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Theory of host sensitized luminescence of rare earth doped materials. I. Parity considerations

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Abstract

The theory of host sensitized luminescence based on the electrostatic model of interaction is extended beyond the free ionic system approximation and improved by the contributions that break the limitations of the single configuration approximation. The approach is based on double perturbation theory and defined in the terms of tensor operators. The parity requirements and consequent selection rules are discussed in the case of various contributions to the energy transfer probability defined up to the third order of perturbation expansion.

Keywords: Host sensitized luminescence; Rare earth doping; Double perturbation theory; Tensor operators

1. Introduction

Although the terms *laser* and *fiber optics* are very modern and almost synonymous with modern technology, the first observations of luminescence from inorganic materials goes back to the 16th century. It was noted in a review article [1], that in 1577 Nicolas Monardes observed a blue tint in water kept in a container made of a special kind of wood [2]. Then, it took almost 300 years for the first experiment to be performed by Stokes in 1852 when fluorescence was introduced as an emission of light; where the first spectroscopic principles were formulated [3], and subsequently used in 1854 as an analytical tool. It took 400 years before laser light was used to warm up and go through metals, alloys and organic tissues; and almost 420 years passed by before a sample was cooled with laser light. Indeed, in 1997 for the first time an optical refrigerator was constructed in the laboratory [4]. In this experiment, due to luminescent cooling, the temperature of Yb^{3+}-doped fluoro-zirconate glass decreased by 16 K! Thus, at the end of this Millennium an optical refrigerator is under construction, while in the second half of the same Millennium, only four centuries ago Monardes, already knowing the phenomenon of luminescence, wrote [2]

> ‘*The other way to make colde, is in a well, wherein they doe put the vessels with water or wine, and there they remayne the moste parte of the daye. This kinde of making colde hath also many inconveniences, as well of the parte of the water, wherewith it is made colde, as of the part of the place where it is put, chiefly in the welles of the cities and townes, that for the most parte are foule and full of filthinesses . . .*’

A vast variety of materials and mechanisms of excitation have led to the present differentiation of luminescence into photoluminescence, fluorescence, phosphorescence, chemiluminescence, bioluminescence, thermoluminescence, electroluminescence, radioluminescence, triboluminescence and sonoluminescence; behind each of these terms various experiments, different theoretical investigations, materials and their applications, even revolutionary discoveries are hidden.

In most cases inorganic crystals do not luminesce at room temperature with detectable efficiency. Thus, from an experimental point of view, having in mind the potential preparation of new materials, doped crystals are most interesting to investigators. Therefore luminescence in crystals is usually understood in terms of the luminescent centers localized at the impurities. This picture has led to a simpler model of luminescence that is associated with a distinct ion. In the particular case of rare earth ions used as impurities, due to their special electronic structure, it is possible in addition to separate the ion from the environment, and describe it as an isolated free system perturbed

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only by the crystal field. In spite of the fact that a great simplification is introduced by the free ionic system approximation, as Dexter stated in his paper in 1953 [5], the theoretical description of luminescence in crystals is a difficult task. The source of this difficulty is not only connected with the fact that luminescence reflects the simultaneous and mutual interaction between matter, radiation and very often the phonons, but with the fact that the accuracy of a theoretical description is very sensitive to the quality of the wavefunctions used for the calculations. This sensitivity is observed when analyzing the properties of the materials with similar impurities in the same hosts, or built of the same impurity atom in various hosts.

Sensitized luminescence is the phenomenon in which the impurity ion is made to radiate upon excitation resulting from the non-radiative transfer of the energy absorbed by another impurity ion or host. In the latter case the host crystal is absorbing the light from the beam used in the experiment, and then it transfers the energy to the impurity. The ion which is made to emit the radiation is called an *activator,* while the donator of the energy is the *sensitizer*. The two sources of the energy transferred to the activator distinguish the so-called impurity-sensitized [6–13] and host-sensitized [14–24] luminescence. At the same time it should be pointed out that the process of energy transfer is realized by a virtual (not real) emission of energy by the donator which is followed by reabsorption of this energy by the acceptor.

From among all references quoted here the papers of Kushida [25–27] and Malta [28] are especially helpful for the present research, since they are devoted to the processes observed in the rare earth doped materials, and their investigations are performed in the language of the second order theory of f↔f one photon electric dipole transitions of Judd and Ofelt [29,30]. While the standard language of f↔f theory might be useful for the interpretation of various terms contributing to the energy transfer amplitude, it should be remembered however that the physical reality of both processes is completely different and therefore it requires separate and independent investigations.

