:

- 1. High absorption of the complex in the UV range as compared to the oxides.
- 2. The energy transfer from the ligands to the lanthanides (a back transfer to the ligands is also possible, but in our case it must be much smaller than the forward transfer).
- 3. For example, multiphonon relaxation populating the emitting ${}^{5}D_{0}$ state of europium and ${}^{5}D_{4}$ state of terbium from their higher energy states.
- 4. Multiphonon relaxation from the emitting ${}^{5}D_{0}$ and ${}^{5}D_{4}$ states of europium and terbium which arise from interaction with water of residual alcohol (formed as a result of the reaction producing the glass) and are decreased strongly in the complex and especially in sol-gel.

The energy-transfer rates between the ligands and the lanthanide ion were calculated for cryptate complexes. Their model includes the direct and exchange Coulomb interaction in the perturbation operator. Namely, the energy-transfer rate W_{ET} is given as follows:

$$W_{ET} = \frac{2\pi}{\hbar} \frac{e^2 S_L}{(2J+1)G} F \sum_{\lambda} \gamma \lambda \langle \alpha' J' \| U^{(\lambda)} \| \alpha J \rangle^2$$
(32)

which corresponds to the dipole- 2^{λ} pole mechanism (λ =2, 4 and 6) and

$$W_{ET} = \frac{2\pi}{\hbar} \frac{e^2 S_L}{(2J+1)GR_L^6} F \sum_{\lambda} \Omega_{\lambda}^{ed} \langle \alpha' J' \| U^{(\lambda)} \| \alpha J \rangle^2$$
(33)

Corresponding to the dipole-dipole mechanism (λ =2, 4 and 6) and

$$W_{ET} = \frac{8\pi}{3\hbar} \frac{e^2 (1-\sigma_0)^2}{2J+1R_L^4} F\langle \alpha' J' \| S \| \alpha J \rangle^2 * \sum_m |\langle \phi | \sum_k \mu_z(k) s_m(k) | \phi' \rangle|^2$$
(34)

corresponding to the exchange mechanism. In the above equations, J represents the total angular momentum quantum number of the lanthanides ion and α specifies a 4f spectroscopic term. G is the degeneracy of the ligand initial state and SL is the electric dipole strength associated with the transition $\phi \rightarrow \phi'$ in the ligand. The quantities $\langle \parallel \parallel \rangle$ are reduced matrix elements and U(λ) is a unit tensor operator and RL the distance from the lanthanides ion nucleus to the region of the ligand molecule in which the ligand donor (or acceptor) state is localized. In Equation (32), S is the total spin operator of the lanthanides ion, μ_z the z component of the electric dipole operator and s_m (m = 0, ±1) a spherical component of the spin operator, both for the ligand electrons, and σ_0 a distance dependent screening factor. The quantities γ_{λ} and F are given by:

$$\gamma_{\lambda} = (\lambda + 1) \frac{\langle r^{\lambda} \rangle^2}{(R_{L}^{\lambda+2})^2} \langle 3 \| C^{(\lambda)} \| 3 \rangle^2 (1 - \sigma_{\lambda})^2$$
(35)

and

$$F = \frac{1}{\hbar_{\gamma L}} \sqrt{\frac{\ln 2}{\pi} \exp\left[-\left(\frac{\Delta}{\hbar_{\gamma L}}\right)^2 \ln 2\right]}$$
(36)

where $\langle r^{\lambda} \rangle$ is the radial expectation value for r^{λ} for 4f electrons, C^{λ} a Racah tensor operator and σ_{λ} are also screening factors. γ_L is the ligand state bandwidth at half-height and Δ the difference between the

donor and acceptor transition energies involved in the transfer process.

7. Discussion

Recent developments in the field of supramolecular chemistry [8,30] have allowed the design of ligands capable of encapsulating lanthanide ions, thus forming kinetically inert complexes. By introduction of chromophoric groups in these ligands, an intense luminescence of the ion can be obtained via the "antenna effect", defined as a light conversion process involving distinct absorbing (ligand) and emitting (metal ion) components. In such a process, the quantities that contribute to the luminescence intensity are the efficiency of the absorption, the efficiency of the ligand-to-metal energy transfer, and the efficiency of the metal luminescence. Encapsulation of lanthanide ions with suitable ligands may therefore give rise to "molecular devices" capable to emit strong, long-lived luminescence.

