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Crystal model for energy-transfer processes in organized media: Higher-order electric multipolar interactions

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The study of the energy-transfer processes is extended, within the conceptual framework of the crystal model, to the electric dipole-electric quadrupole and electric quadrupole-electric quadrupole interactions. The formalisms for the energy-transfer rates are deduced, applying a mixed scheme of Cartesian tensors which are used to establish the geometric aspects of the interaction, and spherical tensors for the electronic part. The dependence of these transfer rates with respect to the geometric factors is discussed, and they are compared with the electric dipole–electric dipole case. In general, and as a consequence of the intrinsically anisotropic character of the quadrupolar operator, the analysis shows formally that those rates are highly anisotropic, suggesting a more careful calculation and interpretation of the transfer rates in organized media, like crystalline phases. This type of analysis shows the faults of the models currently used and cited in the literature, and the importance of the anisotropic effect is illustrated with an application in elpasolite type lattices doped with Ln^{3+} ions which occupy centrosymmetric sites. [S0163-1829(99)12835-2]

I. INTRODUCTION

In the literature of the last decades an important amount of work related to energy-transfer processes in various types of solid-state compounds has been reported, especially those related with experimental studies of these types of effects in a large variety of crystalline systems containing luminescent centers or chromophores such as ions of transition metals, lanthanides, and actinides.[1–6] At the same time, complementary theoretical models explaining those observations were introduced with the pioneering work of Förster,[7] and continued later by Dexter,[8] Inokuti and Hirayama,[9] and others,[10–13] whose main purpose was to estimate the rates W_{DA} of the energy-transfer processes. With varying degrees of acceptance, all these models have been applied to a large variety of crystalline systems, including those in which the ions are found in centrosymmetric as well as noncentrosymmetric point symmetry sites.[14–17] In most cases it has been mentioned that such models can explain correctly the observations. In particular, it is interesting to note that the model of Inokuti and Hirayama[9] has been used extensively in the last three decades, even though its conceptual limitations were rapidly acknowledged after its publication.[18] Later models have not improved that aspect sensibly, since the main contradiction is that they are based on a sum of interactions between ions that assumes a continuous distribution of luminescent centers within the system. This is certainly not the case in crystalline media, where the ions are distributed in very specific positions in the lattice. This points to the need to revise those models and formulate alternative ones that can remove those controversies.[19–22]

The generation of more correct formalisms for the study of energy-transfer processes has had limited success in previous works of this series,[23–25] devoted to the development the crystal model, because it was just applied to dipole-dipole interactions. This model considers in a realistic way both the quantum aspects as well as statistical details of the interaction between the *donor* ions and the *acceptor* ions forming the crystalline system, and has led us to extend its validity by studying other types of interactions. Thus a simultaneous paper[26] tackles the formal analysis of processes mediated by direct exchange interactions, which must be relatively important in systems that have very close together optical centers. However, if the crystallographic arrangement shows greater separations between the interacting atoms, the longer-range interactions, typically electric and/or magnetic multipole interactions, should predominate.

The theoretical estimation of the transfer rates involves the calculation of interactions between a generic *donor-acceptor* ion pair. At the initial instant, $t=0$, the first ion is in an excited state, while the second is in the ground state or in a lower excited state. The relaxation of the donor ion and the transfer of energy to the acceptor ion can occur in several ways; however, for the purpose of this study, and taking into account the properties of the particular lattice chosen as an example, the most important are electric multipolar, magnetic dipolar, and phonon-assisted energy transfer.

The point symmetry site of each one of the chromophores is an important aspect for finding the effective contributions to the global energy-transfer rate. In the case of chromophores at centrosymmetric point sites, the selection rules predict that the most important contributions would be magnetic dipole–magnetic dipole (MD-MD), electric quadrupole–electric quadrupole (EQ-EQ) and electric dipole–electric dipole by a phonon-assisted mechanism or of the vibronic type (EDV-EDV). The theoretical treatment of phonon processes has been attempted by some authors (see, e.g., Refs. 27 and 28), leading to a basic formalism that is valid only in restricted cases.[29] Energy-transfer processes by an electric vibronic dipole mechanism can also be considered, but few papers in the literature refer to that problem from a theoretical standpoint.[30]

Having treated the problem of the energy-transfer processes due to dipole-dipole interactions in previous papers in this series,[23–24] in this paper the analysis is extended to processes that involve higher-order electric multipolar interaction mechanisms. The main purpose of the work is to investigate the effect of the introduction of quadrupole transition momenta in the energy-transfer rate expressions, since it is admitted that the corresponding operator is intrinsically anisotropic.[31] The working hypothesis for this paper is that this must necessarily lead to anisotropic energy-transfer rates, even for highly symmetric systems (such as that of the example discussed below). A similar idea has been considered in the parallel paper,[26] which studies direct exchange interactions. Of course, the mathematical aspects of both papers are closely related, but differ in the structure of the interaction Hamiltonian for each case, and therefore in the explicit final formalism obtained for the energy-transfer rates.

The interaction anisotropy is an aspect that has received little attention in the known models, and in fact most of them have been proposed as if the medium were isotropic and the electric multipolar interaction depended exclusively on the distance according to R^{-s}, where s accounts for the type of mechanism ($s=6$, 8, and 10 for dipole-dipole, dipole-quadrupole, and quadrupole-quadrupole mechanisms, respectively). The transfer rate is usually expressed as $W_{DA}=C^{(s)}\times R^{-s}$, where all the angular, geometric, and electronic dependencies are included in the parameter $C^{(s)}$. A formal expression for this parameter is

$$C^{(s)}=e^2\sum_{k_1,k_2}\frac{(2k_1+2k_2)!}{(2k_1+1)!(2k_1+1)!}\left[\sum_{q_1}|\langle a'|D^{k_1}_{q_1}|a\rangle|^2\right]\times\left[\sum_{q_2}|\langle d|D^{k_2}_{q_2}|d'\rangle|^2\right]\quad[s=2(k_1+k_2+1)],\qquad(1)$$

and in its calculation some approximations have been made that include averages over spatial orientations and 3-j symbols. As a result of that, $C^{(s)}$ is considered identical for all the chromophores, and is treated as a parameter whose magnitude can be deduced from the fitting of the experimental data.[1,27]

Recently,[23–24] the crystal model has been used to characterize the environment around a donor ion (arbitrarily located at the origin of the coordinates), defining a set of angular classes and shell components that account for the complete arrangement of acceptor ions in the system. Under the condition of a binomial type statistical distribution (i.e., a random distribution of luminescent centers as substituents or dopants in the optically inert crystal lattice within the range of excitation energies of interest), it is possible to carry out a statistical analysis under any doping condition in the crystal lattice, and obtain an energy-transfer rate averaged over the whole crystal. This makes it possible finally to obtain a compact formalism for the effective energy-transfer rate.

The general expressions are exemplified through the energy transfer between lanthanide ions Ln^{3+} in the elpasolite-type lattice, a model system that has been thoroughly investigated from the experimental standpoint and has been the target of theoretical interest in recent years.[32–34]

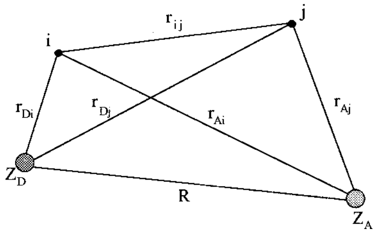

FIG. 1. Typical spatial arrangement of A and B interacting electronic density charges.