The probability of the energy transfer in the rare earth doped materials is expressed in the papers of Kushida in terms of the so-called Judd–Ofelt intensity parameters where all the information about the symmetry of the material (represented by the crystal field parameters) is covered together with the information about the electronic structure of the investigated ion (represented by the radial integrals). Malta in his analysis excludes the radial integrals from the semiempirical parameters, and evaluates them within the assumption that only the perturbing influence of single excitations from the 4f shell to the first excited one electron functions of d and g symmetries are important; due to this assumption it is possible to force the *closure procedure*, but at the same time all the other members of the complete radial basis sets of one electron states of given symmetry are ignored.

It should be pointed out that in both cases the approach presented in these papers is based on the electrostatic model of interaction and includes the quadrupole term of first order and the dipole contribution due to the influence of the odd part of the crystal field potential taken at the second order. In this sense only the latter terms are analogous to the Judd–Ofelt contributions to the transition amplitude.

The semiempirical procedure applied for such calculations, if the number of parameters is large enough, can lead to a proper reproduction of the observed characteristics without introducing any specification of the physical mechanism. However such calculations, even if the accuracy of their results is satisfactory, mean only that the observed property is well described by a one particle parametrization scheme, the commonly used standard scheme of the Judd–Ofelt theory. At the same time, the information about the symmetry of the material, electronic structure, and most of all, about the mechanism of the energy transfer is lost in the process of fitting the parameters. Once the parameters are adjusted, it is impossible to extract from their values any information on, for example, the importance of a particular mechanism. This means that in order to understand the properties of rare earth doped materials, and to establish the model which *reproduces* and *predicts*, the conclusions about physical mechanisms have to be based on the results of ab initio calculations. The success of the theoretical description of energy transfer and the observed cooperative processes, as pointed out by several authors, lies in the accuracy and quality of the wavefunctions describing the energy states of cooperating ions. Thus, there is a demand for a very precise theoretical model of the observed properties.

In the present paper a systematic method of the theoretical description of the host sensitized luminescence is discussed.

2. Experiments

The simplest experiment concerns the impurity ion characterized by an absorption band suitable for the absorption of the energy from the radiating beam. In such a situation the impurity is excited and then returns to its ground state emitting a photon with the so-called Stokes' shift, since it is usually less energetic than the exciting light. In this experiment the impurity acts as a luminescence center. If the radiating light does not match the scheme of the absorption spectra of a given impurity, or in the region of the energy of the light only a forbidden transition is predicted, no excitation of the impurity takes place. It is possible however in some cases that another impurity is introduced to the host crystal. The new impurity is able to absorb the light and through a radiationless process it transfers the energy to the original impurity. In this process the initial impurity is sensitized and becomes a luminescence center. If the transfer of energy is of low probability, the second impurity may itself luminesce with a Stoke's shift; and it is possible to expect two emission bands if these processes appear simultaneously. The line due to the sensitized luminescence is even less energetic than the previous one, because of the relaxation of the energy of the two impurities involved in the cooperative process. The double Stokes' shift, as noted already in 1957 by Dexter [31] might be very well applied to obtain a visible luminescence using for example a convenient source of ultraviolet light; it is rather impossible to obtain such an energy shift in the direct and conventional luminescence process. The cooperative process in which one photon excites two centers simultaneously is very well illustrated by the experiment of Varsanyi and Dieke [32]. The process of infrared-to-visible upconversion also has the cooperative nature [33]. Due to the energy transfer between two centers, for example, the visible green emission arising from infrared excitation was observed for the glass doped by Yb^{3+}–Er^{3+} [34], similarly, blue emission was obtained from the infrared radiation in the case of two impurities Yb^{3+} and Tm^{3+} [35,36], only to mention the pioneering experiments performed in the field which has been rapidly developing over the years.

The conversion process in which more highly energetic visible light is generated using a beam of lower energy, infrared, at first sight seems to be an impossible experiment because of the violation of Stokes' law; the law which is in fact the realization of the energy conservation principle. There is no violation of the law, however, if it is realized that more than one photon of the radiating beam is involved in the process (see for example Refs. [37,38]).

In Fig. 1 various processes originating from the radiationless energy transfer are presented schematically. In all cases $a_{\vec{k}}$ and $a^{+}_{\vec{k}}$ denote the annihilation and creation of a photon $\vec{k}$, b_1 and b_1^{+} are the annihilation and creation operators of energy state 1 of the atom/ion used as an impurity, c and c^{+} are the operators of annihilation and creation of a phonon. In addition, all creation operators are represented by the upward arrows while the annihilation operators are represented by downward arrows. Furthermore, to distinguish the act of donating and accepting the energy with the simultaneous change of the atomic states of the impurities, the single solid (down) and the double solid lines (up) are used, respectively.

Energy transfer takes place in the luminescence when the absorption of the photon from the radiating beam and the emission of the light are taking place on two separate centers. The first diagram in Fig. 1 describes the sensitized luminescence that is the simplest example of this effect.