In conclusion, we have the possibility to strongly increase the emission intensity of lanthanides by incorporating their macrocyclic complexes in stable glasses [24].

In order to use the model for exchange interaction, which arise from the overlap of the ligands function with the excited state of the lanthanides we need to know the geometry of the complex and the distances between the lanthanides and the ligand atoms. This information for the lanthanides chelates with phosphoro-azoderivatives of β -diketonates and 2,2'-bipyridine can be found in [31].

The efficiency of luminescence of lanthanides complexes depends on several processes, among others light absorption by the complex, energy transfer from the ligand to the Ln(III) ion, multiphonon relaxation and energy-back transfer.

The charge-transfer states can also play an important role. The studies of the decay times and the respective rate constants of these processes in many systems can finally lead to finding new materials with highly efficient emission at room temperature [32].

As mentioned above the weak luminescence of lanthanides arising from Laporte forbidden f–f transition can be strongly enhanced by preparing a complex with strong light-absorbing ligand followed by energy transfer from the ligand to the lanthanides ion. Such complexes could be seen as light conversion molecular devices (LCMDs), coining the term "antenna effect" to donate the absorption, energy- transfer, emission sequence involving distinct absorbing (the ligand) and emitting (the lanthanides ion) components, thus overcoming the very small absorption coefficients of the lanthanide ions. The design of efficient lanthanide complexes has become an important research goal. The interest in the photophysical properties of lanthanides ion complexes has grown considerably since Lehn proposed the system then being pursued by several groups, working with many different classes of ligands (e.g. cryptands, podands, calixarenes, macrocyclic ligands, 1,3-diketones, heterobiaryl ligands, carboxylic acid derivatives, terphenyl ligands, proteins, etc.) [33–35].

The oscillator strength of lanthanides ions embedded in oxide glasses is very low, the phenomena are a result of the fact that the transitions are forbidden by the Laport rule. The intensities of the luminescence of the lanthanides can be strongly increased by incorporating the ion into a complex. Such complexes could be seen as light conversion molecular devices (LCMDs), coining the term "antenna effect" which includes the absorption, energy transfer, emission sequence involving distant absorbing (the ligand) and emitting (the lanthanide ion) components, thus overcoming the very small absorption coefficient of the lanthanide ions. The design of efficient

lanthanide complexes has become an important research goal. The transitions can be intensified by incorporating the ions in complexes. Interest in the photophysical properties of lanthanide ion complexes has grown considerably since Lehn [29,30,34,35] proposed the system then being pursued by several group, working with many different classes of ligands (e. g. cryptands, podandts, calixarenes, macrocyclic ligands, b-diketones, heterobiaryl ligands, carboxylic acid derivatives, terphenyl ligands, proteins, ets.). Most of the complexes investigated emit red or green light (Eu³⁺ and Tb³⁺ luminescence respectively). However there are also complexes of different Ln³⁺ ions that luminescence in other spectral regions: the near IR (Yb³⁺, Nd³⁺, Er³⁺), orange (Sm³⁺), yellow (Dy³⁺), blue(Tm³⁺), or the near UV (CE³⁺, Gd³⁺) and IR Yb3⁺ [34].

Efficient light emitting complexes (LEC) may find the several applications, such as luminescent probes in biomedical assays and time resolved microscopy, fluorescent lighting and luminescent sensors for chemical species (H⁺, halide ions, OH⁻), electroluminescent devices, UV dosimeters, or antireflection coating for solar cells. Beside the quantum yield of LEC, other aspects such as light output, solubility, volatility, and photo-, thermal- and thermodynamic stabilities may be critical to many applications, and must also be controlled. In addition, incorporation of lanthanides complexes into sol-gel glasses increases their mechanical and photostability. Silicon inorganic-organic hybrids, synthesized through a sol-gel [24,34] process, it have been successfully employed for many purposes, such as sequestrating agents, and it has shown that the sol-gel process could be used to produce silica glasses with trapped Eu(III) fluorescent compounds. Silicon hybrids have, as an advantage, their very low solubility in water and many polar and apolar solvents, as well as their high thermal stability [35].