The particular choice of this cubic system has a twofold justification: In the first place, the distance between optical centers is relatively important, allowing very short-range contributions such as direct exchange to be neglected. In the second place, structurally the system has high symmetry, which allows the effect of the interaction anisotropy on the energy-transfer rates to be seen more clearly.

II. INTERACTION POTENTIAL

Using a general type of electrostatic perturbation, and within a model of independent systems, the various multipolar contributions are specified initially by means of their Cartesian operators, coupled to a symmetric tensor (also Cartesian) that contains the system's geometric information. For the purpose of this study, and considering a situation of chromophores separated by sufficient distance as to neglect the contributions due to exchange, the perturbation Hamiltonian, H', of the interacting electronic densities D and A, is usually expressed as[35]

$$\begin{aligned}H'_{DA}&=\sum_{j=1}^{s}\sum_{i=1}^{t}\frac{e^2}{\mathbf{r}_{ij}}\\&=\sum_{j=1}^{s}\sum_{i=1}^{t}\frac{e^2}{R\left[1+\left(\dfrac{|\mathbf{r}_{Aj}-\mathbf{r}_{Di}|^2+2\mathbf{R}\cdot(\mathbf{r}_{Aj}-\mathbf{r}_{Di})}{R^2}\right)\right]^{1/2}},\end{aligned}\qquad(2)$$

where conventional subscripts have been used for the distances shown in Fig. 1. From Eq. (2) the multipolar expansion is easily found, because the condition $R\gg r_{Di},r_{Aj}$, is satisfied for sufficiently separated chromophores.

In what follows, and for simplicity, the different electric multipolar interactions will be referred to as: d-d (dipole-dipole), d-q (dipole-quadrupole), and q-q (quadrupole-quadrupole). In vector notation, they correspond to

$$H'^{d\text{-}d}_{DA}=R^{-3}\left\{\left(\sum_{i=1}^{s} e\mathbf{r}_{Di}\right)\cdot\left(\sum_{j=1}^{t} e\mathbf{r}_{Aj}\right)-3\sum_{i=1}^{s}\sum_{j=1}^{t}(e\mathbf{r}_{Aj}\cdot\hat{\mathbf{R}})(\hat{\mathbf{R}}\cdot e\mathbf{r}_{Di})\right\}, \tag{3}$$

$$H'^{d\text{-}q}_{DA}=\tfrac{3}{2}\mathbf{R}^{-4}\left\{\sum_{i=1}^{s}\sum_{j=1}^{t}[e(\mathbf{r}_{Di}\cdot\mathbf{r}_{Di})-5e(\mathbf{r}_{Di}\cdot\hat{\mathbf{R}})(\hat{\mathbf{R}}\cdot\mathbf{r}_{Di})-2e(\mathbf{r}_{Aj}\cdot\mathbf{r}_{Di})](\hat{\mathbf{R}}\cdot e\mathbf{r}_{Aj})-\sum_{i=1}^{s}\sum_{j=1}^{t}[e(\mathbf{r}_{Aj}\cdot\mathbf{r}_{Aj})-5e(\mathbf{r}_{Aj}\cdot\hat{\mathbf{R}})(\hat{\mathbf{R}}\cdot\mathbf{r}_{Aj})\right.$$
$$\left.-2e(\mathbf{r}_{Aj}\cdot\mathbf{r}_{Di})](\hat{\mathbf{R}}\cdot e\mathbf{r}_{Di})\right\}, \tag{4}$$

$$H'^{q\text{-}q}_{DA}=\tfrac{3}{4}R^{-5}\left\{\sum_{i=1}^{s}\sum_{j=1}^{t}[e(\mathbf{r}_{Aj}\cdot\mathbf{r}_{Aj})e(\mathbf{r}_{Di}\cdot\mathbf{r}_{Di})-5e(\mathbf{r}_{Di}\cdot\mathbf{r}_{Di})e(\hat{\mathbf{R}}\cdot\mathbf{r}_{Aj})^2-5e(\mathbf{r}_{Aj}\cdot\mathbf{r}_{Aj})e(\hat{\mathbf{R}}\cdot\mathbf{r}_{Di})^2-20e^2(\mathbf{r}_{Aj}\cdot\mathbf{r}_{Di})(\hat{\mathbf{R}}\cdot\mathbf{r}_{Aj})\right.$$
$$\left.\times(\hat{\mathbf{R}}\cdot\mathbf{r}_{Di})+35e^2(\hat{\mathbf{R}}\cdot\mathbf{r}_{Aj})^2(\hat{\mathbf{R}}\cdot\mathbf{r}_{Di})^2+2e^2(\mathbf{r}_{Aj}\cdot\mathbf{r}_{Di})(\mathbf{r}_{Aj}\cdot\mathbf{r}_{Di})]\right\}. \tag{5}$$

In this notation, $\hat{\mathbf{R}}=\mathbf{R}/R$ is a unit vector that accounts for the direction of interaction between both multipoles. The expansion has been truncated because it is expected that the remaining higher-order multipoles will not contribute significantly, particularly if the distances between the optical centers are relatively important. However, they could be easily deduced from Eq. (2). The formal attack that will be followed allows Eqs. (3) and (5) to be expressed in a more compact form in which the multipole operators are coupled by means of a second-rank symmetric tensor which shows the geometric dependence of the interaction, of a form similar to that of the already known dipole-dipole case.[19,23,25] For the sake of completeness, this latter case is presented briefly in the equation

$$H'^{d\text{-}d}_{AB}=R^{-3}\{\mu_D\cdot\tilde{C}^{dd}\cdot\mu_A\}, \tag{6}$$

where the second-rank symmetric coupling tensor $\tilde{\mathbf{C}}^{dd}$ is established by the following matrix elements $C^{dd}_{\alpha\beta}$ (Refs. 19 and 23):

$$C^{dd}_{\alpha\beta}=\left\{\delta_{\alpha\beta}-3\,\frac{R_\alpha R_\beta}{R^2}\right\},\quad \forall\alpha,\beta=x,y,z. \tag{7}$$

From Eqs. (4) and (5), the multipolar contributions related to the $(d\text{-}q)$ and $(q\text{-}q)$ terms can be expressed in a similar way:

$$H'^{d\text{-}q}_{DA}=\tfrac{3}{2}R^{-4}\left\{\sum_{i=1}^{s}\sum_{j=1}^{t}\hat{\mathbf{R}}\cdot\{\tilde{Q}_{Di}\cdot\tilde{\mathbf{C}}^{dq}\cdot\mu_{Aj}\}\right.$$
$$\left.-\sum_{i=1}^{s}\sum_{j=1}^{t}\hat{\mathbf{R}}\cdot\{\tilde{Q}_{Aj}\cdot\tilde{C}^{dq}\cdot\mu_{Di}\}\right\}. \tag{8}$$

In this equation, $\tilde{Q}$ is the *traceless* formalism of the quadrupolar symmetric tensor,[36] with the following six components:

$$Q^{\alpha\beta}=e\{\mathbf{r}^\alpha\mathbf{r}^\beta-\tfrac{1}{3}\mathbf{r}^2\delta_{\alpha\beta}\},\quad\forall\alpha,\beta=x,y,z. \tag{9}$$

Similarly, the symmetric coupling tensor $\tilde{C}^{dq}$ in Eq. (8) has elements of the following form:

$$C^{dq}_{\alpha\beta}=\left\{2\,\delta_{\alpha\beta}-5\,\frac{R_\alpha R_\beta}{R^2}\right\},\quad\forall\alpha,\beta=x,y,z. \tag{10}$$

By inspecting Eq. (8), it is seen that it considers a pair of ''mirror image'' contributions depending on the ion in which the electric dipolar or electric quadrupolar transition is localized. Thus, in specific examples, it is necessary to determine whether one of these contributions or both of them are considered, depending on the degree of complexity of the energy-transfer processes.