Many materials become fluorescent when doped with the lanthanides [11,12,39–41]. In the case of phosphors the luminescent spectra of Ce^{3+} is in the far infrared, Gd^{3+} in the ultraviolet while for the other ions of the lanthanide series the spectra are in the visible and near infrared regions. The lanthanide acceptors might be divided into categories characterized by the kind of luminescence. The luminescence excitation of Ce^{3+}, Pr^{3+} and Tb^{3+} occurs in a broad 4f–5d absorption band, in the case of Sm^{3+} and Eu^{3+} in a charge transfer band and Tm^{3+} in narrow bands due to 4f–4f transitions which in the majority of cases have a form of atomic-like spectroscopic lines [1]. In fact, using appropriate rare earth ions and particular host lattices it is possible to select the light emission with the desired wavelength from the visible and near infrared regions of spectra. For example, Er^{3+} has its dominant emission at 1.5 μm which is the preferred wavelength for long distance fiber-optic communication [42]. This property of rare earth ions has caused an increasing interest in the application of rare earth semiconductors as active media for light emitting diodes, injection lasers and other optoelectronic devices [43–45].

The first two and the third diagrams in Fig. 1 show the difference between the resonant and non-resonant energy transfer. In the latter case, in addition to the excitation of the activator to the state with the energy smaller than the portion emitted by the sensitizer, a phonon is emitted, and as a consequence the energy conservation principle is again satisfied [46–48]. It is interesting to mention that these two different processes of energy transfer are distinguishable from an experimental point of view. Indeed, it was observed [49] that the transfer via the resonant process depends on the concentration of the ions while the non-resonant case strongly depends on the structure of the crystal.

3. Electrostatic model

What is the mechanism of the energy transfer between the sensitizer and activator? What is the efficiency of the energy transfer and the sensitized luminescence? The importance of these questions and also the expected precision of their answers are defined in an illustrative and convincing way by just a single experiment in which the host-sensitized luminescence of Tb^{3+} is observed as a result of the energy transfer from a nearby tryptophan, a crystalline aromatic essential amino acid, a crucial element for the nutrition of animals [50]. Thermolysin, a proteolytic enzyme which breaks down proteins into simpler compounds (as in digestion) possesses the ability of binding the lanthanides which replace the four sites of calcium. In such a material a strong luminescence sensitized by tryptophan, which provides the energy, is observed. Since the structure of thermolysin with substituted lanthanides is known, the luminescence spectroscopy is used here to *measure* the distance between the metals [51–53].

The answers to the above questions were addressed in many publications. In some of them the energy transfer processes are regarded as a resonance between two allowed electric dipole transitions which is the common case observed in organic systems; there are also investigations devoted to the transition processes that result from the resonance of an allowed electric dipole transition in the