We have seen the ways in which the electronic f levels of lanthanides ions are populated and depopulated by radiative and non-radiative transitions. As already mentioned, the population density of luminescent levels is generally weak because of the low transition probabilities. However, there are other possibilities to increase the luminescence, mainly by creating strongly absorbing species that will transfer the energy to the lanthanides ion. The three main ways of such excitation are:

(I) Exciting closed shell of transition metal complexes such as tungstates, molybdates, vanadates, titanates ets. This way of excitation and its transfer to the lanthanides has been known since the late fifties. The method has been applied to phosphors for luminescent lamps and television screens. There is a vast literature and many reports by Philips, General Electric, Westinghouse, etc. The method is applied to solid melting at high temperatures.

(II) Energy transfer from a strongly absorbing lanthanides due to f-d transitionsor charge transfer; the literature is very large.

(III) Energy transfer between the ligands and the lanthanides ion in complexes [36].

An example of experimental results of ligand to Eu energy (or charge transfer), showing the intensification of Eu emission is presented in figure 4 and for Tb in figure 5.



Figure 4. Partial energy diagram for Eu^{3+} , $4f^{6}$ ions are showing the related magnitude of the interelectronic repulsion, spin-orbit coupling and ligand field effects. Downward arrows indicate the most luminescent excited level.

8. Applications

The lanthanides have found in the past applications in colour TV and in permanent magnets. The modern applications include:

Luminescent solar concentrators [37,38];

Computer displays;

Light emitting diodes [39] and semiconductor quantum dots [40];

Luminescent biosensors [41] and bioassays [42];

Active optical waveguide [43];

Materials based on upconversion from IR to visible light [44];

Materials for optoelectronics [45].

The importance of lanthanides in solar energy conversion can be found in excellent book by [46].



Figure 5. Partial energy diagram for Tb^{3+} , $4f^8$ ions are showing the related magnitude of the interelectronic repulsion, spin-orbit coupling and ligand field effects. Downward arrows indicate the most luminescent excited level.

9. Conclusion

The transition between the four f-levels which give rise to the luminescence are forbidden by Laporte rule. Therefore in order to obtain efficient luminescence there are ways to increase the population of the emitting levels since the luminescence intensity is a combination of the transition probability and the population of the excited state levels.

The ways to obtain increase intensity include incorporation of the lanthanide ions into complexes and transfer energy to the emitting lanthanides. This way named by J.-M. Lehn "The antenna effect".

In this paper I have outlined the theoretical approaches by which electronic levels of trivalent lanthanidess can be calculated. Radiative transitions between the levels are obtained from the matrix elements of the two relevant levels which are similar for a giver lanthanides but dependent of the host material, and the three intensity parameters which are specific for a given ion. The non-radiative transitions between the emitting level and the lower levels depend on the number of lattice phonons

connecting the emitting level and the lower levels depend on the number of lattice phonons connecting the emitting level and the next lower level.

Several recent reviews described in details how increasing of luminescence of lanthanide complexes can be achieved by using macrocyclic ligands [47]. Design of luminescent lanthanide complexes to efficient photo-emitting materials can be found in [48].

The energy transfer mechanisms are presented for a transfer between two lanthanides ions, between strongly absorbing charge transfer bands of host matrices and between strongly absorbing ligand states of complexes to the lanthanides ion. Application sin nanotechnology, optics, television screens, sensors and biology were outlined.

Acknowledgments

I am very grateful to Viktoria Levchenko for her important assistance for preparation of the manuscript.

My deep gratitude goes to Jean-Claude G. Bünzli and Jean-Marie Lehn for most illuminating discussions.

Conflict of Interest

All authors declare no conflicts of interest in this paper.

