

## Cross-relaxation process between +3 rare-earth ions in LiYF<sub>4</sub> crystals

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The cross-relaxation probability ( $\text{sec}^{-1}$ ) involving the  $^5S_2$  and  $^5I_8$  levels of holmium ions in LiYF<sub>4</sub> was investigated and its concentration dependence determined. By using a random distribution function of ions in the crystal, it was possible to determine the concentration dependence of the nonradiative probability for the ion-ion energy transfer by dipole-dipole, dipole-quadrupole, and quadrupole-quadrupole electric interactions. The applied model shows that the ion-ion cross-relaxation transfer between Ho<sup>3+</sup> ions in LiYF<sub>4</sub> crystals, cannot account for the experimental results. At a high concentration level of activators (>1%), the excited ion must interact with two neighbors of same specie competing with the single ion cross-relaxation transfer. [S0163-1829(96)01229-5]

### I. INTRODUCTION

In a recent paper<sup>1</sup> we reported the strong quenching of the  $^5S_2 \rightarrow ^5I_7$ ,  $^5I_8$  luminescent transitions in high-doped LiYF<sub>4</sub> with Ho<sup>3+</sup> by two possible cross-relaxation processes with almost zero mismatch energy, favoring the population of the  $^5I_5$ ,  $^5I_6$ , and  $^5I_7$  levels. A quantitative spectroscopic study of the luminescence of the HoLiF<sub>4</sub> crystal<sup>1</sup> showed that there is a total quenching of the 490-, 540-, 749-, and 900-nm luminescent channels, starting from the  $^5F_3$ ,  $^5S_2$ , and  $^5I_5$  levels, respectively. These partial luminescence quenchings are independent of the temperature, indicating that there is some energy transfer between neighboring excited Ho<sup>3+</sup> ions (Ho\*) with approximately zero mismatch energy ( $\Delta E \approx 0$ ). These processes are responsible for the conversion of visible and near-infrared transitions into the midinfrared ones.

When investigating the schematic energy level diagram of the Ho<sup>3+</sup> ions in high-doped LiYF<sub>4</sub> crystals, two resonant cross-relaxation processes were found:  $P_1$  and  $P_3$  ( $\Delta E \approx 0$ ), and a nonresonant  $P_2$  with  $\Delta E > 0$ , involving two nearest-neighbor Ho<sup>3+</sup> ions. These processes are generically represented by the sequence [Ho\*(1), Ho(2)]  $\rightarrow$  [Ho\*(1), Ho\*(2)], respectively,

$$P_1: (^5F_3, ^5I_8) \rightarrow (^5F_5, ^5I_7) \quad \text{resonant } \Delta E \approx 0,$$

$$P_2: (^5S_2, ^5I_8) \rightarrow (^5I_6, ^5I_6) \quad \text{energy mismatch } \Delta E \\ = 1047 \text{ cm}^{-1},$$

$$P_3: (^5I_4, ^5I_8) \rightarrow (^5I_6, ^5I_7) \quad \text{resonant } \Delta E \approx 0.$$

The  $P_1$  process short circuits the  $^5S_2$  state and populates the  $^5F_2$  level, besides quenching the 490-nm fluorescence. Clearly, the  $P_1$  and  $P_2$  processes quench the green emission from the  $^5S_2$  level. At 300 K,  $P_2$  is more probable than  $W_2$ , a multiphonon emission rate from the  $^5S_2$  level, according to the rate equation model presented in the previous paper.<sup>1</sup> In this paper, we present the results from an investigation of the nature of the  $P_2$  cross-relaxation process, determining its mean value for several Ho<sup>3+</sup>-doped crystals with 0.001–0.1 and 1 mol fractions.

The previous quantitative luminescence measurements in LiYF<sub>4</sub> doped with low Ho<sup>3+</sup> concentration showed that the 490-nm and 790-nm emissions, respectively, from the  $^5F_3$  and  $^5I_4$  levels, are much weaker than the 540-nm emission (from the  $^5S_2$  level), by a factor of 364 times. This fact makes difficult the use of these two weaker fluorescences for investigating the nature of cross-relaxation processes between activators. The 540-nm emission from the  $^5S_2$  level was then chosen for that investigation.

