

Impurity-sensitized luminescence of rare earth-doped materials[☆]

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Abstract

The accuracy of the theoretical model of impurity-sensitized luminescence in rare earth-doped materials presented here is adjusted to the demands of precise modern experimental techniques. The description is formulated within the double perturbation theory, and it is based on the assumption that electrostatic interactions between the subsystems that take part in the luminescence process are the most important ones. The amplitude of the energy transfer is determined by the contributions that represent the perturbing influence of the crystal-field potential and also electron correlation effects taken into account within the rare earth ions. In this way, the model is defined beyond the standard free ionic system and single configuration approximations. The new contributions to the energy transfer amplitude are expressed in the terms of effective tensor operators, and they contain the perturbing influence of various excited configurations. In order to maintain the high accuracy of the model, the radial integrals of all effective operators are defined within the so-called perturbed function approach. This means that they are evaluated for the complete radial basis sets of one electron functions of given symmetry, including the continuum.

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1. Introduction

“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?”—these are the questions that were asked at the beginning of the series of papers devoted to the theoretical description of the host-sensitized luminescence observed in the rare earths-doped materials [1–4]

(hereafter denoted by I–IV). These questions are also valid in the case of an impurity, and also the cooperative sensitization of luminescence.

The approach presented here originates from the concept of the first quantum mechanical investigations performed by Förster [5], that subsequently has been developed by Dexter [6–8] as a model based on electrostatic interactions between the sensitizer and activator. Kushida [9–11] improved the description of the energy transfer by including at the second order the perturbing influence of the crystal-field potential by means of the standard Judd Ofelt theory developed for the description of electric dipole $f \leftrightarrow f$ transitions [12,13]. At the same time, a detailed analysis of the impact of electron correlation effects upon the electric dipole transition amplitude demonstrated that it is crucial for a theoretical description of these radiative processes to break down the single configuration approximation of the standard model, and to

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compensate its limitations. These conclusions are supported by the results of ab initio numerical calculations performed for ions across the lanthanide series. Similarly as in the case of the host-sensitized luminescence, that has been described within the model extended by the impact due to the electron correlation effects, here the concept is applied for the energy transfer between two lanthanide ions. At the same time, the analysis presented here defines the starting point for further investigations on the cooperative processes and migration of the energy between various centers [14–17].

In the particular case of the impurity-sensitized luminescence the impact of the crystal environment is taken into account in a rather passive way. Indeed, the ligands surrounding the central ion are included only as a source of a perturbing operator, the crystal-field potential, that modifies the description of the electronic structure of free lanthanide ions. The act of sensitization results from the energy transfer understood as a consequence of the electrostatic interaction between the donor and acceptor ions. By means of the multipole expansion, this interaction is represented in terms of dipoles, quadrupoles and higher multipoles localized on both centers. The probability of the energy transfer is described in an elegant way by a simple expression in which the interactions between various multipoles are distinguished by the power of the inter-center distance R , namely

$$\mathcal{P}_{S \rightarrow A} = \frac{T_6}{R^6} + \frac{T_8}{R^8} + \frac{T_{10}}{R^{10}} + \dots \quad (1)$$

where T_6 , T_8 and T_{10} are associated with the dipole–dipole, dipole–quadrupole and quadrupole–quadrupole interactions, respectively. The values of the terms contributing to \mathcal{P} in Eq. (1) are determined by rather complex matrix elements. The choice of various contributions that are taken into account depends on the physical model applied for the description of the sensitizer–activator interaction, and on the required precision of theoretical approach.

In the present analysis, both of the lanthanide ions involved in the energy transfer process are described in the language of the perturbation theory applied for the hamiltonian that describes each ion separately. Due to this independent-systems approximation, in each hamiltonian the perturbing influence of the crystal-field potential and also electron correlation effects are taken into account separately. In this way the contributions to T_6 , T_8 and T_{10} in Eq. (1) represent the effects that result from breaking down the limitations of the single configuration approximation (electron correlation) and free ionic system approximation (lower symmetry represented by the crystal-field potential).