In the same way, the quadrupole-quadrupole interaction [Eq. (5)] is straightforwardly expressed in terms of coupled quadrupolar tensor operators:

$$H'^{q\text{-}q}_{DA}=\tfrac{3}{4}R^{-5}\left\{\sum_{i=1}^{s}\sum_{j=1}^{t}\hat{R}\cdot(\tilde{Q}_{Aj}\cdot\tilde{C}^{qq}\cdot\tilde{Q}_{Di})\cdot\hat{R}\right.$$
$$\left.+2\sum_{i=1}^{s}\sum_{j=1}^{t}\mathrm{Tr}(\tilde{Q}_{Aj}\cdot\tilde{Q}_{Di})\right\}. \tag{11}$$

The first term on the right of this equation corresponds to the electric quadrupolar operators coupled by a geometric tensor of the same structure as in the previous cases, but with an additional dependence in $\hat{\mathbf{R}}^2$. The algebraic structure of this product is essentially anisotropic, due precisely to the double dot product with $\hat{\mathbf{R}}$. The second term corresponds to a contracted second-rank tensor that shows the direct interaction between the components of the operators located on each ion, which is particularly interesting because it corresponds to an isotropic contribution independent of the relative positions of the donor-acceptor pair.

The $C^{qq}_{\alpha\beta}$ elements of the symmetric coupling tensor $\tilde{C}^{qq}$ are the following:

$$C^{qq}_{\alpha\beta}=\left\{-20\delta_{\alpha\beta}+35\,\frac{R_\alpha R_\beta}{R^2}\right\},\quad\forall\alpha\beta=x,y,z. \tag{12}$$

III. ENERGY-TRANSFER RATES

The energy-transfer rate W_{DA} between two chromophores D and A, one acting as a donor (D) and the other acting as an acceptor (A) of energy, can be written according to Fermi's golden rule,

$$W_{DA}=\frac{2\pi}{\hbar}|(d'a|H'_{DA}|da')|^2\int f_D(\omega)f_A(\omega)d\omega, \tag{13}$$

where H'_{DA} is the electrostatic interaction potential that connects two terminal states: an initial state $|1\rangle=|d'a\rangle=|d'\rangle|a\rangle$ and a final state $|2\rangle=|da'\rangle=|d\rangle|a'\rangle$. Here, the primed labels mean excited electronic states. The functions $f_D(\omega)$ and $f_A(\omega)$, correspond to the spectral form functions of the ions D and A within the frequency range ω of the relevant transitions.

Since according to Fermi's golden rule the energy-transfer rates depend on the squares of the matrix elements, and H'_{AB} includes the three predominant contributions mentioned earlier, there will be pure (d-d), (d-q), and (q-q) processes. The first case was analyzed in great detail for cubic lattices in previous papers,[23,24] achieving, for cubic systems, a compact formalism,

$$|\langle 1|H'^{d\text{-}d}_{DA}|2\rangle|^2=R^{-6}|\mu_{d'd}|^2|\mu_{aa'}|^2G^{dd}_{DA}. \tag{14}$$

This is a very simple equation in which G^{dd}_{DA} is the global geometric factor of the interaction, and is the result of the symmetry of the lattice. The explicit form of that factor for the dipole-dipole case is

$$G^{dd}_{DA}=\frac{1}{9}\left\{\sum_{\alpha,\beta=x,y,z}(C^{dd}_{\alpha\beta})^2\right\}. \tag{15}$$

It should be noted that this is the result of the properties of the cubic crystals, for which it is true that $|\mu^x|^2=|\mu^y|^2=|\mu^z|^2=\frac{1}{3}|\mu|^2$. Work on crystals having different symmetries is underway.

With respect to the dipole-quadrupole contribution, finding the analog of Eq. (15) is less direct. Using reasons identical to those given earlier, and taking advantage of the hermitic and real character of the components of the quadrupolar tensor in Cartesian coordinates,[36] a derivation of the squared matrix elements is easily deducible. In matrix notation we obtain

$$|\langle 1|H'^{d\text{-}q}_{DA}|2\rangle|^2=\tfrac{9}{4}R^{-8}\{(\alpha^*\cdot\tilde{\mathbf{R}}\cdot\alpha)\}, \tag{16}$$

where $\alpha=\tilde{Q}_D\cdot\tilde{C}^{dq}\cdot\mu_A$ is, obviously, a Cartesian vector, and $\tilde{\mathbf{R}}=(\hat{\mathbf{R}}^*\hat{\mathbf{R}})$ is a second- rank unit tensor. This product follows the same behavior of Eq. (6), although the greater complexity of the mechanism is reflected in the algebra. Work with Eq. (16) must take into account two aspects that distinguish this case from that of the d-d interaction: In the first place, it can be shown that the product $(\alpha^*\cdot\tilde{\mathbf{R}}\cdot\alpha)$ includes not only diagonal quadratic contributions, but also some not nonzero cross-product-type terms $(\alpha^*_\beta\hat{\mathbf{R}}_\beta\hat{\mathbf{R}}_\gamma\alpha_\gamma)$, $\forall\beta\neq\gamma=x,y,z$. Second, it is necessary to stress that the Cartesian representation of the quadrupolar tensor is symmetric and reducible (with six components Q^{xy}; Q^{yz}, Q^{zx}, Q^{x^2}, Q^{y^2}, and Q^{z^2}), so that some cross products between Q^{x^2}, Q^{y^2}, and Q^{z^2} are nonzero, the same as some integrals of type $(\alpha^*_\beta\alpha_\gamma)$ derived from those nonvanishing cross terms $(\alpha^*_\beta\hat{\mathbf{R}}_\beta\hat{\mathbf{R}}_\gamma\alpha_\gamma)$ mentioned earlier. For the purpose of later calculations, a more appropriate form should give the expressions in terms of the five-component irreducible real base (Q^{xy}; Q^{yz}, Q^{zx}, $Q^{x^2-y^2}$, and Q^{z^2}). This can be done easily by writing the Cartesian quadrupolar operators in terms of spherical tensors, $C_{2q}=\sqrt{4\pi/5}Y_{2q}$, according to Griffith's convention.[37] This makes it possible to simplify the estimation of the electronic part of the calculation and to express the squares of the matrix elements x^2 and y^2 of the quadrupolar operator and cross products as combinations that include z^2 and (x^2-y^2) components; for example, for Q^{x^2},

$$|\langle 1|Q^{x^2}|2\rangle|^2=\tfrac{1}{4}|\langle 1|Q^{zz}|2\rangle|^2+\tfrac{1}{4}|\langle 1|Q^{x^2-y^2}|2\rangle|^2. \tag{17}$$

A final relevant aspect in this analysis of the components of the quadrupolar transition moment is the one that refers to the different weight that each one has in the total transition moment. In fact, the squares of the matrix elements take different values even in high-symmetry systems such as the Ln^{3+} ions in octahedral point symmetry, as has been shown by Chua and Tanner.[20] This leads to drastic changes in the form of the geometric factor in the dipole-quadrupole case.