### II. EXPERIMENTAL TECHNIQUES

The samples used in this investigation were single crystals of doped LiYF<sub>4</sub> containing several Ho<sup>3+</sup> concentrations from 0.001 to 0.1 and 1 mol fractions. The starting material for the crystal growth were synthesized from ultrapure rare-earth oxides by a conventional hydrofluorination procedure. The Ho<sup>3+</sup>:LiYF<sub>4</sub> thus synthesized was grown by the conventional Czochralski method under an argon atmosphere. Samples were extracted from the boule after the appropriate choice of a region free of scattering defects. The holmium concentrations were determined by an x-ray fluorescence technique.

The lifetimes of excited Ho<sup>3+</sup> ions were measured using a pulsed laser excitation (10 nsec) from a dye-pumped nitrogen laser tuned at 450 nm. The time-dependent signal was detected by a fast S-20 extended-type photomultiplier detector and analyzed using a signal-processing Box-Car averager (PAR 4402).

### III. RESULTS AND DISCUSSION

Figure 1 shows the schematic energy level diagram of the Ho<sup>3+</sup> ions in the LiYF<sub>4</sub> crystal where the nonresonant single-ion process ( $P_2$ ) involving two nearest-neighbor Ho<sup>3+</sup> ions may be responsible for the luminescence quenching of the  $^5S_2$  level. In addition to that, the double-ion process is proposed for the  $^5S_2$  level deexcitation.

The experimental value of  $P_2$  was obtained from the total lifetime ( $\tau$ ) measured after a pulsed laser excitation (10 nsec) from a dye-pumped nitrogen laser tuned at 450 nm. The following relation between the total lifetime ( $\tau$ ) and the mi-

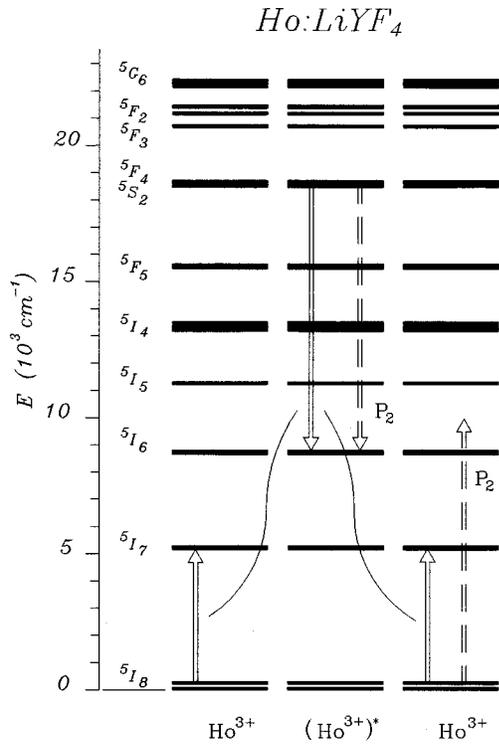


FIG. 1. Energy level diagrams illustrating the single-ion ( $P_2$ ) and the double-ion energy transfer in  $\text{Ho}^{3+}$ -doped  $\text{LiYF}_4$  crystals. The double-ion mechanism involves a cooperative absorption of the excitation energy by both neighbor (acceptor) ions located at the same distances from the donor.

microscopic transfer rate was obtained using the  $f(R)dR$  distribution function of ions:

$$\frac{1}{\tau} = \frac{1}{\tau_r} + W_2 + P_2 = \frac{1}{\tau_r} + W_2 + \int_{R_{\min}}^{\infty} W_{D-A}(R)f(R)dR. \quad (1)$$

$\tau_r^{-1}$  and  $W_2$  are the radiative transition and multiphonon decay rates of the  $^5S_2$  level, which are not concentration dependents. Only the  $P_2$  transfer rate is strongly dependent on the Ho concentration.