The crucial role of the crystal-field potential in the description of the radiative $f \leftrightarrow f$ transitions is obvious, and it defines the basis for the Judd Ofelt theory. The

perturbing influence of electron correlation effects upon the amplitude of electric dipole transitions changes dramatically the description based on the single configuration approximation. Therefore it is expected that the non-radiative energy transfer is also sensitive to these two physical mechanisms. The accuracy of the description of the electron correlation effects is especially important in the case of the impurity-sensitized processes in which the electronic structures of two lanthanide ions are directly involved.

2. Perturbation approach

In general the amplitude of the energy transfer that gives rise to the impurity-sensitized luminescence is determined by a product of matrix elements localized on both centers involved in the process,

$$\langle 1f, 2f | V | 1i, 2i \rangle \sim \sum_{k_1 q_1} \sum_{k_2 q_2} \langle \Psi_{1f} | D_{q_1}^{(k_1)} | \Psi_{1i} \rangle \langle \Psi_{2f} | D_{q_2}^{(k_2)} | \Psi_{2i} \rangle \quad (2)$$

where V represents the electrostatic interactions between the multipoles $D_{q_1}^{(k_1)}$ localized on the first lanthanide ion, and $D_{q_2}^{(k_2)}$ on the second ion. The interaction of the multipoles is defined by a general expansion presented in Eq. (1) of II, and the multipole operators are defined as follows

$$D_q^{(k)} = \sum_i r_i^k C_{q,i}^{(k)}$$

The functions that are used for the evaluation of the matrix elements in Eq. (2) are obtained by means of the perturbation approach applied for the hamiltonian that is defined in the same way for each ion

$$H = H_0 + \lambda V_{\text{CF}} + \mu V_{\text{corr}} \quad (3)$$

where H_0 is the zeroth order hamiltonian (usually defined at the level of the Hartree Fock model), and V_{CF} denotes the crystal-field potential

$$V_{\text{CF}} = \sum_{t,p}^{\text{even+odd}} B_p^t \sum_i^N r_i^t C_p^{(t)}(\vartheta_i, \phi_i)$$

where B_p^t are the structural parameters (the crystal-field parameters), and the radial dependence of V_{CF} is explicitly presented, since all the radial integrals in the future numerical ab initio calculations are evaluated directly. The operator that is responsible for the electron correlation effects is defined by a non-central part of the Coulomb interaction, namely

$$V_{\text{corr}} = \sum_s \sum_{i < j} \frac{r_i^s}{r_{ij}^{s+1}} (C^{(s)}(\vartheta_i \phi_i) \cdot C^{(s)}(\vartheta_j \phi_j)) - \sum_i u_{\text{HF}}(r_i)$$

The wavefunction that describes the energy levels of a separate lanthanide ion has the standard form of a series (in practice limited to a sum) of corrections of various orders that are of two different origins. Namely, for each ion the energy state of the $4f^N$ configuration, Ψ_k , is described by the function

$$\Psi_k = \Psi_0^k + \lambda \Psi_k^{10} + \mu \Psi_k^{01} + \lambda \mu \Psi_k^{11} + \theta(\lambda^n \mu^m), \quad n, m \geq 2$$

where the expansion is limited here to the terms of second order in both perturbations included simultaneously. In the present approach, each matrix element in Eq. (2) is expressed as a sum of terms that arise at different orders of perturbation expansion, and that originate from V_{CF} and V_{corr} .

Only the first order contribution to the energy transfer amplitude has the simple form of a single matrix element,

$$\Gamma^1(1) = \langle \Psi_{1f}^0 | D_{q_1}^{(k_1)} | \Psi_{1i}^0 \rangle. \quad (4)$$

The same term, with appropriate functions Ψ_{2f} and Ψ_{2i} , represents the first order contribution which originates from the multipoles localized on the second center. The general expression of Eq. (4) defines the theoretical background of the standard theoretical analysis of energy transfer presented in the literature. This is the amplitude of the energy transfer defined within the single configuration approximation applied for the free ionic system.