Finally, Eq. (17) is rewritten as

$$|\langle 1|H'^{d\text{-}q}_{DA}|2\rangle|^2=R^{-8}|\mu_{aa'}|^2 \times\left\{\frac{3}{4}\sum_{\substack{\alpha\beta=xy,xz,yz,\\ z^2,x^2-y^2}}|Q^{\alpha\beta}_{d'd}|^2(g^{dq(\alpha\beta)}_{DA})\right\}, \tag{18}$$

where $|Q^{\alpha\beta}_{d'd}|^2$ are the five components of the quadrupolar transition moment for the transition $|d'\rangle\rightarrow|d\rangle$ in the donor ion, and $g^{dq(\alpha\beta)}_{DA}$ are the particular geometric factors of each dipole-quadrupole interaction component. The converse term accounts for probable $|d'\rangle\rightarrow|d\rangle$ electric dipole and $|a\rangle\rightarrow|a'\rangle$ electric quadrupole transitions.

The same procedure is used to express the term corresponding to the quadrupole-quadrupole interaction, which would have matrix elements

$$|\langle 1|H'^{q\text{-}q}_{DA}|2\rangle|^2=R^{-10}\left\{\tfrac{9}{16}\sum_{\substack{\alpha\beta,\gamma\delta=xy,yz,xz,\\ x^2-y^2,z^2}} \times|Q^{\alpha\beta}_{d'd}|^2|Q^{\gamma\delta}_{aa'}|^2g^{qq(\alpha\beta\gamma\delta)}_{DA}\right\}. \tag{19}$$

The number of geometric factors, both for (d-q) as well as for (q-q) interactions, is important, so a detailed list may be requested from the author.

Summarizing, and by inspection of the previous equations, the anisotropic properties of the energy-transfer processes that involve higher-order multipoles can be observed. In the electronic part, this is reflected in the fact that the electric quadrupolar operator has symmetry properties that are different from those of the electric dipolar operator. In fact, and as an example, we will mention the case of ions in octahedral sites, for which the three components of the dipolar transition moments transform according to T_{1u}. In contrast, of the five components of the quadrupolar transition moments, three transform according to the symmetry species

T_{2g} (xy, yz, and xz), while the remaining two (z^2 and x^2-y^2) do so according to E_g,[38] leading to a different behavior when applied to the calculation of transition moments. This point will be explained with a specific calculation example in Sec. V. Similarly, the anisotropic character of the electric quadrupolar operator transforms, moreover, the interaction geometric factors into local parameters which weight the product between components of the quadrupolar transition moments. Certainly, in a detailed calculation of the rates W_{DA}, each contribution must be scaled by a product of parameters that accounts for the properties of the medium (dielectric constant) and other factors, in agreement with Dexter's pioneering work.[8]

IV. EFFECTIVE ENERGY-TRANSFER RATE AND THE DECAY CURVES

Having shown the intrinsic anisotropy of the electric quadrupole transition momenta, a realistic relaxation rate from the excited states must be established. This is achieved by adding contributions to W_{DA} [Eq. (13)] over all possible orientations and distances between donor ions and the set of acceptor ions in the crystal. This procedure has been described in previous papers,[23–25] and their most relevant aspects are summarized in this section.

The crystal model is based on an ''angular class'' structure to allow counting the acceptor ions that surround a donor ion. For a stoichiometric-type crystal (in which the allowed crystallographic sites are occupied exclusively by chromophores), an angular class is defined as the set of acceptor ions that have the same angular orientation with respect to the donor ion. For cubic lattices, it can be immediately shown that each of those angular classes is formed of shell subclasses made of m members (with $m\rightarrow\infty$) located at increasing distances, as a result of periodic translations within the crystal for a given angular orientation. The first member of a shell subclass is the closest acceptor ion, which is at a distance, R_l^g and which we have called the ''generator of the lth angular class.''[23,24] Certainly, the remaining members of a shell subclass correspond to crystallographic points whose position with respect to the donor ion is $R_{l,m}=mR_l^g$.

In this same approach it has been shown that the probability for the donor ion system to continue in an excited state, for all $t>0$, after the excitation, is given by the general formalism

$$\rho(t)=\Delta_{\text{stat}}(X,Wt)*\exp\left[-\left(\gamma+\sum_l \overline{n_l}W_{DA}(mR_l^g)\right)t\right], \tag{20}$$

where

$$\Delta_{\text{stat}}(X,Wt)=\frac{1}{N_D}\left\{\sum_{j=1}^{N_D}\exp\left(\sum_{l,m}-t\Delta n_{l,m}^{(j)}W_{DA}(mR_l^g)\right)\right\}. \tag{21}$$

Since the probability $\rho(t)$ is directly proportional to the time evolution of the intensity of the luminescence due to the relaxation of the excited states, then Eq. (20) can be related directly to the experimental information. In that equation, $\overline{n_l}$ corresponds to the average fraction of sites actually occupied by chromophores in the case of nonstoichiometric crystals of relative concentration X, [$\overline{n_l}=Xn_l^{\max}$ $(0\leqslant X\leqslant 1)$]. In turn, $n_l^{\max}$ is the maximum number of chromophores that the crystal lattice can contain (i.e., a crystal with $X=1$) and the function $\Delta_{\text{stat}}(X,Wt)$ includes all the information related to the effect of the statistical fluctuations in the chromophores population, $\Delta n_{l,m}^{(j)}$, in the actual crystal.

Under the considerations of the crystal model, and in the analyzed cases, the analytical estimation of an effective transfer rate at a macroscopic scale $\Sigma_l\overline{n_l}W_{DA}(mR_l^g)=k_{\text{eff}}$ leads to the following:

$$k_{\text{eff}}^{d\text{-}d}=\frac{2\pi\int f_D(\omega)f_A(\omega)d\omega}{\hbar(R_1^g)^6}X\zeta(6)\times\left\{\sum_{\varepsilon,\phi}\sum_l n_l^{\max}|\mu^\varepsilon|^2|\mu^\phi|^2\left(\frac{R_1^g}{R_l^g}\right)^6 g_{dd}^{\varepsilon-\phi}(l)\right\}, \tag{22a}$$

$$k_{\text{eff}}^{d\text{-}q}=\frac{2\pi\int f_D(\omega)f_A(\omega)d\omega}{\hbar(R_1^g)^8}X\zeta(8)\times\left\{\sum_{\varepsilon,\alpha\beta}\sum_l \tfrac{3}{4}\,n_l^{\max}|\mu^\varepsilon|^2|Q^{\alpha\beta}|^2\left(\frac{R_1^g}{R_l^g}\right)^8 g_{dq}^{\varepsilon-\alpha\beta}(l)\right\}, \tag{22b}$$

$$k_{\text{eff}}^{q\text{-}q}=\frac{2\pi\int f_D(\omega)f_A(\omega)d\omega}{\hbar(R_1^g)^{10}}X\zeta(10)\times\left\{\sum_{\alpha\beta,\gamma\delta}\sum_l \tfrac{9}{16}\,n_l^{\max}|Q^{\alpha\beta}|^2|Q^{\gamma\delta}|^2\left(\frac{R_1^g}{R_l^g}\right)^{10}\times g_{qq}^{\alpha\beta-\gamma\delta}(1)\right\}. \tag{22c}$$

In the case of dipole-dipole interactions in cubic systems,[23] the interaction is isotropic (i.e., it is easy to decouple electronic and geometrical factors) and Eq. (22a) is reduced to $k_{\text{eff}}^{d\text{-}d}=X\zeta(6)w_{DA(0)}^{dd}L_{dd(0)}$; a compact final expression which is a function of the transfer rate for the nearest-neighbor donor-acceptor pair, $w_{DA(0)}^{dd}$; the relative concentration of chromophores in the lattice, X; the Riemann's zeta function $\zeta(6)$, which accounts for the translations in the shell subclasses; and a lattice parameter $L_{dd(0)}$ which includes exclusively the geometric properties of the interacting chromophores.