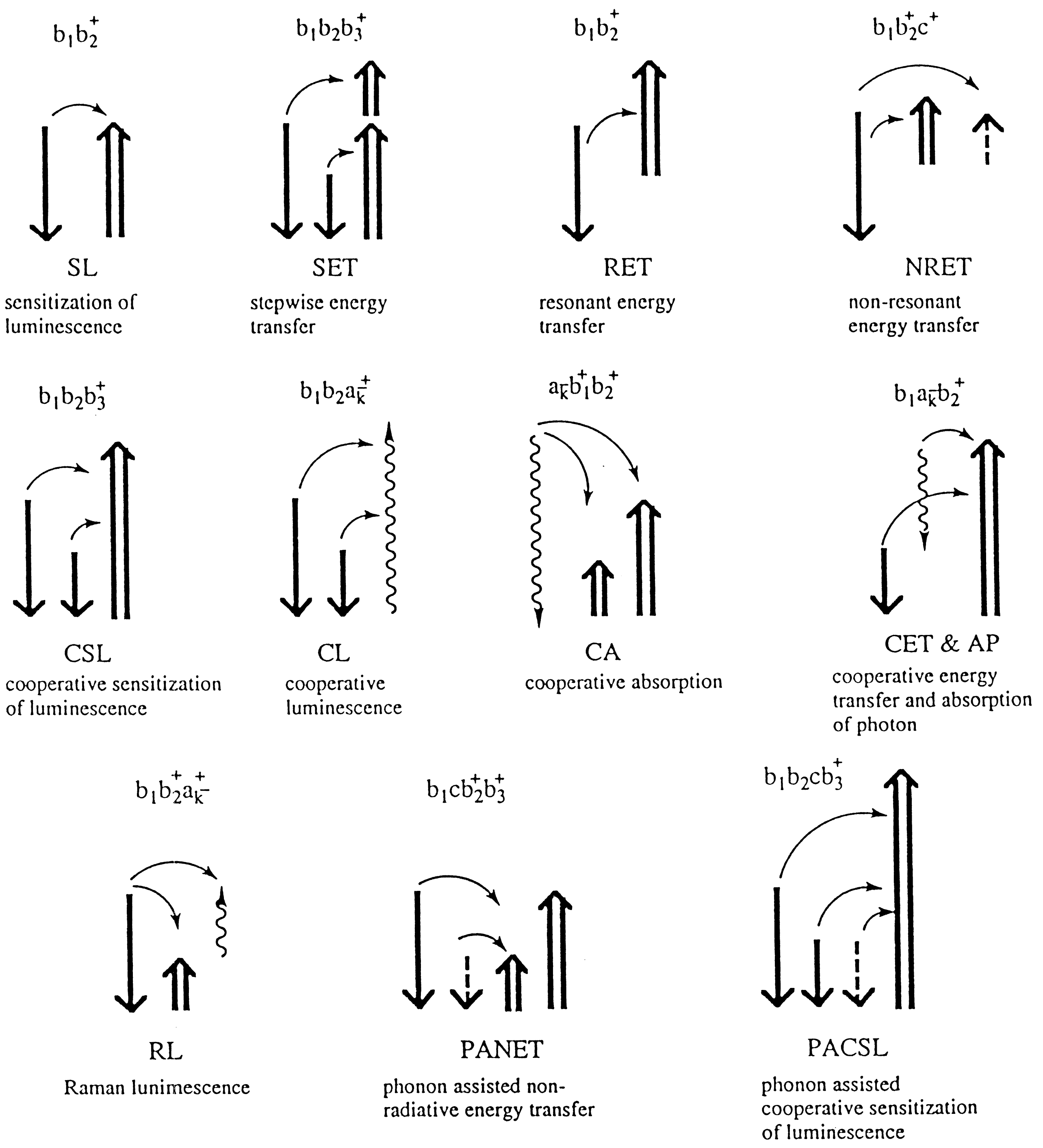

Fig. 1. Illustration of various processes originating from the non-radiative energy transfer, where $a_{\bar{k}}$ (↓), $a_{\bar{k}}^+$ (↑) represent anihilation and creation of photons; b_1 (↓), b_1^+ (⇑) represent anihilation and creation of atomic/ionic states; c (↓), c^+ (⇑) represent anihilation and creation of phonons.

sensitizer and forbidden transitions in the activator as it is observed in inorganic materials. While the first quantum mechanical investigations were performed by Föster in 1948 [54] only in the 1960s did Dexter develop the approach which defines the starting point for theoretical investigations based on the electrostatic model of mutual interactions between the sensitizer and activator [5,31,55].

In the electrostatic model of interactions between the activator and sensitizer [56] the transfer rate depends in various ways on the distance between the cooperating centers. In general, the probability of energy transfer is proportional to the matrix element of the perturbing operator representing the interaction between two ions with the functions which describe the initial and final states of both subsystems [57].

The multipole expansion applied for the electrostatic interaction potential leads to a very clear general expression for the probability of energy transfer, where the dependence on various powers of the distance between the impurities is explicitly exposed, namely

$$\mathscr{P}_{\mathrm{S}\to\mathrm{A}} = \frac{T_6}{R^6} + \frac{T_8}{R^8} + \frac{T_{10}}{R^{10}} + \dots \tag{1}$$

where T_6, T_8 and T_{10} are the terms associated with the dipole–dipole, dipole–quadrupole and quadrupole–quadrupole interactions, respectively. In general, these terms are determined by appropriate matrix elements of electric dipole, electric quadrupole, and higher multipole radiation operators between the functions describing the energy states of activator and sensitizer.

It is possible also to include in the theoretical description of the energy transfer the impact due to the electromagnetic interactions [57]. However, it has been estimated in the case of allowed transitions that the electro-magnetic interactions are negligible in comparison to the terms arising from electrostatic interactions. The relative importance of electrostatic and electromagnetic interactions might be changed in the case of rare earth impurities. Indeed, this is the case where the effect of energy transfer is associated with the forbidden electric dipole transitions, and therefore for very small transition amplitudes the ratio between the mechanisms might be changed.

In fact, the above matrix elements have a form of the product of two matrix elements associated separately with both centers.

$$\langle f|V|i\rangle \sim \sum_{kq}\sum_{m\,\mu} \langle \Psi_f^{\mathrm{RE}}|D_q^{(k)}|\Psi_i^{\mathrm{RE}}\rangle\langle \Phi_f^{\mathrm{L}}|D_\mu^{(m)}|\Phi_i^{\mathrm{L}}\rangle. \tag{2}$$

In the particular case of the present discussion, the first matrix element describes the lanthanide ion, and its evaluation is the task of the present investigation, while the second element is associated with the host, and its evaluation depends on the particular choice of ligands [28].