The second order contributions have more complex structure, and they are determined by a sum of four general terms for each lanthanide ion, namely in the case of the first center

$$\begin{aligned} \Gamma^2(1) = & \lambda_1 \{ \langle \Psi_{1f}^0 | D_{q_1}^{(k_1)} | \Psi_{1i}^{10} \rangle + \langle \Psi_{1f}^{10} | D_{q_1}^{(k_1)} | \Psi_{1i}^0 \rangle \} \\ & + \mu_1 \{ \langle \Psi_{1f}^0 | D_{q_1}^{(k_1)} | \Psi_{1i}^{01} \rangle + \langle \Psi_{1f}^{01} | D_{q_1}^{(k_1)} | \Psi_{1i}^0 \rangle \} \end{aligned} \quad (5)$$

with the same expression for the second center.

The first two terms in Eq. (5), that are associated with λ , represent the perturbing impact due to the crystal-field potential. The terms proportional to μ_1 include the effects of electron correlation within each ion. The structure of these contributions indicate, that each term represents the impact due to a particular mechanism which is included via the first order corrections to the wavefunctions, either Ψ^{10} or Ψ^{01} . The interplay of both mechanisms is represented by the third order contributions where both perturbing operators are regarded simultaneously via the correction to the wavefunction $\Psi^{(11)}$.

Due to the complex nature of the analyzed expressions, in order to keep the clarity of presentation of the approach, the expansion of the wavefunctions is limited to a sum of the first three components. This means that the first order corrections to the wavefunction, due to each mechanism separately, are included. Furthermore,

as a result of the standard definition of the first order corrections to the wavefunctions, each function provides to the final expression for the matrix elements in Eq. (2) one energy denominator. At the same time, the number of the energy denominators determines the order of the expression, and this rule is followed here to identify various contributions to the energy transfer amplitude.

Thus, in general, the amplitude of the energy transfer is defined in the terms of contributions of certain orders that are presented separately for sensitizer and activator,

$$\begin{aligned} \langle 1f, 2f | V | 1i, 2i \rangle \\ \sim \Gamma^1(1)\Gamma^1(2) + (\Gamma^2(1)\Gamma^1(2) + \Gamma^1(1)\Gamma^2(2)) \\ + (\Gamma^2(1)\Gamma^2(2) + \Gamma^3(1)\Gamma^1(2) + \Gamma^1(1)\Gamma^3(2)) \end{aligned} \quad (6)$$

where the first term is a product of the first order terms that are defined in Eq. (4); each term is evaluated for a separate center that takes part in the process. This product defines the first order contribution of the standard approach (no energy denominator). The second part of the expression in Eq. (6) defines the second order contributions to the energy transfer amplitude, and they contain one energy denominator. Indeed, they are defined by Γ^2 (the second order term for individual center), that in turn contains Ψ^{10} or Ψ^{01} . The last part of Eq. (6) is of the third order, and these expressions contain two energy denominators (one from each Γ^2). Among them, however, the very last two terms of Eq. (6) are defined by Γ^3 . The latter contribution is determined by the matrix element with the functions $\Psi^{(11)}$, that are excluded from present analysis. These terms represent the interplay of both perturbing mechanisms taken into account within one center. The complexity of the third order terms require a separate analysis (see for example third order contributions to the energy transfer in the case of the host-sensitized luminescence as described in II).

The second order terms of each lanthanide ion contributing in Eq. (6) consist of three different components, namely

$$\Gamma^2(j) = \Gamma_\lambda^2(j) + \Gamma_\lambda^{2'}(j) + \Gamma_\mu^2(j) \quad (7)$$

where j denotes the number of a center.