In general, the k_{eff} transfer rates are referred only to the properties of the angular class generators. For d-q and q-q interactions, a further simplification results from the analysis of the properties of the terms $(R_1^g/R_1^g)^s g(l)$ in Eqs. (22b) and (22c). Since the higher-order interactions ($s=8$ and 10) cancel out very rapidly with distance, it is easy to show that the summations over l converge rapidly and, for practical purposes, they do not differ significantly from its first members [i.e., those evaluated in the first and second angular classes ($l=1$ and 2)]. This is shown with an example in Appendix A.

In the d-q and q-q cases, the geometric factors cannot be added together directly to give a global magnitude (as in the

d-d case in cubic systems), so that they must be retained as local properties characteristic of each product of the components of multipole transition momenta $(\varepsilon-\alpha\beta)$ and $(\alpha\beta-\gamma\delta)$, respectively. In this way, restricting the summation to $l=1$ and 2 and defining the global energy transfer rate at a microscopic scale W_{DA}, then k_{eff} in each case is

$$k_{\mathrm{eff}}^{d\text{-}q}=X\zeta(8)W_{DA}^{d\text{-}q}=X\zeta(8)\,\frac{2\pi\int f_D(\omega)f_A(\omega)d\omega}{\hbar(R_1^g)^8}\times\left\{\sum_{\varepsilon,\alpha\beta}\sum_{l=1,2}\frac{3}{4}n_l^{\max}|\mu^{\varepsilon}|^2|Q^{\alpha\beta}|^2\left(\frac{R_1^g}{R_l^g}\right)^8 g_{dq}^{\varepsilon-\alpha\beta}(1)\right\}, \tag{23a}$$

$$k_{\mathrm{eff}}^{q\text{-}q}=X\zeta(10)W_{DA}^{q\text{-}q}=X\zeta(10)\,\frac{2\pi\int f_D(\omega)f_A(\omega)d\omega}{\hbar(R_1^g)^{10}}\times\left\{\sum_{\alpha\beta,\gamma\delta}\sum_{l=1,2}\frac{9}{16}n_l^{\max}|Q^{\alpha\beta}|^2|Q^{\gamma\delta}|^2\times\left(\frac{R_1^g}{R_l^g}\right)^{10} g_{qq}^{\alpha\beta-\gamma\delta}(l)\right\}. \tag{23b}$$

On the other hand, the statistical term for fluctuations, $\Delta_{\mathrm{stat}}(X,Wt)$ [Eq. (21)], may be rewritten in the form of an expanded McLaurin series:

$$\Delta_{\mathrm{stat}}(X,Wt)=\frac{1}{N_D}\sum_{j=1}^{N_D}\left\{1-t\sum_{l,m}\Delta n_{l,m}^{(j)}W_{DA}(mR_l^g)+\frac{t^2}{2!}\left(\sum_{l,m}\Delta n_{l,m}^{(j)}W_{DA}(mR_l^g)\right)^2-\frac{t^3}{3!}\left(\sum_{l,m}\Delta n_{l,m}^{(j)}W_{DA}(mR_l^g)\right)^3+\cdots\right\}. \tag{24}$$

It has been shown that the first-order contribution in this series is identically zero,[23] so that only the higher-order contributions in $\Delta_{\mathrm{stat}}(X,Wt)$ establish its temporal behavior. Assuming a binomial statistical contribution for the population of chromophores in the lattice, in the dipole-quadrupole case we have

$$\Delta_{\mathrm{stat}}^{dq}(X,Wt)=\left\{1+\frac{(X-X^2)t^2}{2!}\zeta(16)[W_{DA}^{d\text{-}q}]^{(2)}-\frac{X(1-X)(1-2X)t^3}{3!}\zeta(24)[W_{DA}^{d\text{-}q}]^{(3)}+[(X(1-X)-6(1-X)^2X^2]+3X^2(1-X)^2\frac{\zeta(32)t^4}{4!}[W_{DA}^{d\text{-}q}]^{(4)}+\cdots\right\}, \tag{25}$$

and, for the quadrupole-quadrupole,

$$\Delta_{\mathrm{stat}}^{qq}(X,Wt)=\left\{1+\frac{(X-X^2)t^2}{2!}\zeta(20)[W_{DA}^{q\text{-}q}]^{(2)}-\frac{X(1-X)(1-2X)t^3}{3!}\zeta(30)[W_{DA}^{q\text{-}q}]^{(3)}+[(X(1-X)-6(1-X)^2X^2]+3X^2(1-X)^2\frac{\zeta(40)t^4}{4!}[W_{DA}^{q\text{-}q}]^{(4)}+\cdots\right\}, \tag{26}$$

where, for instance, a representative expression for the $[W_{DA}]^{(k)}$ parameters for q-q interaction is

$$[W_{Da}^{q\text{-}q}]^{(2)}=\frac{2\pi\int f_D(\omega)f_A(\omega)d\omega}{\hbar(R_1^g)^{10}}\times\left\{\sum_{\alpha\beta,\gamma\delta}n_1^{\max}[\tfrac{9}{16}|Q^{\alpha\beta}|^2|Q^{\gamma\delta}|^2 g_{qq}^{\alpha\beta-\gamma\delta}(1)]^2\right\}. \tag{27}$$

Appendix C includes other $[W_{DA}]^{(k)}$ parameters. Rigorously, the effect of the anisotropy produces a very complex expression for $\Delta_{\mathrm{stat}}(X,Wt)$; however, for simplicity it was preferred to leave it in reference to average properties of the first angular class. The error that this introduces is marginal and does not change the shape of the calculated decay curves.

Finally, since the higher-order multipole interactions have a shorter range than those of the dipole-dipole type, a simple calculation is made, analyzing only the first two angular classes ($l=1$ and 2) for the cubic lattice of the elpasolite type, $\mathrm{Cs_2NaY_{1-x}Ln_xCl_6}$. Figure 2 shows a comparison between the shape and slope of the decay curves for (d-d), (d-q), and (q-q) processes, with identical values of W_{DA}, showing that the differences between the shapes of the multipole-multipole interactions studied are small. Moreover, for large energy transfer rates [Fig. 2(b)] it is impossible, in practice, to distinguish between each decay curve. This behavior is due solely to the statistical effect of the actual chromophores population in the crystal system, and it is in contrast with the discussions of a series of works.[22,27]

V. CALCULATION OF THE CROSS-RELAXATION $(^1G_4,\,^3H_6)\rightarrow(^3H_5,\,^3H_4)$ IN $\mathrm{Cs_2NaYCl_6{:}TmCl_6}$

One of the possible examples of energy-transfer processes due to an electric quadrupole-electric quadrupole interaction is that of the cross-relaxation of $\mathrm{Tm^{3+}}$ ions $(^1\boldsymbol{G}_4,\,^3\boldsymbol{H}_6)\rightarrow(^3\boldsymbol{H}_5,\,^3\boldsymbol{H}_4)$ in $\mathrm{Cs_2NaYCl_6{:}TmCl_6}$. Interest in this particular system and process of energy transfer is due to the high-symmetry properties of the lattice, which will make it possible to show more clearly the importance of the anisotropic effect of the quadrupole operator. This example has been recently studied by Chua and Tanner.[20]