The main aim of the present analysis is to demonstrate the structure of particular contributions to the probability of energy transfer. This presentation is formulated in the terms of perturbation expansion performed for the Hamiltonian in which the interaction with the environment and electron correlation effects are taken into account. It should be pointed out that such detailed analysis defines the first step on the path to identifying those physical mechanisms that are the most important; the results presented here form the indispensable background for properly defined ab initio calculations that provide the information on the hierarchy of various contributions.

4. Perturbing influence of crystal field potential and electron correlation effects

The first order contributions to the energy transfer amplitude are determined by a simple matrix element of the form

$$\Gamma^1 = \langle \Psi_f^0|D_q^{(k)}|\Psi_i^0\rangle. \tag{3}$$

Due to the same parity of both wavefunctions describing the energy levels of $4\mathrm{f}^N$ configuration, for the non-vanishing matrix element in Eq. (3) the rank of tensor operator k must be even. This means that the first order terms contribute only to the mechanisms caused by even-multipole interactions, with the quadrupole term initializing the expansion. It should be pointed out that this term is defined within the free ionic system approximation, and is determined by the functions defined within the single configuration approximation.

The results of ab initio calculations performed for several ions across the lanthanide series have proven that the single configuration approximation of the standard approach of Judd and Ofelt does not provide an adequate description of f↔f transitions, and electron correlation effects must be taken into account in any reliable theoretical analysis [58–61]. One has to realize at the same time that in order to create a theoretical model of spectroscopic properties of rare earth doped materials, the model which would be able to reproduce the observations, some other physical mechanisms have to be incorporated in addition to electron correlation effects. Thus, in order to improve the model of the description of host sensitized luminescence the theory has to be defined beyond the free ionic system approximation and it should break the limitations of the single configuration approximation. Therefore, the Hamiltonian for which the perturbation expansion is performed has the following form [62]

$$H = H_0 + \lambda V_{\mathrm{CF}} + \mu V_{\mathrm{corr}} \tag{4}$$

where H_0 denotes the Hamiltonian of zeroth order with the central part defined usually within the Hartree–Fock approach, and possibly containing in addition all the operators which are necessary for a proper description of the electronic structure of a given ion; V_{CF} denotes the crystal field potential due to which the model is extended beyond the free ionic system approximation. Electron correlation effects are represented here by the perturbation V_{corr} that contains the non-central part of Coulomb interaction. The perturbing operators are assisted on both sides by the projection operators that divide the space into the two complementary subspaces. Namely, each operator V in fact stands for

$$V \equiv PVQ + QVP + QVQ \tag{5}$$

where P is the projection operator onto the space spanned by the solutions of the zeroth order problem, and Q is its orthogonal complement. This particular construction of the perturbing operators assures ones that the eigenvalues of zeroth order Hamiltonian are not changed, while the remaining part of the perturbing interactions PVP is possibly included within H_0.

Using the standard procedure of double perturbation theory and taking into account the corrections to the wavefunctions up to the second order

$$\Psi_k = \Psi_k^0 + \lambda\Psi_k^{10} + \mu\Psi_k^{01} + \lambda\mu\Psi_k^{11} + \lambda^2\Psi_k^{20} + \mu^2\Psi_k^{02} + \theta(\lambda^n\mu^m), n+m \geq 3,$$

the matrix element of the multipole radiation operator has the general form of contributions of first, Γ^1, second, Γ^2, and third order, Γ^3. The parity requirements for the nonvanishing matrix elements define the selection rules and, at the same time, they identify the nature of the contributing mechanism.

4.1. Second order contributions

The second order terms are determined by the matrix elements that involve the first order corrections to the wavefunctions due to both perturbations separately. Indeed, there are separate terms proportional to the perturbing parameters λ (crystal field potential) and μ (electron correlation effects), namely

$$\begin{aligned}\Gamma^2 &= \lambda\left\{\langle\Psi_f^0|D_q^{(k)}|\Psi_i^{10}\rangle + \langle\Psi_f^{10}|D_q^{(k)}|\Psi_i^0\rangle\right\}\\ &\quad + \mu\left\{\langle\Psi_f^0|D_q^{(k)}|\Psi_i^{01}\rangle + \langle\Psi_f^{01}|D_q^{(k)}|\Psi_i^0\rangle\right\}.\end{aligned} \tag{6}$$

When the appropriate expressions for the particular corrections to the wavefunctions are applied (see Eqs. (12) and (13) in Ref. [62]), one of the possible choices of intermediate states is the following

$$\begin{aligned}\Gamma_\lambda^2 = \sum_{Xx}&\left\{\langle\Psi_f^0|D_q^{(k)}|Xx\rangle\langle Xx|QV_{\mathrm{CF}}P|\Psi_i^0\rangle/(E_i^0 - E_{Xx}^0)\right.\\ &\left.+\langle\Psi_f^0|PV_{\mathrm{CF}}Q|Xx\rangle\langle Xx|D_q^{(k)}|\Psi_i^0\rangle/(E_f^0 - E_{Xx}^0)\right\}.\end{aligned} \tag{7}$$

In these second order terms the intermediate configurations Xx are of opposite parity to the parity of $4f^N$ and therefore k in the multipole expansion must be odd. At the same time the rank of the tensor operator of the crystal potential V_{CF} is limited also to the odd values. In particular, when $k=1$, these terms determine formally the transition amplitude of electric dipole transitions defined within the standard Judd Ofelt theory. Thus, the parity requirements demonstrate that interspace interactions via the odd part of crystal field potential contribute to the dipole (and all odd-rank multipoles) part of the energy transfer amplitude. The terms defined by Eq. (7) for $k=1$ is the only one of second order included by Malta in his considerations.