Γ_λ^2 and $\Gamma_\lambda^{2'}$ arise from the interactions via the crystal-field potential that is divided into even and the odd parts. This distinction is based on the availability of the crystal-field parameters that define V_{CF} . The even part of V_{CF} modifies the energy, and therefore in practice it is possible to evaluate even crystal parameters from a fitting procedure. The odd part does not contribute to the energy, but it plays a crucial role in the description of electric dipole $f \leftrightarrow f$ transitions, and unfortunately there is no reliable source of their values available. These terms if second order that arise from V_{CF} are defined as

follows in the case of the even part of V_{CF}

$$\Gamma_{\lambda}^2(j) = \sum_{Xx} \{ \langle \Psi_f^0 | D_q^{(k)} | Xx \rangle \langle Xx | Q V_{CF} P | \Psi_i^0 \rangle / (E_i^0 - E_{Xx}^0) + \langle \Psi_f^0 | P V_{CF} Q | Xx \rangle \times \langle Xx | D_q^{(k)} | \Psi_i^0 \rangle / (E_f^0 - E_{Xx}^0) \}_j \quad (8)$$

and in the case of the odd part of V_{CF}

$$\Gamma_{\lambda}^2(j) = \sum_{Bb} \{ \langle \Psi_f^0 | D_q^{(k)} | Bb \rangle \langle Bb | Q V_{CF} P | \Psi_i^0 \rangle / (E_i^0 - E_{Bb}^0) + \langle \Psi_f^0 | P V_{CF} Q | Bb \rangle \times \langle Bb | D_q^{(k)} | \Psi_i^0 \rangle / (E_f^0 - E_{Bb}^0) \}_j. \quad (9)$$

The third term in Eq. (7) originates from the perturbing influence of the electron correlation effects taken into account within each lanthanide ion; it is defined by the following perturbative expression

$$\Gamma_{\mu}^2(j) = \sum_{Bb} \{ \langle \Psi_f^0 | D_q^{(k)} | Bb \rangle \langle Bb | Q V_{corr} P | \Psi_i^0 \rangle / (E_i^0 - E_{Bb}^0) + \langle \Psi_f^0 | P V_{corr} Q | Bb \rangle \times \langle Bb | D_q^{(k)} | \Psi_i^0 \rangle / (E_f^0 - E_{Bb}^0) \}_j. \quad (10)$$

The subscript j in all these expressions means that all the objects in the matrix elements above have to be assigned to each center of the energy transfer. $|Xx\rangle$ and $|Bb\rangle$ denote the energy states x , b of the excited configurations X and B , respectively, and Q and P that accompany the perturbing operators are the projection operators. P projects onto the subspace spanned by the eigenfunctions of H_0 , and Q is its orthogonal complement.

The general structure of Eqs. (8)–(10) indicates that the intermediate configurations X and B represent single excitations from the $4f$ shell to one electron states of appropriate parity. The two-particle nature of the Coulomb interaction that together with the Hartree Fock potential defines the electron correlation operator allows one to include in Eq. (10) the perturbing influence of doubly excited configurations. However the other matrix element of the product vanishes in such a case, since the multipole operator is one particle. In summary it means that at the second order analysis only the impact due to singly excited configurations is taken into account.

3. Effective operators

To simplify and make numerical calculations possible in practice, the contributions to the amplitude of the energy transfer between two lanthanide ions have to be expressed in the terms of effective operators. In the particular case of the theoretical description of the interaction of two separate subsystems (two ions), the effectiveness of the tensor operators is understood

in the usual way. However, it should be clearly stated that in the effective form of the amplitude each center is represented by an operator that acts within the ground configuration of this particular ion.

In order to perform the so-called *partial closure*, all the approximations about the relative magnitude of the energies of ground and excited configurations introduced within the standard Judd Ofelt theory are adopted. The procedure of derivation of the effective operators of Eqs. (7)–(10) is similar to that applied in the case of the energy transfer amplitude for the host sensitized process; therefore all details, since they are presented in II, are not repeated here. The general expressions derived previously are adopted here to new conditions of the experiment in which two lanthanide ions are involved. The ligands are not playing any active role in the interaction between the ions, but as mentioned before, they are included only as a source of the electrostatic field that surrounds the centers of the luminescence.