Partially considering their calculations, the magnitudes of the five components $|Q^{xy}|^2$, $|Q^{yz}|^2$, $|Q^{yz}|^2$, $|Q^{x^2-y^2}|^2$, and $|Q^{zz}|^2$ can be established immediately both in the donor as well as in the acceptor ion. Using the *JM* wave function basis and assuming pure states, the squares of the matrix elements $|\langle 1|H_{DA}'^{q\text{-}q}|2\rangle|^2$ can be calculated in terms of the products

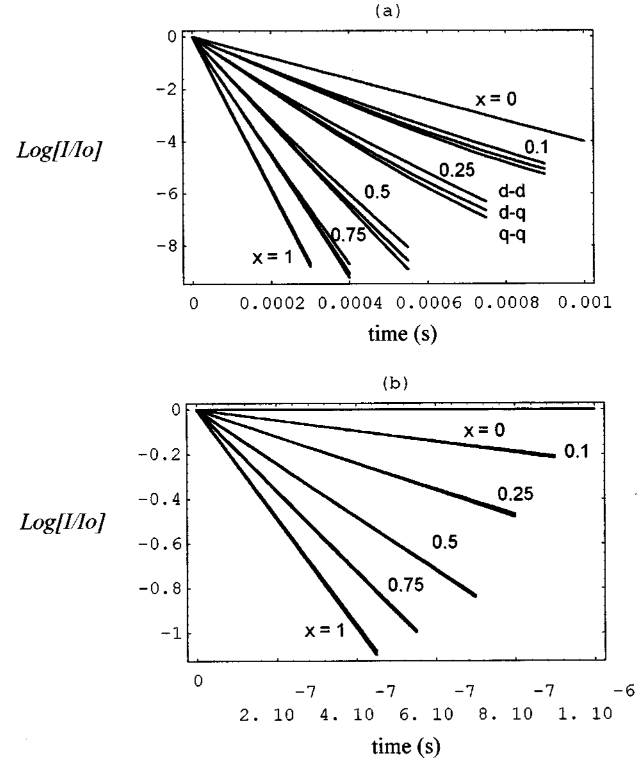

FIG. 2. Typical shape of the decay curves. (a) $\gamma = 4\times10^3\,(\mathrm{s}^{-1})$ and $W_{DA(0)}^{q\text{-}q} = 2.4\times10^4\,(\mathrm{s}^{-1})$ and (b) $\gamma = 4\times10^2\,(\mathrm{s}^{-1})$ and $W_{DA(0)}^{q\text{-}q} = 2.4\times10^6\,(\mathrm{s}^{-1})$, for different relative concentrations x of optical centers. Note the difference in the scale of the plots.

between components $Q^{\alpha\beta}$. For example, for the $(^1G_4)\rightarrow(^3H_5)$ transition in the donor ion, we find the ratios

$$|Q_{d'd}^{x^2-y^2}|^2 : |Q_{d'd}^{z^2}|^2 : |Q_{d'd}^{xy}|^2 : |Q_{d'd}^{yz}|^2 : |Q_{d'd}^{xz}|^2 = 1 : \tfrac{1}{2} : \tfrac{3}{8} : \tfrac{3}{16} : \tfrac{3}{16}$$

while for the $(^3H_4)\rightarrow(^3H_6)$ transition in the acceptor ion, the components take relative values

$$|Q_{aa'}^{x^2-y^2}|^2 : |Q_{aa'}^{z^2}|^2 : |Q_{aa'}^{xy}|^2 : |Q_{aa'}^{yz}|^2 : |Q_{aa'}^{xz}|^2 = 1 : \tfrac{2}{3} : \tfrac{3}{8} : 0 : 0.$$

In the first place, this shows the strong variations that can appear in the products between components $(\alpha\beta-\delta\gamma)$ of both quadrupole moments.

A complete calculation of this process considering the first two angular classes gives a value of $W_{DA}^{q\text{-}q} = 2.42\times10^6$ (s^{-1}) for the energy-transfer rate. Appendix B shows details of the calculation. This result is more than twice the one calculated in Ref. 20, and this is due to the way in which the crystal model establishes the geometrical effects of the interaction and global properties. The authors of Ref. 20 did the calculation using a shell model, considering just one generic donor-acceptor pair in each shell and multiplying this result by the number of ions in each shell. Rigorously, the anisotropic effect of the electric quadrupole operator causes that the geometric factors $g_{qq}^{(\alpha\beta-\gamma\delta)}(l)$ change their magnitude significantly depending on the angular orientation between the donor ion and the acceptor ion, even within the same angular class l, as can be verified from the tables included in Appendix B. Thus, in spite of the system's high symmetry, the geometric factors become local properties in the higher order multipole interactions, and this results in a change of the magnitude of $W_{DA}^{q\text{-}q}$. We could predict that differences should be larger in systems of lower symmetry where the anisotropic effects are stronger.

VI. CONCLUSIONS

The crystal model has been extended to account for the most relevant higher-order electric multipole contributions which are responsible for the energy-transfer processes in crystalline phases doped with luminescent ions that are relatively separated. This results in the predominance of long-range interactions, and permits to neglect other short-range interactions such as direct exchange, studied in the parallel paper.[26]

Even in crystals with high symmetry, and in contrast with the purely dipolar case, the electric quadrupole operator introduces an expected decrease in the isotropicity of the interaction which is observed in both electronic as well as geometric contributions to the energy-transfer rates. Similar effects have been observed in the parallel study on energy-transfer rates induced by direct exchange interaction, although the specific mechanisms are very different. For instance, this study shows clearly how the geometric factors of the electric dipole–electric quadrupole and electric quadrupole–electric quadrupole interactions depend explicitly on the angular orientation (θ,ϕ) between the *donor-acceptor* pair, and become local parameters that have to be estimated carefully. These geometric factors have been mentioned ambiguously in some works,[22] and they have been defined analytically only in this paper, to our knowledge. In contrast, as a result of the anisotropy, the geometric factors in direct exchange energy transfer are also local parameters but are related to the relative orientation of the electron clouds, which affects the electronic overlap between the interacting ions.

The anisotropy of the electric quadrupole operator leads to a higher degree of complexity in the crystal model expressions, because the process of summation and averaging of interactions over angular orientations and distances is more cumbersome. However, with the approximations mentioned in this study, the expressions obtained for the decay curves show full formal agreement with those that correspond to the dipole-dipole mechanism previously established by the author.[23,24]

This approach has the advantage of expressing the temporal evolution of the decay processes in terms of average parameters that have a precise physical meaning that is known from the synthesis data (X) or are easily calculated from the crystallographic information [geometric factors $g_{dq}^{(\varepsilon-\alpha\beta)}(l)$ and $g_{qq}^{(\alpha\beta-\gamma\delta)}(l)$]. The only parameter that is adjustable from the experimental information is the global energy-transfer rate at a microscopic scale, W_{DA}, which, however, can be calculated from the theory, as has been illustrated with a particular example in Sec. V, based partially on the results of Chua and Tanner.[20]

Since the effective energy-transfer rate k_{eff} [see Eqs. (20) and (22)], is a macroscopic magnitude and additive to the radiative decay rate γ, the energy-transfer processes produce rather rapid relaxations from the excited states. Using the well-known results of Inokuti and Hirayama,[16] it has become common to differentiate the multipolar mechanism of the transfer processes from the shape of the decay curve, with the one corresponding to quadrupole-quadrupole interactions mentioned as faster and sharper for early relaxation intervals.[1–3,12,16]