There is another possibility of intermediate configurations chosen in the case of Γ_λ^2, namely

$$\begin{aligned}\Gamma_\lambda^{2\prime} = \sum_{Xx}&\left\{\langle\Psi_f^0|D_q^{(k)}|Bb\rangle\langle Bb|QV_{\mathrm{CF}}P|\Psi_i^0\rangle/(E_i^0 - E_{Bb}^0)\right.\\ &\left.+\langle\Psi_f^0|PV_{\mathrm{CF}}Q|Bb\rangle\langle Bb|D_q^{(k)}|\Psi_i^0\rangle/(E_f^0 - E_{Bb}^0)\right\}.\end{aligned} \tag{8}$$

Here the intermediate excited configurations are of the same parity as the parity of $4f^N$, and therefore the perturbing influence of the even part of crystal field potential is taken into account. As a result, these interactions contribute to the even-rank multipole mechanism, in particular to the quadrupole terms.

At this point of analysis one may ask the question which from among the second order terms defined by Eqs. (7) and (8) is the most important; unfortunately, it is impossible to provide the information for such a judgment from the general analysis of the structure of these expressions. This means that the choice of various contributions to the amplitude should not be made ad hoc, and numerical analysis is required to verify all possibilities.

Summarizing, it should be pointed out that these second order contributions represent the perturbing influence of crystal field potential and therefore they go beyond the free ionic system approximation of the first order approach.

The second part of the second order contributions that are caused by electron correlation effects (proportional to μ) has the standard perturbative form, namely

$$\begin{aligned}\Gamma_\mu^2 = \sum_{Xx}&\left\{\langle\Psi_f^0|D_q^{(k)}|Bb\rangle\langle Bb|QV_{\mathrm{corr}}P|\Psi_i^0\rangle/(E_i^0 - E_{Bb}^0)\right.\\ &\left.+\langle\Psi_f^0|PV_{\mathrm{corr}}Q|Bb\rangle\langle Bb|D_q^{(k)}|\Psi_i^0\rangle/(E_f^0 - E_{Bb}^0)\right\}.\end{aligned} \tag{9}$$

Realizing that the V_{corr} as the non-central part of Coulomb interaction involves also the two-particle operator, it is easily seen that these contributions are more complex than the previous ones. In the case of Hartree–Fock potential and also Coulomb interaction potential, the parity requirements limit the intermediate configurations to those which are of the same parity $4f^N$. At the same time it should be remembered that two particle character of V_{corr} allows the inclusion of the perturbing influence of doubly excited configurations in addition to those describing a single excitation from the 4f shell.

In all cases the rank of multipole interaction operator k in Eq. (9) must be even, and therefore it is seen that electron correlation contributes at the second order only to the quadrupole terms (and all the even-rank poles).

4.2. Third order contributions

At the third order of analysis there is an explosion of various terms contributing to the energy transfer amplitude. In general, the perturbing expressions have the form

$$\begin{aligned}\Gamma^3 &= \lambda\mu\left\{\langle\Psi_f^{10}|D_q^{(k)}|\Psi_i^{01}\rangle + \langle\Psi_f^{01}|D_q^{(k)}|\Psi_i^{10}\rangle\right.\\ &\quad\left. + \langle\Psi_f^0|D_q^{(k)}|\Psi_i^{11}\rangle + \langle\Psi_f^{11}|D_q^{(k)}|\Psi_i^0\rangle\right\}\\ &\quad + \lambda^2\left\{\langle\Psi_f^{10}|D_q^{(k)}|\Psi_i^{10}\rangle + \langle\Psi_f^{20}|D_q^{(k)}|\Psi_i^0\rangle\right.\\ &\quad\left. + \langle\Psi_f^0|D_q^{(k)}|\Psi_i^{20}\rangle\right\}\\ &\quad + \mu^2\left\{\langle\Psi_f^{01}|D_q^{(k)}|\Psi_i^{01}\rangle + \langle\Psi_f^{02}|D_q^{(k)}|\Psi_i^0\rangle\right.\\ &\quad\left. + \langle\Psi_f^0|D_q^{(k)}|\Psi_i^{02}\rangle\right\}\end{aligned} \tag{10}$$

where Ψ^{11}, Ψ^{20} and Ψ^{02} satisfy the Eqs. (16) and (19) in Ref. [62].