3.1. First order contributions γ^1 —standard approach

The first order contributions to the amplitude of the energy transfer are determined as a product of matrix elements of effective operator Ω^0 defined in the terms of unit tensor operators in the following way

$$\Omega^0 = \langle 4f | r^k | 4f \rangle \langle f | C^{(k)} | f \rangle U^{(k)}(ff) \quad (11)$$

and the contributions $\gamma^1 = \Gamma^1(1)\Gamma^1(2)$ (the first term in Eq. (6)) has the following effective form

$$M^1(Q - Q) = \langle 4f | r^{k_1} | 4f \rangle_1 \langle 4f | r^{k_2} | 4f \rangle_2 \langle f | C^{(k_1)} | f \rangle \times \langle f | C^{(k_2)} | f \rangle \langle \Psi_{1f} | U^{(k_1)}(ff) | \Psi_{1i} \rangle \times \langle \Psi_{2f} | U^{(k_2)}(ff) | \Psi_{2i} \rangle. \quad (12)$$

Due to the parity requirements for the non-vanishing matrix elements of spherical tensor operators, the values of k_1 and k_2 , that determine the multipoles localized on center 1 and 2, are even. From a physical point of view this means that the first order terms contribute to the quadrupole–quadrupole mechanism. Therefore the expression in Eq. (12) is denoted by $M^1(Q - Q)$, and in particular $k_1 = k_2 = 2$.

3.2. Second order contributions γ^2

At the second order the perturbing influence of various excited configurations is taken into account via the crystal-field potential and electron correlation operator. As a consequence, the distinct contributions are characterized by the kind of excitation that is included in the effective operator.

The impact due to the singly excited configurations $4f^{N-1}n'd$ and $4f^{N-1}n'g$ for all n' , are represented by the effective operator associated with particular lanthanide ion of the following form for given k and q , in general

$$\Omega_{\lambda}(\ell') = \sum_{ip}^{\text{odd}} B_p^i \sum_{rq} (-1)^{r-q} [r]^{1/2} R_{\text{CF}}^{ik}(\ell') A_k^r(\ell') \times \begin{pmatrix} t & k & r \\ p & q & -q \end{pmatrix} U_q^{(r)}(ff) \quad (13)$$

where $\ell' = d, g$, and the angular part of the effective operator is defined in the same way as in the case of the Judd Ofelt theory of electric dipole $f \leftrightarrow f$ transition, namely

$$A_k^r(\ell') = [r]^{1/2} \begin{Bmatrix} k & r & t \\ f & \ell' & f \end{Bmatrix} \langle f \| C^{(t)} \| \ell' \rangle \langle \ell' \| C^{(k)} \| f \rangle \quad (14)$$

and the radial term has the following form

$$R_{\text{CF}}^{ik}(\ell') = \langle q^i(4f \rightarrow \ell') | r^k | 4f \rangle \quad (15)$$

where $q^i(4f \rightarrow \ell')$ is the perturbed function [18] defined in Appendix A. In general all the perturbed functions contain within their definition the troublesome summation over the complete basis sets of the one electron functions to which an electron from the $4f$ shell is promoted. Due to this approach, instead of such summations of the first order contributions caused by certain perturbation operator (in this particular case the V_{CF} potential), the radial terms of effective operators are expressed by a single integrals with newly defined functions (see Appendix A).

For $\ell' = \text{even}$, due to the parity requirements for the non-vanishing matrix elements in Eq. (14), the rank of the tensor operators of crystal-field potential must be odd. This means that this particular contribution arises from the odd part of the crystal-field potential. At the same time the selection rules for the second matrix element of spherical tensor in Eq. (14) indicates that also the rank of the multipole tensor operator, k , has to be odd. The same situation is valid in the case of the other center. Thus, the product of matrix elements of $\Omega_{\lambda}(\ell')$ for one ion, and $\Omega_{\lambda}(\ell'')$ for the second one, contributes to the dipole–dipole mechanism of interactions between both centers. These are the third order contributions, since each Ω_{λ} provides one energy denominator through the radial integral defined in Eq. (15).