The results summarized in Fig. 2, where the condition of equal magnitude in $W_{DA(0)}$ for the three types of electric multipole interaction for several system compositions has been enforced, indicate that there are no sensible differences between the shape of decay curves of the different multipolar order processes. Inspecting Eqs. (22) and (23), it is obvious that only the values of Riemann's zeta function, $\zeta(s)$, change, $\zeta(6)>\zeta(8)>\zeta(10)$, and therefore the magnitude of the effective energy transfer rates decreases very slightly with an increase in the order of the multipolar interaction: $k_{\mathrm{eff}}^{d\text{-}d}>k_{\mathrm{eff}}^{d\text{-}q}>k_{\mathrm{eff}}^{q\text{-}q}$. The function $\Delta_{\mathrm{stat}}(X,w_{DA})$ and its temporal evolution is also affected, but in a somewhat different sense: although the Riemann zeta functions involved in $\Delta_{\mathrm{stat}}(X,w_{DA})$ are very similar [for instance, $\zeta(12)\cong\zeta(18)\cong\zeta(20)$], the differences of shape are mainly related to the magnitude of the $[W_{DA}]^{(k)}$ parameters. However, the change is so small that, in practice and particularly if the W_{DA} energy-transfer rate is large, the curves overlap [see Fig. 2(b)]. For smaller energy-transfer rates, there are some differences between the shape of the decay curves [see Fig. 2(a)], in such a way that they are more pronounced for the higher-order interactions, but changes are again small and not conclusive for the purposes of fitting experimental data and deciding the order of the multipolar interaction. Thus the results of this part of the study contradict numerous analyses in the literature.[1–3,12,16] Moreover, rigorously, the assignment of the type of predominant multipolar mechanism by analysis and fitting of the decay curves loses its meaning in view of the slight differences in shape of the decay curves of one type or the other seen in Figs. 2(a) and 2(b). These results point to the importance of theoretical calculations of the energy-transfer rates to achieve a correct assignment of the multipolar mechanism.

From the point of view of the crystal model, the only important information that can be extracted from the experimental data is the effective energy-transfer rate k_{eff}, which can be deduced from the initial slope of the decay curves. In fact, if $t\rightarrow 0$, then $\Delta_{\mathrm{stat}}(X,wt)\rightarrow 1$ and

$$\left.\frac{d\ln\rho(t)}{dt}\right|_{t\rightarrow 0}=-(\gamma+k_{\mathrm{eff}})=-[\gamma+X\zeta(s)W_{DA}],$$

$$s=6,8,10$$

is true.

With γ known (from very slightly doped crystals), and with data for a series of increasingly doped samples (X), it is possible to deduce the global energy-transfer rate and compare it with the theoretically calculated magnitudes.

Leaving the multipolar transition moments as the only parameters, the method seems to be robust and easy to use in a realistic estimation of the energy-transfer rates for solid-state compounds.

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APPENDIX A: AN APPROXIMATE CALCULATION OF THE EFFECT OF DISTANCE IN $\boldsymbol{\Sigma_{\varepsilon,\alpha\beta}\Sigma_l|\mu^{\varepsilon}|^2|Q^{\alpha\beta}|^2(R_1^g/R_l^g)^8 g_{dq}^{(\varepsilon-\alpha\beta)}(l)}$

It is easy to show with an example that the geometric factors $g_{dq}^{(\varepsilon-\alpha\beta)}(1)$ and $g_{qq}^{(\alpha\beta-\gamma\delta)}(1)$ for the first angular class are the dominant terms in these summations. In fact, choosing the $(x-xy)$ component of the dipole-quadrupole interaction, the analytic form of $g_{dq}^{(x-xy)}$ is as follows:

$$g_{dq}^{(x-xy)}=4\left(1-10\frac{R_x^2}{R^2}+25\frac{R_x^4}{R^4}\right)\frac{R_y^2}{R^2}.$$

Evaluating for all the ions of the first three angular classes ($l=1$, 2, and 3) and considering data on donor-acceptor distances (see Refs. 23 and 39) in the elpasolite lattice, we obtain

$\left(\frac{R_1^g}{R_1^g}\right)^8 g_{dq}^{(x-xy)}(1)$	$\left(\frac{R_1^g}{R_2^g}\right)^8 g_{dq}^{(x-xy)}(2)$	$\left(\frac{R_1^g}{R_3^g}\right)^8 g_{dq}^{(x-xy)}(3)$
1×26	0.0625×8	$0.012\,34\times 0.444$

and the $g_{dq}^{(x-xy)}(1)$ parameter alone accounts for 98.1% of the total $(x-xy)$ component of the d-q interaction. Adding contributions up to the second angular classes makes it possible to account for approximately 99.9%. This criterion is rather general, with slight variations for other components of both $(\varepsilon-\alpha\beta)$ for d-q and $(\alpha\beta-\gamma\delta)$ for q-q, and allows simpler formalisms for the global transfer rates.

APPENDIX B: CALCULATION OF THE $\boldsymbol{q}$-$\boldsymbol{q}$ ENERGY-TRANSFER PROCESS IN $\mathbf{Cs_2NaYCl_6{:}TmCl_6}$

The calculation of $k_{\mathrm{eff}}^{q\text{-}q}$ and $\Delta_{\mathrm{stat}}(X,Wt)$ in the case of the energy process of transfer between Tm^{3+} ions in $\mathrm{Cs_2NaYCl_6{:}TmCl_6}$ is made considering the first two angular classes and pertinent crystallographic data.[39] The nonzero geometric factors for the angular classes $l=1,2$ are

$l=1$ (12 acceptor ions, four in each Cartesian plane. $R=a/\sqrt{2}$. Typical Cartesian coordinates$(\lvert R_x\rvert,\lvert R_y\rvert,\lvert R_z\rvert)$.		$l=2$ (six acceptor ions, two in each Cartesian axis. $R=a$. Typical Cartesian coordinates $(\lvert R_x\rvert,\lvert R_y\rvert,\lvert R_z\rvert)$.	
(i) plane *x*-*y*: $(a/2,a/2,0)$		(i) *x* axis: $(a,0,0)$	
$g_{qq}^{xy\text{-}xy}=361$	$g_{qq}^{zz\text{-}zz}=\frac{729}{16}$	$g_{qq}^{xy\text{-}xy}=256$	$g_{qq}^{zz\text{-}zz}=\frac{729}{16}$
$g_{qq}^{yz\text{-}yz}=36$	$g_{qq}^{(x^2-y^2)-(x^2-y^2)}=\frac{823}{128}$	$g_{qq}^{yz\text{-}yz}=256$	$g_{qq}^{(x^2-y^2)-(x^2-y^2)}=\frac{361}{16}$
$g_{qq}^{xz\text{-}xz}=36$		$g_{qq}^{xz\text{-}xz}=256$	
$g_{qq}^{yz\text{-}xz}=100$	$g_{qq}^{zz-(x^2-y^2)}=\frac{5}{4}$		$g_{qq}^{zz-(x^2-y^2)}=\frac{3145}{16}$
$g_{qq}^{xy\text{-}zz}=\frac{225}{4}$			
(ii) Plane *y*-*z*: $(0,a/2,a/2)$		(ii) *y* axis: $(0,\alpha,0)$	
$g_{qq}^{xy\text{-}xy}=36$	$g_{qq}^{zz\text{-}zz}=\frac{13\,689}{526}$	$g_{qq}^{xy\text{-}xy}=256$	$g_{qq}^{(x^2-y^2)-(x^2-y^2)}=\frac{361}{16}$
$g_{qq}^{yz\text{-}yz}=361$	$g_{qq}^{yz-(x^2-y^2)}=225/16$	$g_{qq}^{yz\text{-}yz}=256$	
$g_{qq}^{xz\text{-}xz}=36$	$g_{qq}^{(x^2-y^2)-(x^2-y^2)}=\frac{5021}{256}$	$g_{qq}^{xz\text{-}xz}=256$	$g_{qq}^{zz-(x^2-y^2)}=\frac{3145}{16}$
$g_{qq}^{yz\text{-}zz}=\frac{225}{4}$		$g_{qq}^{zz\text{-}zz}=\frac{729}{16}$	
$g_{qq}^{xy\text{-}xz}=100$	$g_{qq}^{zz-(x^2-y^2)}=\frac{5465}{256}$		
(iii) Plane *x*-*z*: $(a/2,0,a/2)$		(iii) *z* axis: $(0,0,a)$	
$g_{qq}^{xy\text{-}xy}=36$	$g_{qq}^{zz\text{-}zz}=\frac{13\,689}{256}$	$g_{qq}^{xy\text{-}xy}=16$	$g_{qq}^{zz\text{-}zz}=\frac{1573}{8}$
$g_{qq}^{yz\text{-}yz}=36$	$g_{qq}^{xz-(x^2-y^2)}=\frac{225}{16}$	$g_{qq}^{yz\text{-}yz}=256$	$g_{qq}^{(x^2-y^2)-(x^2-y^2)}=1$
$g_{qq}^{xz\text{-}xz}=361$	$g_{qq}^{(x^2-y^2)-(x^2-y^2)}=\frac{5021}{256}$	$g_{qq}^{xz\text{-}xz}=256$	
$g_{qq}^{yz\text{-}zz}=\frac{225}{16}$			
$g_{qq}^{xy\text{-}xz}=100$	$g_{qq}^{zz-(x^2-y^2)}=\frac{5465}{256}$		