Table I shows the measured lifetimes values of the  $^5S_2$  level in  $\text{LiYF}_4$  crystals with several Ho concentrations, and the obtained values of  $P_2$  using Eq. (1). It is important

TABLE I. Experimental lifetimes values for  $\text{Ho}^{3+}$  ( $^5S_2$ ):  $\text{LiYF}_4$  crystals, measured at 300 K, for several Ho concentrations ( $x_A$ ). The cross-relaxation probability rate [ $P_2$  ( $\text{sec}^{-1}$ )], was calculated using Eq. (1) and the measured lifetimes.

$x_A$	$P_2$ ( $\text{sec}^{-1}$ )	$\tau$ ( $\mu\text{sec}$ )
0.002 0	957	131.2
0.005 2	2 608	107.8
0.007 3	3 793	95.6
0.016 9	12 217	53
0.050 9	46 946	18.7
0.107 2	132 222	7.2

to note that the extrapolated value of the  $(\tau_r^{-1} + W_2)$  intracenter transition rate is equal to  $6666.7 \text{ sec}^{-1}$ .

Assuming a multipolar electric interaction between two  $\text{Ho}^{3+}$  ions separated by the distance  $R$ , one must have the microscopic cross-relaxation rate given by  $W_{D-A}(R) = \sum_{s=6,8,10} (C_s/R^s)$ , where  $C_s$  is the transference constant ( $\text{cm}^s/\text{sec}$ ), and  $s$  the order of the multipolar electric interaction, i.e.,  $s=6$  for dipole-dipole,  $s=8$  for dipole-quadrupole, and  $s=10$  for the quadrupole-quadrupole interaction. Using a random ion distribution in the crystal, it was possible to define the  $f(R)dR$  function which specifies the fraction of  $\text{Ho}^{3+}$  ions which have an  $\text{Ho}^{3+}$  ion as the closest neighbor inside of a shell between the distances  $R$  and  $R+dR$ . Since the  $4f^N$  orbital of the ( $3+$ ) rare-earth ions is always shielded by the most external fulfilled orbital ( $5p^6$ ), one expects a negligible interaction between them in the ground state which in turn produces no tendency for either preference or rejection of a closer pair configurations away from statistical distribution. This argument justifies the use of a random distribution of Ho ions in the host at relatively high concentrations ( $x_A > 0.01$ ), in the deexcitation model. This function was successfully applied to describe the  $F$  center- $\text{OH}^-$  interaction in KCl crystals.<sup>2</sup>

The  $f(R)dR$  distribution function is given by

$$f(R)dR = \frac{4\pi R^2}{AR_0^3} x_A(1-x_A)^{4\pi R^3/3R_0^3-2} dR \quad (2)$$

with  $x_A$  the activator concentration given in mol fraction.  $R_0^3 = 1/N$ , where  $R_0 = 4.16 \text{ \AA}$  and  $N = 1.41 \times 10^{22} \text{ Y ions/cm}^3$  for  $\text{LiYF}_4$  crystals.  $A$  is the normalization constant obtained by the following relation:  $A = \int_{R_{\min}}^{\infty} f(R)dR$ , where  $R_{\min}$  is the nearest-neighbor (Y-Y) distance equal to  $3.72 \text{ \AA}$ .

The average value of the cross-relaxation probability  $P_2(\text{sec}^{-1})$  can be evaluated using the following expression:

$$P_2 = \langle W_{\text{tr}} \rangle_{\text{av}} = \sum_{s=6,8,10} C_s \left\{ \int_{R_{\min}}^{\infty} \left[ \left( \frac{1}{R^s} \right) f(R) dR \right] \right\}. \quad (3)$$

$C_s = R_C^s/\tau_r$ , where  $R_C$  is the critical distance for the interaction.  $\tau_r$  is the radiative lifetime of the  $^5S_2$  level which has been estimated to be  $0.67 \text{ msec}$ .<sup>3</sup>

By substituting  $f(R)dR$  in Eq. (3), one obtains  $P_2$ . The integration part is defined in the following:

$$I(s, x_A) = \int_{R_{\min}}^{\infty} \left[ \left( \frac{1}{R^s} \right) f(R) \right] dR. \quad (4)$$