The perturbing influence of the singly excited configurations of the same parity as the parity of the ground configuration of each lanthanide ion is represented by two kinds of effective operators that originate from the crystal-field potential and also from the electron correlation operator. In the case of $4f^{N-1}n'f$ for all n' ,

the contributions resulting from V_{CF} have the form

$$\Omega_{\lambda}(f) = \sum_{ip}^{\text{even}} B_p^i \sum_{rq} (-1)^{r-q} [r]^{1/2} R_{\text{CF}}^{ik}(f) A_k^r(f) \times \begin{pmatrix} t & k & r \\ p & q & -q \end{pmatrix} U_q^{(r)}(ff) \quad (16)$$

where the same angular part from Eq. (14) is used, and the radial integrals are defined by Eq. (15). The selection rules for these matrix elements limit t and also k to even values. This means that even part of the crystal-field potential is the source of these second order terms, and that they are associated with the quadrupoles localized on lanthanide ion.

In the case of interactions via the electron correlation, the effective operator of second order is defined as follows

$$\Omega_{\mu}(f) = \langle f \| C^{(k)} \| f \rangle \left(R_{\text{HF}}^k(f) + \frac{7}{2}(N-1)R^{0k}(f) + \frac{N-1}{2[k]} \langle f \| C^{(k)} \| f \rangle^2 R^{kk}(f) \right) U^{(k)}(ff). \quad (17)$$

The first term originates from the perturbing influence of the Hartree Fock potential, the second and the third terms are associated with the Coulomb interaction. The appropriate radial terms are defined by single radial integrals as follows: in the case of the Hartree Fock potential taken as a perturbation

$$R_{\text{HF}}^k(\ell'') = \langle q_{\text{HF}}(4f \rightarrow \ell'') | r^k | 4f \rangle \quad (18)$$

and for the Coulomb interaction

$$R^{sk}(\ell'') = \langle q^s(4f \rightarrow \ell'') | r^k | 4f \rangle \quad (19)$$

where the perturbed functions are defined in Appendix A. It is interesting to mention that due to the two-particle character of the Coulomb interaction potential, two particle effective operators also contribute to the energy transfer amplitude. Consequently, in general the expression in Eq. (17) should be extended by such terms (see II). However, the results of the numerical analysis performed on the importance of electron correlation effects in the description of the radiative transitions demonstrated that the major part of electron correlation effects in the description of the radiative transitions is represented by one-particle effective operators (see for example Ref. [19]). These conclusions have been applied here, and consequently only the one-particle effective operators are analyzed in Eq. (17).

It is seen from Eq. (17) that, since $k = \text{even}$, this effective operator also represents the quadrupoles localized on a luminescence center, and together with the counterpart arising from the second ion, it contributes to the quadrupole–quadrupole mechanism of mutual interaction between the centers.

For the completeness of the analysis, another class of singly excited configurations of the same parity as the parity of $4f^N$, namely $4f^{N-1}n'p$ should be considered. In this particular case, for $\ell' = p$, the impact due to the crystal-field potential has the following form

$$\Omega_{\lambda}(\ell') = \sum_{ip}^{\text{even}} B_p^i \sum_{rq} (-1)^{r-q} [r]^{1/2} R_{\text{CF}}^{ik}(\ell') A_k^{r'}(\ell') \times \begin{pmatrix} t & k & r \\ p & q & -q \end{pmatrix} U_q^{(r)}(ff) \quad (20)$$

and in the case of electron correlation perturbing operator

$$\Omega_{\mu}(\ell') = \frac{N-1}{2[k]} \langle f \| C^{(k)} \| f \rangle \langle f \| C^{(k)} \| \ell' \rangle^2 R^{kk}(\ell') U^{(k)}(ff). \quad (21)$$

The angular terms and the radial integrals of $\Omega_{\lambda}(\ell')$ and $\Omega_{\mu}(\ell')$ are defined by Eqs. (14), (15), (18) and (19), respectively.