It is seen from Eq. (10) that the third order terms contain the inter-play of both perturbations, and these terms (proportional to $\lambda\mu$) define a new category, and therefore they are the most interesting ones. In addition, there are also contributions that are associated with the second order corrections to the wavefunctions caused by a distinct mechanism, these are the terms proportional to λ^2 and μ^2.

In the case of the first matrix element it is possible to perform the following selection of intermediate configurations

$$\Gamma^{3}_{\lambda\mu} = \sum_{Xx}\sum_{Bb} \times \left\{ \frac{\langle \Psi^0_f |PV_{\mathrm{corr}}Q|Bb\rangle \langle Bb|D^{(k)}_q|Xx\rangle \langle Xx|QV_{\mathrm{CF}}P|\Psi^0_i\rangle}{(E^0_i - E^0_{Xx})(E^0_f - E^0_{Bb})} + \frac{\langle \Psi^0_f |PV_{\mathrm{CF}}Q|Xx\rangle \langle Xx|D^{(k)}_q|Bb\rangle \langle Bb|QV_{\mathrm{corr}}P|\Psi^0_i\rangle}{(E^0_f - E^0_{Xx})(E^0_i - E^0_{Bb})} \right\} \tag{11}$$

where the excited configurations Xx are of the opposite parity while Bb are of the same parity as parity of the $4\mathrm{f}^N$. Consequently, the crystal field potential is limited to the odd parts, and the whole term contributes to the dipole mechanism, and to all the others caused by the odd rank poles. In addition, due to the two particle nature of the Coulomb potential operator Eq. (11) represents also the perturbing influence of doubly excited configurations. This means that, for example, the parity requirements allow the following pair of configurations to be included in Eq. (11), for example

$$Bb = 4\mathrm{f}^{N-2}\, n''\ell'' n'\ell' \Leftrightarrow Xx = 4\mathrm{f}^{N-1} n'\ell'$$

where ℓ' and ℓ'' are of even parity.

At the same time, the other choice of the perturbing configurations leads to the contributions

$$\Gamma^{3'}_{\lambda\mu} = \sum_{Aa}\sum_{Bb} \times \left\{ \frac{\langle \Psi^0_f |PV_{\mathrm{corr}}Q|Bb\rangle \langle Bb|D^{(k)}_q|Aa\rangle \langle Aa|QV_{\mathrm{CF}}P|\Psi^0_i\rangle}{(E^0_i - E^0_{Aa})(E^0_f - E^0_{Bb})} + \frac{\langle \Psi^0_f |PV_{\mathrm{CF}}Q|Aa\rangle \langle Aa|D^{(k)}_q|Bb\rangle \langle Bb|QV_{\mathrm{corr}}P|\Psi^0_i\rangle}{(E^0_f - E^0_{Aa})(E^0_i - E^0_{Bb})} \right\}. \tag{12}$$

Here, the even part of the crystal field potential is included and this kind of interaction with the environment, together with electron correlation effects, contribute to the quadrupole mechanism. In the case of Eq. (12) where only the intermediate configurations of the same parity are chosen, it is possible to include again the impact due to doubly excited configurations. In all these cases, the inter-space interactions via the particular perturbation are taken into account since all the operators are accompanied by P at one side, and by Q operators at the other.

A completely different expression is obtained when the intra-space interactions are taken into account. For example, it is possible to consider the following terms

$$\begin{aligned}\Gamma^{3''}_{\lambda\mu} &= \sum_{Xx}\sum_{Yy} \times \left\{ \frac{\langle 4\mathrm{f}^N\Psi^0_f |D^{(k)}_q|Yy\rangle \langle Yy|QV_{\mathrm{corr}}Q|Xx\rangle \langle Xx|QV_{\mathrm{CF}}P|4\mathrm{f}^N\Psi^0_i\rangle}{(E^0_i - E^0_{Yy})(E^0_i - E^0_{Xx})} + \frac{\langle 4\mathrm{f}^N\Psi^0_f |PV_{\mathrm{CF}}Q|Xx\rangle \langle Xx|QV_{\mathrm{corr}}Q|Yy\rangle \langle Yy|D^{(k)}_q|4\mathrm{f}^N\Psi^0_i\rangle}{(E^0_f - E^0_{Yy})(E^0_f - E^0_{Xx})} \right\} \\ &+ \sum_{Bb}\sum_{Yy} \left\{ \frac{\langle 4\mathrm{f}^N\Psi^0_f |D^{(k)}_q|Yy\rangle \langle Yy|QV_{\mathrm{CF}}Q|Bb\rangle \langle Bb|QV_{\mathrm{corr}}P|4\mathrm{f}^N\Psi^0_i\rangle}{(E^0_i - E^0_{Yy})(E^0_i - E^0_{Bb})} + \frac{\langle 4\mathrm{f}^N\Psi^0_f |PV_{\mathrm{corr}}Q|Bb\rangle \langle Bb|QV_{\mathrm{CF}}Q|Yy\rangle \langle Yy|D^{(k)}_q|4\mathrm{f}^N\Psi^0_i\rangle}{(E^0_f - E^0_{Yy})(E^0_f - E^0_{Bb})} \right\}.\end{aligned} \tag{13}$$