A numerical calculation of the integration part was performed for each type of individual interaction (i.e.,  $s=6,8,10$ ). The results are shown in Fig. 2 (full squares) for dipole-dipole ( $d-d$ ), dipole-quadrupole ( $d-q$ ), and quadrupole-quadrupole ( $q-q$ ) interactions. There it is seen, a linear dependence of  $I(s, x_A)$  with the activator concentration for  $x_A \leq 0.12$ , i.e.,  $I(s, x_A) = I(s)x_A$ . The same behavior is obtained for the concentration range where  $x_A \leq 0.3$ , when using an exponential-type law for the exchange ion-ion transfer (see Fig. 2). The exchange microscopic interaction between rare-earth ions at distances  $R \gg R_0$  ( $R_{\min} = 3.72 \text{ \AA}$  for YLF), can be given as  $W_{\text{exch}} = W_0 \exp(-2R/R_0)$ , where  $R_0$  is the Bohr radius.  $R_0$  is equal to  $\sim 0.4 \text{ \AA}$  for rare-earth ions.

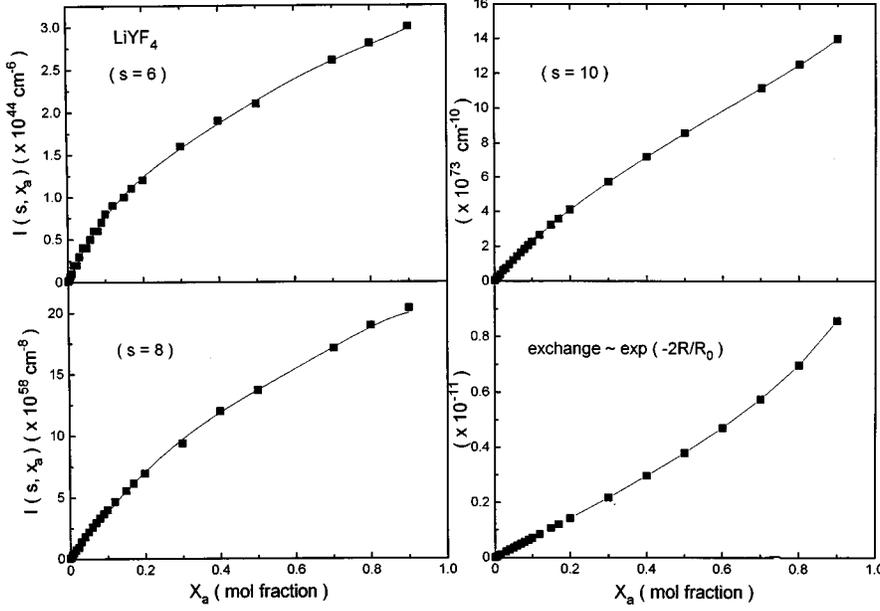


FIG. 2. Numeric calculated values (represented by full squares), for the integration part  $I(s, x_A)$  using the  $(d-d)$ ,  $(d-q)$ , and  $(q-q)$  interaction (i.e.,  $s=6, 8, 10$ , respectively). The exchange was also considered. The calculation was performed for a  $\text{LiYF}_4$  crystal lattice with an activator concentration variation from 0 to 0.9 mol fraction. Full lines represent the computer fittings using a fifth-order polynomial function.

Figure 2 also shows the result obtained for the numerical calculation of the integration part used for the exchange interaction which is given by

$$I(\text{exch}, x_A) = \int_{R_{\min}}^{\infty} \left[ \exp\left(\frac{-2R}{R_0}\right) f(R) \right] dR.$$

There it is also seen, a linear dependence of  $I(\text{exch}, x_A)$  with the activator concentration when  $x_A \leq 0.3$ .