4. Summary

The first order contributions to the amplitude of the energy transfer is determined by the matrix elements of the following effective operators that contribute to the quadrupole–quadrupole mechanism,

$$M^1(Q - Q) = \Omega^0(1)\Omega^0(2) \sim R^{-5} \quad (22)$$

where Ω^0 is defined by Eq. (11) for each ion, and these contributions are associated with R^{-5} . In the general expression for the probability of the energy transfer the first order term $M^1(Q - Q)$ contributes to T_{10} in Eq. (1). There are no first order contributions originating from the interactions between the dipoles localized on the centers.

The second order contributions that determine the impact of the dipole–quadrupole mechanism consist of the matrix elements of the following effective operators

$$M^2(D - Q) = [\Omega_{\lambda}(d) + \Omega_{\lambda}(g)]_1 \Omega^0(2) + \Omega^0(1) [\Omega_{\lambda}(d) + \Omega_{\lambda}(g)]_2 \sim R^{-4} \quad (23)$$

and these terms are associated with R^{-4} ; they contribute to T_8 of Eq. (1).

The quadrupole–quadrupole mechanism is described by the second order contributions by the following operators

$$M^2(Q - Q) = [\Omega_{\lambda}(f) + \Omega_{\mu}(f) + \Omega_{\mu}(p)]_1 \Omega^0(2) + \Omega^0(1) [\Omega_{\lambda}(f) + \Omega_{\mu}(f) + \Omega_{\mu}(p)]_2 \sim R^{-5}. \quad (24)$$

These terms are also associated with R^{-5} , and they contribute to T_{10} of Eq. (1) (together with the first order terms of Eq. (22)).

The first non-vanishing contributions to the dipole–dipole mechanisms of interaction between two centers appear at the third order analysis. In particular, γ^3 built of two second order terms arising from each center, $\Gamma^2(1)\Gamma^2(2)$ has the following general form

$$M^3(D - D) = [\Omega_{\lambda}(d) + \Omega_{\lambda}(g)]_1 [\Omega_{\lambda}(d) + \Omega_{\lambda}(g)]_2 \sim R^{-3}. \quad (25)$$

In this particular case the perturbing influence of the single excitations $4f \rightarrow d, g$ is included via the crystal-field potential taken into account for both centers. When the second order terms of separate ions are of mixed origin, and for example, the interactions via V_{CF} on the first center and via the operator of electron correlation on the other center are taken into account, the single excitations of opposite parities are included. This situation is represented by the following third order effective operators that contribute to the dipole–quadrupole mechanism.

This product of second order terms provides also third order contributions to the other mechanisms, namely

$$M^3(D - Q) = [\Omega_{\lambda}(d) + \Omega_{\lambda}(g)]_1 \times [\Omega_{\lambda}(f) + \Omega_{\mu}(f) + \Omega_{\mu}(p)]_2 \sim R^{-4}. \quad (26)$$

Finally, electron correlation effects included on both centers are represented by the third order terms that contribute to the quadrupole–quadrupole mechanism, and that have the following form:

$$M^3(Q - Q) = [\Omega_{\lambda}(f) + \Omega_{\mu}(f) + \Omega_{\mu}(p)]_1 \times [\Omega_{\lambda}(f) + \Omega_{\mu}(f) + \Omega_{\mu}(p)]_2 \sim R^{-5}. \quad (27)$$

Summarizing, the results of the present analysis provide information about the physical mechanisms that contribute to the distinct terms T_6 , T_8 and T_{10} in a general expression of Eq. (1) that determines the probability of the energy transfer between two lanthanide ions playing the role of luminescence centers. Thus, in the terms of the transition amplitude of the energy transfer, a general Eq. (2) is now understood in the following way:

$$\langle 1f, 2f | V | 1i, 2i \rangle \sim \frac{M^3(D - D)}{R^3} + \frac{(M^2 + M^3)(D - Q)}{R^4} + \frac{(M^1 + M^2 + M^3)(Q - Q)}{R^5} \quad (28)$$

where the distinct mechanisms and their theoretical description are indicated.