In this way, the different contributions to $k_{\text{eff}}^{q\text{-}q}$ are established, forming the products

$$\sum_{\alpha\beta,\gamma\delta}\sum_{l=1,2}|Q^{\alpha\beta}|^2|Q^{\gamma\delta}|^2\left(\frac{R_1^g}{R_l^g}\right)^{10}g_{qq}^{(\alpha\beta-\gamma\delta)}(l).$$

Taking the magnitudes for the integral of the spectral form functions, dielectric constant and field correction factor from Chua and Tanner's work,[20] this finally gives a value of $k_{\text{eff}}^{q\text{-}q}=2.42\times 10^6\ \text{s}^{-1}$.

APPENDIX C: LIST OF THE $[W_{DA}]^{(k)}$ PARAMETERS

The $[W_{DA}]^{(k)}$ parameters arise from the statistical term $\Delta_{\text{stat}}(X,Wt)$, and the first $(k)=2,3,4$ parameters have the following analytical expressions:

$$[W_{DA}^{d\text{-}q}]^{(2)}=\frac{4\pi^2(\int f_D(\omega)f_A(\omega)d\omega)^2}{\hbar^2(R_1^g)^{16}}\left\{\sum_{\varepsilon,\alpha\beta}n_1^{\max}[\tfrac{3}{4}\,|\mu^{\varepsilon}|^2|Q^{\alpha\beta}|^2g_{dq}^{\varepsilon-\alpha\beta}(1)]^2\right\},$$

$$[W_{DA}^{d\text{-}q}]^{(3)}=\frac{8\pi^3(\int f_D(\omega)f_A(\omega)d\omega)^3}{\hbar^3(R_1^g)^{24}}\left\{\sum_{\varepsilon,\alpha\beta}n_1^{\max}[\tfrac{3}{4}\,|\mu^{\varepsilon}|^2|Q^{\alpha\beta}|^2g_{dq}^{\varepsilon-\alpha\beta}(1)]^3\right\},$$

$$[W_{DA}^{d\text{-}q}]^{(4,1)}=\frac{16\pi^4(\int f_D(\omega)f_A(\omega)d\omega)^4}{\hbar^4(R_1^g)^{32}}\left\{\sum_{\varepsilon,\alpha\beta}n_1^{\max}[\tfrac{9}{16}\,|\mu^{\varepsilon}|^2|Q^{\alpha\beta}|^2g_{dq}^{\varepsilon-\alpha\beta}(1)]^4\right\},$$

$$[W_{DA}^{d\text{-}q}]^{(4,2)}=\frac{16\pi^4(\int f_D(\omega)f_A(\omega)d\omega)^4}{\hbar^4(R_1^g)^{32}}\left\{\sum_{\varepsilon,\alpha\beta}(n_1^{\max})^2[\tfrac{9}{16}\,|\mu^{\varepsilon}|^2|Q^{\alpha\beta}|^2g_{dq}^{\epsilon-\alpha\beta}(1)]^4\right\}.$$

For the q-q interaction,

$$[W_{DA}^{q\text{-}q}]^{(2)}=\frac{4\pi^2(\int f_D(\omega)f_A(\omega)d\omega)^2}{\hbar^2(R_1^g)^{20}}\left\{\sum_{\epsilon\beta,\gamma\delta}n_1^{\max}[\tfrac{9}{16}\,|Q^{\alpha\beta}|^2|Q^{\gamma\delta}|^2g_{qq}^{\alpha\beta-\gamma\delta}(1)]^2\right\},$$

$$[W_{DA}^{q\text{-}q}]^{(3)}=\frac{8\pi^3(\int f_D(\omega)f_A(\omega)d\omega)^3}{\hbar^3(R_1^g)^{30}}\left\{\sum_{\alpha\beta,\gamma\delta}n_1^{\max}[\tfrac{9}{16}\,|Q^{\alpha\beta}|^2|Q^{\gamma\delta}|^2g_{qq}^{\alpha\beta-\gamma\delta}(1)]^3\right\},$$

$$[W_{DA}^{q\text{-}q}]^{(4,1)}=\frac{16\pi^4(\int f_D(\omega)f_A(\omega)d\omega)^4}{\hbar^4(R_1^g)^{40}}\left\{\sum_{\alpha\beta,\gamma\delta}n_1^{\max}[\tfrac{9}{16}\,|Q^{\alpha\beta}|^2|Q^{\gamma\delta}|^2g_{qq}^{\alpha\beta-\gamma\delta}(1)]^4\right\},$$

$$[W_{DA}^{q\text{-}q}]^{(4,2)}=\frac{16\pi^4(\int f_D(\omega)f_A(\omega)d\omega)^4}{\hbar^4(R_1^g)^{40}}\left\{\sum_{\alpha\beta,\gamma\delta}(n_1^{\max})^2[\tfrac{9}{16}\,|Q^{\alpha\beta}|^2|Q^{\gamma\delta}|^2g_{qq}^{\varepsilon-\alpha\beta}(1)]^4\right\}.$$

Evaluating these expressions for the $({}^1G_4,\,{}^3H_6)\rightarrow({}^3H_5,\,{}^3H_4)$ $(q\text{-}q)$ energy transfer process in the Tm^{3+} elpasolite lattice up to $k=4$, the following values are obtained:

$[W_{DA}^{q\text{-}q}]^{(2)}$ (s^{-2})	$[W_{DA}^{q\text{-}q}]^{(3)}$ (s^{-3})	$[W_{DA}^{q\text{-}q}]^{(4.1)}$ (s^{-4})	$[W_{DA}^{d\text{-}q}]^{(4.2)}$ (s^{-4})
2.31×10^{7}	6.90×10^{15}	1.81×10^{21}	7.26×10^{21}

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