The observed behavior of the integration part for each type of microscopic interaction, verified for  $I(s, x_A)$  and  $I(\text{exch}, x_A)$ , states that the average rate probability for the single-ion transfer model, where  $\langle W_{\text{tr}} \rangle_{\text{av}} = \sum_s C_s I(s, x_A) = [\sum_s C_s I(s)] x_A$ , must have a linear dependence on  $x_A$  in the range of  $x_A \leq 0.12$ . This general conclusion is not satisfied for the most of the  $\text{TR}^{3+}$  systems.<sup>4</sup> In particular, that linear behavior is not in agreement with the estimated values of  $P_2$ , obtained from the experimental lifetime of the  ${}^5\text{S}_2$  level of  $\text{Ho}^{3+}$  ions in  $\text{LiYF}_4$  (YLF) crystals. These experimental values are exhibited in Fig. 3 which are represented by full squares.

That result evidences the need of extending this model to include the ion- (two ions) transfer competing with the actual ion-ion energy transfer (single-ion transfer). In this proposed mechanism (double-ion transfer), the excitation energy is splitted and transferred to both neighboring ions situated at the same distance  $R$  from the donor (see Fig. 1 for the  $\text{Ho}^{3+}$ : YLF system). The microscopic transfer probability  $W_{D-2A}(R)$  for the double-ion transfer was obtained by extending the overlap integral between either the acceptor absorption and donor emission line shape, derived elsewhere for the case of the ion-ion transfer probability.<sup>5</sup> It was done by replacing the individual absorptions by a cooperative one composed by the sum of both absorption's line shape. For a  $(d-d)$  interaction, one must have

$$W_{D-2A}(R) = \frac{3\hbar c^2 \sigma_{A_1} \sigma_D}{4\pi^3 n^2 R^6} \int \frac{f_D(E)}{E^2} \left[ F_{A_1}(E+E_2) + \left( \frac{\sigma_{A_2}}{\sigma_{A_1}} \right) F_{A_2}(E+E_1) \right] dE,$$

where  $E_1$  and  $E_2$  are the average absorption energies from acceptors  $A_1$  and  $A_2$ , evaluated using the following expressions:

$$E_1 = \int E F_{A_1}(E) dE \quad \text{and} \quad E_2 = \int E F_{A_2}(E) dE.$$

$\sigma_D$  is the integrated emission cross section of donors (D).  $\sigma_{A_1}$  and  $\sigma_{A_2}$  are the integrated absorption cross sections of acceptors,  $A_1$  and  $A_2$ , respectively.  $f_D(E)$  is the normalized line shape of the donor emission.  $F_{A_1}(E+E_2)$  and

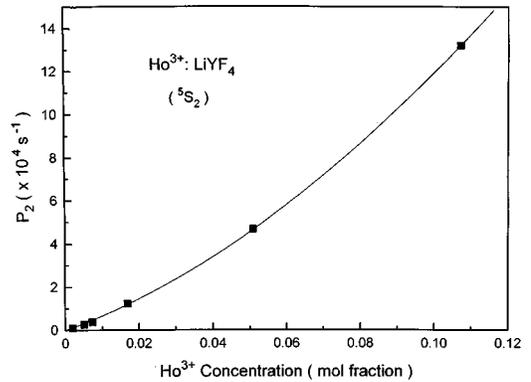


FIG. 3. Concentration dependence of the nonradiative deexcitation probability rate [ $P_2(\text{sec}^{-1})$ ] of the  ${}^5\text{S}_2$  level of  $\text{Ho}^{3+}$  ions in a  $\text{LiYF}_4$  crystal. The experimental values were obtained from the measured lifetimes and are represented by full squares. Full lines represent the computer best fit using Eq. (7) from the present model for the average rate probability  $\langle W_{\text{tr}} \rangle_{\text{av}}$ , which includes the double-ion transfer in addition to the single-ion transfer.

$F_{A_2}(E+E_1)$  are the absorption line shape of the two individual absorptions of acceptors ions  $A_1$  and  $A_2$ , translated to the  $(E_1+E_2)$  average energy position.

This proposed interaction must produce a nonlinear concentration effect on the activator concentration dependence of the average transfer rate probability in the range of interest, i.e.,  $x_A > 1\%$ .