It should be mentioned that the contributions defined by Eq. (13) arise from the general matrix element that involves the correction Ψ^{11}. In the first two expressions the odd part of the crystal field potential is included, and the rank of multipole operator k is also odd. This means that the electron correlation effects within the Q-space contribute at the third order to the dipole terms of the amplitude. The same kind of terms contributing to the energy transfer amplitude are modified by the intra-space interactions via the crystal field potential (last two expressions). The parity requirements show that in this case even part of the crystal field potential is included and k is again odd.

The remaining third order terms, those proportional to λ^2 and μ^2 lead to new classes of terms. A similar analysis provides information on selection rules that have to be satisfied for the non-vanishing contributions. Unfortunately, these parity considerations do not give any information on the relative importance of various contributions. At this point of analysis it is clearly seen that in order to establish the hierarchy of important terms first of all the general expressions have to be transformed to the form that is suitable for numerical calculations; the next and the final step of the procedure of establishing the reliable model of host sensitized luminescence in rare earth doped materials is to perform ab initio calculations for several ions from the lanthanide series.

5. Summary and the strategy of further investigations

The results of parity considerations showed that at the second order analysis electron correlation effects contribute to those parts of energy transfer amplitude that is caused by the even-parity multipoles. In this particular case the inter-space interactions via V_{corr} are taken into account and the perturbing influence of excited configurations of the same parity as the parity of $4f^N$ configuration is included. The odd parity multipole contributions, such as the dipole terms, are modified by electron correlation effects only at the third order where the simultaneous influence of crystal field potential is taken into account.

The crystal field potential influence is represented also by the terms of second order. The even part of V_{CF} contributes to the terms of even ranks while the odd part of the potential gives the contributions to the odd parity multipoles, including the dipole term.

In summary, the second order terms Γ_λ^2 associated with V_{CF}(odd), and representing the perturbing influence of $4f^{N-1}n'd$ and $4f^{N-1}n'g$ for all n', contribute to the dipole part of T_6 of the Förster model and T_8 of Dexter, both introduced in Eq. (1). At the same time, $\Gamma_\lambda^{2\prime}$ caused by V_{CF}(even), and Γ_μ^2, arising from the electron correlation effects, contribute to the quadrupole term T_{10} in Eq. (1); in both cases these contributions involve the impact due to the single excitations $4f^{N-1}n''f$, for all n''.

The variety of new contributions to the amplitude of energy transfer is much richer at the third order where in addition to the inter-space interactions also intra-space interactions do appear. Since the so-called properties are analyzed here rather than the energy for which each perturbation expansion is defined and oriented, it is impossible to expect that, for example, the third order contributions have to be smaller than the second order ones. Indeed, only in the case of the energy series, when the Hamiltonian is well defined, one can expect that the perturbation expansion is convergent. This means that it is impossible to use here the strategy, commonly used in the energy investigations, based on the procedure in which the most important term at certain order is identified, and the summation of this particular kind of term is performed up to infinity, while the remaining terms are neglected. In the case of the contributions to the energy transfer amplitude (not corrections as in the case of energy series) the only possibility is to perform the analysis of all contributions at a given order, and then analyze all the terms at higher order.

As demonstrated, very interesting information on the physical mechanisms of the host sensitized luminescence is provided by the second order terms. However, the only way to establish the hierarchy of the various contributions, to verify the relative importance of the perturbing influence of crystal field potential and electron correlation effects, to find out which kind of excited intermediate configurations play the dominant role is to perform numerical calculations with the aim of establishing the general tendencies. Indeed, there is no a priori information about the relative magnitude of contributions of various orders and, for example, it is impossible to predict that the third order contributions must be smaller than the second order ones. Just the contrary, it has been found that in the case of certain kinds of effective operators the third order electron correlation contributions are larger than the components evaluated within the standard second order formulation [53–66].

In particular, this means that the following steps have to be undertaken:

1. the assumptions of the standard Judd–Ofelt theory of f↔f transitions on the energy denominators of the perturbing expressions have to be adopted;
2. the partial closure has to be performed in order to obtain the effective operator form of all contributions;
3. the radial terms of all effective operators should be re-defined within the perturbed function approach;
4. finally, ab initio calculations for several ions of lanthanide series should be performed.

Work along this line is in progress.

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