References

- 1. Jorgensen CK (1971) Modern aspects of ligand field theory, North-Holland Pub. Co, 538 pages.
- 2. Reisfeld R, Jorgensen CK (1977) Lasers and Excited States of Lanthanidess. *Springer-Verlag*, Berlin Heidelberg, New-York.
- 3. Condon EU, Shortley GH (1963) The theory of atomic spectra, University Press Cambridge. See also Slater, J. C., (1929) *Phys Rev* 34: 1293–1322.
- 4. Racah G (1949) Theory of complex spectra, *Phys Rev* 76: 1352.
- 5. Bünzli JC, Chauvin AS (2014) Lanthanides in Solar Energy Conversion. *Handbook on the Physics and Chemistry of Lanthanidess. Elsevier B.V.*, Amsterdam, chapter 261, 44: 169–281.
- 6. Jorgensen CK, Reisfeld R (1982) Chemistry and spectroscopy of lanthanidess. *Topics in Current Chemistry* 100: 126–166.
- 7. Reisfeld R, Jorgensen CK (1987) Chapter 58 Excited state phenomena in vitreous materials. *Handbook on the Physics and Chemistry of Lanthanidess* 9: 1–90.
- 8. Lehn JM (1987) Supramolecular chemistry scope and perspectivesmolecules supermolecules molecular devices. *Nobel lecture*.
- 9. Reisfeld R, Jorgensen CK (1992) Optical properties of colorants or luminescent species in sol-gel glasses. *Struct Bond* 77: 207–256.
- 10. Reisfeld R, Saraidarov T, Panzer G, et al. (2011) New Optical Material Europium EDTA complex in polyvinyl pyrrolidone films with fluorescence enhanced by silver plasmons. *Opt Mater* 34: 351–355.
- 11. Levchenko V, Grouchko M, Magdassi S, et al. (2011) Enhancement of luminescence of Rhodamine B by gold nanoparticles in thin films on glass for active optical materials applications.

Opt Mater 34: 360-365.

- Reisfeld R, Grinberg M, Levchenko V, et al. (2014) Sol-gel glasses with Enhanced Luminescence of Laser Dye Rhodamine B due to Plasmonic Coupling by Copper Nanoparticles. *Opt Mater* 36: 1611–1615.
- 13. Gaft M, Reisfeld R, Panczer G (2004) Luminescence Spectroscopy of Minerals and Materials. Springer Verlag, New-York.
- 14. Gan F (1992) Optical and Spectroscopic Properties of Glass, Springer Verlag, New York.
- 15. Reisfeld R (1975) Radiative and nonradiative transition of lanthanidess in glasses, *Structure and Bonding* 22: 123-175; Reisfeld, R. (1976) Excited states and energy transfer from donor cations to lanthanidess in the condensed phase. *Struct Bond* 30: 65–97.
- Reisfeld R (1980) Multiphonon relaxation in glasses, Internat. School of Atomic and Molecular Spectroscopy, In: DiBartolo B., Goldberg V., NATO Advanced Study Institute on Radiationless Processes, Erice, Italy, 1979. Radiationless Processes, Plenum, 489–498.
- 17. Binnemans K (2009) Lanthanide-Based Luminescent Hybrid Materials. *Chem Rev* 109: 4283–4374.
- 18. Judd BR (1962) Optical absorptionintensities of lanthanides ions. Phys Rev 127: 504.
- 19. Ofelt GS (1962) Intensities of crystal spectra of lanthanides ions. J Chem Phys 3: 37-511.
- 20. Wybourne BG (1965) Spectra of Lanthanidess Salts, 11 Spectroscopic Properties of Lanthanidess, In: *Interscience Publishers*, New York, London, Sydney, 210–219.
- Dieke GH (1968) Spectra and Energy Levels of Lanthanidess Ions in Crystals, In: Crosswhite, H. M., Crosswhite, H., *Interscience Publishers*, New York, London, Sydney, Toronto.
- 22. Görller-Walrand C, Binnermans K (1998) Spectral Intensities of f-f Transitions. *Handbook on Physics and Chemistry of Lanthanidess* Elsevier Science B. V. 25: 101–261.
- 23. Jorgensen CK, Judd BR (1964) Hypersensitive pseudoquadrupole transition in lanthanides. *Mol Phys* 8: 281–290.
- 24. Reisfeld R (2004) Lanthanides Ions: Their Spectroscopy of Cryptates and Related Complexes in Glasses, In: Schonherr, T.. *Struct Bond* 106: 209–235.
- 25. Luminescence and energy transfer (1980) Struct Bond 42.
- 26. Reisfeld R (1976) Excited states and energy transfer from donor cations to lanthanidess in the condensed phase. *Struct Bond* 30: 65–97.
- 27. Longo R, Goncalves FR, Silva E, et al. (2000) Europium bipyridil cryptates. *Chem Phys Lett* 328: 67–74.
- 28. De Sa GF, Malta OL, de Donega CM, et al. (2000) Spectroscopic properties and design of highly luminescent lanthanide coordination complexes. *Coordin Chem Rev* 196:165-195.
- 29. Demendoza J, Mesa E, Rodriguezubis JC, et al. (1991) A new macrobicyclic tris-bipyridine ligand and its CU-2(I) and AG-3(I) complexes. *Angewandte Chemie-International* (English edition) 30: 13331–13333.
- 30. Sabbatini N, Guardigli M, Manet I, et al. (1995) Lanthanide complexes of encapsulating ligands: Luminescent devices at the molecular level. *Pure App Chem* 67: 135–140.
- Borzechowska M, Trush V, Turowska-Tyrk I, et al. (2002) Spectroscopic and magnetic studies of mixed lanthanide complexes: LnL₃α,α'Dipy in solution and in solid. J Alloys Compd 341: 98–106.
- 32. Reisfeld R (2004) Sol gel processed lasers, In: Sakka, S., *Sol-Gel Technology Handbook 3, NATO Science Series, Springer*, Netherlands, 239–261.