The statistical model including this proposed double-ion interaction is obtained from the random walk probability. Let the  $h(r)dR$  function describe the probability of finding one or two activator ions in the shell between the distances  $R$  and  $R+dR$  from the donor. It can also be written in terms of the two individuals statistical distributions;  $f(R)dR$  which is related to the single-ion transfer, and  $g(R)dR$  related to the double-ion transfer, as follows:

$$h(R)dR = \frac{Af(R)dR + g(R)dR}{B}, \quad (5)$$

where  $B$  is the normalization constant given by  $B = \int_{R_{\min}}^{\infty} h(R)dR$ .

$f(R)dR$  was given in Eq. (2).  $g(R)$  specifies the fraction of activator ( $A^{3+}$ ) ions which will have two  $A^{3+}$  ions as the closest neighbors inside of the shell between the distances  $R$  and  $R+dR$  from the donor.  $g(R)dR$  is also obtained from the random walk problem, and is given by

$$g(R)dR = \frac{4\pi R^2}{R_0^3} x_A^2 (1-x_A)^{4\pi R^3/R_0^3-3} dR. \quad (6)$$

If the energy transfer is dominated by one type of the multipolar electric dipole interactions, the double-ion and single-ion microscopic rates can be written as  $W_{D-2A}(R) = C_s^{(2)}/R_s$  and  $W_{D-A}(R) = C_s^{(1)}/R_s$ , respectively. Using the fact that the  $f(R)dR$  distribution should be used to perform the average value of the microscopic single-ion rate and that  $g(R)dR$  must be used for averaging the double-ion microscopic rate, one must have the following expression for the observable probability rate in the crystal:

$$\langle W_{tr} \rangle_{av} = \frac{1}{B} \left\{ C_s^{(1)} \int_{R_{\min}}^{\infty} \left[ \left( \frac{1}{R^s} \right) Af(R) \right] dR + C_s^{(2)} \int_{R_{\min}}^{\infty} \left[ \left( \frac{1}{R^s} \right) g(R) \right] dR \right\}.$$

TABLE II. Parameter values obtained from the best fit of data using Eq. (7) from the present model which includes the double-ion transfer in the cross-relaxation process between  $\text{Ho}^{3+}$  ions in  $\text{LiYF}_4$  crystals.  $C_s^{(1)}$  ( $R_C^{(1)}$ ) and  $C_s^{(2)}$  ( $R_C^{(2)}$ ) refer to single-ion and double-ion processes, respectively.

$s$	$C_s^{(1)}$ ( $\text{cm}^s/\text{sec}$ )	$R_C^{(1)}$ ( $\text{\AA}$ )	$a$	$C_s^{(2)}$ ( $\text{cm}^s/\text{sec}$ )	$R_C^{(2)}$ ( $\text{\AA}$ )
6	$5.1 \times 10^{-40}$	8.4	23.6	$1.2 \times 10^{-38}$	14.2
8	$1.4 \times 10^{-54}$	7.5	13.8	$2.0 \times 10^{-53}$	10.4
10	$2.2 \times 10^{-69}$	6.6	16.1	$3.6 \times 10^{-68}$	8.7

Using the approximation that  $(1-x_A)^{4\pi R^3/R_0^3-3} \cong (1-x_A)^{4\pi R^3/R_0^3-2}$ , and the following ratio between the two normalization constants  $(A/B) = 1/(1+x_A)$ , we have that

$$\langle W_{tr} \rangle_{av} = C_s^{(1)} \left( \frac{1+ax_A}{1+x_A} \right) I(s, x_A), \quad (7)$$

where  $C_s^{(2)} = aC_s^{(1)}$ .  $I(s, x_A)$  is the integration part defined in Eq. (4), involving only the  $f(R)dR$  distribution function.