It is interesting to note that the new effective operators that describe electron correlation effects within each center contribute to D–Q and Q–Q mechanisms at the second and third order. As mentioned, the third order analysis should also include the terms in which both perturbations are taken into

account simultaneously for each ion. In fact, a general analysis of the impurity sensitized luminescence based on the electrostatic model, has to be extended also by the so-called exchange interactions, similarly as in the case of the host sensitized processes [20]. However, since the number of effective operators is large already in the case of the analysis that is presented here, the main task is to eliminate all objects that are relatively negligible at the level of the amplitude of the energy transfer. With a limited number of contributing terms it will be much easier to address the additional problem of the so-called cross-terms when evaluating the probability of the process.

The relative importance of various effective operators has to be established through the numerical calculations performed for a particular experiment; work along this line is in progress, and the results will be reported in a separate analysis.

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Appendix A

Radial integrals of effective operators contributing to the amplitude of the energy transfer between two luminescence centers are defined in the terms of the perturbed functions [18]. Each function is a linear combination of the first order corrections taken into account via certain perturbing operator. In the particular case of V_{CF} , and the effective operators defined in Eq. (13) the originally derived radial term has the form

$$R_{CF}^{tk}(\ell') = \sum_{n'} \frac{\langle 4f|r^t|n'\ell'\rangle\langle n'\ell'|r^k|4f\rangle}{(\varepsilon_{4f} - \varepsilon_{n'\ell'})}. \quad (\text{A.1})$$

With the aid of the perturbed function defined as follows

$$q^t(4f \rightarrow \ell') = \sum_{n'} \frac{\langle 4f|r^t|n'\ell'\rangle}{(\varepsilon_{4f} - \varepsilon_{n'\ell'})} P_{n'\ell'} \quad (\text{A.2})$$

where the summation over the complete radial basis sets of one electron functions of ℓ' symmetry is included within the definition of the perturbed function. As a consequence, the initial radial term in Eq. (A.1) is reduced to the single radial integral presented in Eq. (15) of the main text.

Similarly in the case of the effective operators defined by Eqs. (17) and (12) the original radial terms

have the form

$$R_{HF}^k(\ell'') = \sum_{n''} \frac{\langle 4f|u_{HF}|n''\ell''\rangle\langle n''\ell''|r^k|4f\rangle}{(\varepsilon_{4f} - \varepsilon_{n''\ell''})} \quad (\text{A.3})$$

in the case of the perturbing influence of the Hartree Fock potential, and

$$R^{sk}(\ell'') = \sum_{n''} \frac{R^s(4f4f4fn''\ell'')\langle n''\ell''|r^k|4f\rangle}{(\varepsilon_{4f} - \varepsilon_{n''\ell''})} \quad (\text{A.4})$$

in the case of the Coulomb interaction taken as a perturbation.

These terms are represented by single radial integrals of Eqs. (18) and (19), when the following perturbed functions are introduced,

$$q_{HF}(4f \rightarrow \ell'') = \sum_{n''} \frac{\langle 4f|u_{HF}|n''\ell''\rangle}{(\varepsilon_{4f} - \varepsilon_{n''\ell''})} P_{n''\ell''} \quad (\text{A.5})$$

and

$$q^s(4f \rightarrow \ell'') = \sum_{n''} \frac{R^s(4f4f4fn''\ell'')}{(\varepsilon_{4f} - \varepsilon_{n''\ell''})} P_{n''\ell''}. \quad (\text{A.6})$$

The details of the perturbed function approach may be found in Ref. [18]. The properties of various radial integrals contributing to the amplitude of the energy transfer are presented in II for various ions of the lanthanide series. It should be mentioned however, that the values of radial integrals, due to the perturbed function approach, are evaluated for the complete radial basis sets of one electron function of given symmetry; including the discrete and also the continuum part of the spectrum.

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