- Bünzli JCG (1989) Chemical and Earth Sciences, Theory and Practice, In: Bünzli, J. C., Chopin, G. R., *Elsevier* Amsterdam, 219–293.
- 34. Comby S, Gummy F, Bunzli JC, et al. (2006) Luminescence Properties of an Yb podate in Sol-Gel Silica Films Solution, and Solid State. *Chem Phys Lett* 432: 128–132.
- 35. Reisfeld R (1996) Lasers based in sol-gel technology, Optical and Modern Application, In: Reisfeld, R., Jorgensen, C. K.. *Struct Bond* 85: 215–217.
- 36. Balzani V, Lehn JM, Vandeloosdrect J, et al. (1991) Luminescence properties of Eu³⁺ and Tb³⁺ complexes of branched macrocyclic ligands containing 4 2,2'-bipyridine units. *Angewandte Chemie-International* (English edition) 30: 190–191.
- 37. Reisfeld R (2015) Luminescent solar concentrators and the ways to increase their efficiencies, *Handbook Sol-Gel* Vol. 3 to be published by Wiley-VCH.
- 38. Reisfeld R (2010) Invited paper, New Developments in Luminescence for Solar Energy Utilization. *Opt Mater* 32: 850–856.
- 39. Bunzli JC, Piguet C, (2005) Taking advantage of luminescent lanthanide ions. *Chem Soc Rev* 34: 1048–1077.
- 40. Reisfeld R, Gaft M, Saraidarov T, et al. (2000) Nanoparticles of cadmium sulfide with europium and terbium in zirconia films having intersified luminescence. *Materials Letters* 45: 154–156.
- 41. Zhang J, Fu Y, Ray K, et al. (2013) Luminescent Properties of Eu(III) Chelates on Metal Nanorods. *J Phys Chem C* 117: 9372–9380.
- 42. Zhou S, Zheng W, Chen Z, et al. (2014) Dissolution-Enhanced Luminescent Bioassay Based on Inorganic Lanthanide Nanoparticles. *Angew Chem Int Ed* 53: 12498–12502.
- 43. Reisfeld R (2014) Fluorescence-active Waveguides by the Sol-Gel Method. Theory and Application, *Zeitschrift fur Naturforsch B*, Band 69, Heft 2: 131–140.
- 44. Auzel F (2004) Upconversion and Anti-Stokes Processes with f and d Ions in Solids. *Chem Rev* 104: 139–173.
- 45. Kenyon AJ (2002) Review Recent developments in rare-earthdoped materials for optoelectronics. *Prog Quant Electron* 26: 225–284.
- 46. Bünzli J-CG, Chauvin A-S (2014) Lanthanides in Solar Energy Conversion. *Handbook on the Physics and Chemistry of Lanthanidess* Elsevier B.V. North-Holland.
- 47. Leif RC, Vallarino LM, Becker MC, et al. (2006) Increasing the luminescence of lanthanide complexes. *Cytometry Part A* 69A: 767–778.
- 48. Armelao L, Quici S, Barigelletti F, et al. (2010) Design of luminescent lanthanide complexe: From molecules to highly efficient photo-emitting materials. *Coordin Chem Rev* 254: 487–505.

© 2015, Renata Reisfeld, licensee AIMS Press. This is an open access article distributed under the terms of the Creative Commons Attribution License (http://creativecommons.org/licenses/by/4.0)