Figure 3 (solid line) shows the computer best fit of the experimental data. The  $x_A$  dependence of  $I(s, x_A)$  term, was obtained by fitting the numerical integration values (calculated for each  $x_A$ ) with a polynomial function of fifth order. From these results one sees that once starting with any of the microscopic electric interactions [i.e.,  $(d-d)$ ,  $(d-q)$  and  $(q-q)$ ], the present model describes the observed deexcitation probability only if the double-ion interaction is used in addition to the single-ion process for Ho-doped systems.

Table II shows the  $C_s^{(1)}$ ,  $C_s^{(2)}$ ,  $R_C^{(1)}$ , and  $R_C^{(2)}$  (for  $s=6, 8, 10$ ), values obtained from the best fit. The  $C_{d-d}^{(1)}$ ,  $C_{d-q}^{(1)}$ , and  $C_{q-q}^{(1)}$  obtained values are of the same order of magnitude than the theoretical values given in Ref. 6.

Using the  $I(s, x_A) = I(s)x_A$  verified when  $x_A < 0.12$  from the numerical calculations, in Eq. (7), one must find that

$$\langle W_{tr} \rangle_{av} \propto C_s^{(1)} \left( \frac{1+ax_A}{1+x_A} \right) x_A.$$

It shows that the nonlinear interaction (double-ion transfer) will be important only if  $a \gg 1$  (i.e.,  $C_s^{(2)} \gg C_s^{(1)}$ ). The  $\text{Tm}^{3+}$  ( ${}^3\text{F}_4$ ):  $\text{Y}_3\text{Al}_5\text{O}_{12}$  system certainly is an example where  $a \leq 1$ .<sup>7</sup> It seems that in this particular case, the cross-relaxation probability follows a single-ion behavior, i.e., a linear dependence on  $x_A$ .

In this paper the Ho system was used as a probe for the investigation of the cross-relaxation mechanism between  $\text{TR}^{3+}$  ions in crystals as a function of  $\text{TR}^{3+}$  concentration. The result derived from the present model states that, independently of the microscopic electric interactions  $(d-d)$ ,  $(d-q)$ , and  $(q-q)$  considered, one always expects from the theory a linear concentration dependence of the cross-relaxation probability ( $\text{sec}^{-1}$ ) as a function of the activator doping for  $x_A \leq 0.12$ , when using a single-ion transfer only. In order to account for the experimental observation (i.e., a nonlinear concentration dependence), the double-ion interaction must be considered in addition to the actual single-ion transfer mechanism at a higher concentration level of the activator (i.e.,  $x_A \geq 1\%$ ).

#### IV. CONCLUSIONS

The concentration dependence of the cross-relaxation probability derived from the present model for Ho ions in the  $\text{LiYF}_4$  crystal can be extended to any other  $\text{TR}^{3+}$ -doped ionic crystals. The behavior of the concentration dependence of the integration part,  $I(s, x_A)$ , obtained from the numerical calculations for each type of interaction ( $s$ ), is a general result and does not depend on a specific  $\text{TR}^{3+}$  ion and host lattice considered.

It is expected for rare-earth (3+) ions in solids, a quadrupole-quadrupole electric coupling dominating the dipole-quadrupole (which in turn dominates dipole-dipole)

transfer for distances of  $\approx (10-20)$  Å separation.<sup>8</sup> Some experimental investigations have indicated that the resonance energy transfer between rare-earth (3+) ions in a glass host is governed by the dipole-quadrupole interaction.<sup>9</sup> The non-resonant energy transfer from  $\text{Eu}^{3+}$  ( $^5D_0$ ) to  $\text{Yb}^{3+}$  ( $^2F_{7/2}$ ) in the  $\text{Y}_2\text{O}_3$  crystal is claimed to be dominated by the dipole-quadrupole interaction.<sup>10</sup> In the literature, the interpretation of the data is based on the observed fluorescence time decay of donors which has been described by Inokuti and Hirayama.<sup>11</sup> Usually this investigation is restricted to a few combinations of donor and acceptor concentrations. Also the luminescence quenching of the  $^5S_2$  level has been investigated<sup>6</sup> in  $\text{LiY}_{1-x}\text{Ho}_x\text{F}_4$  for Ho doping between 0.01 and 1 mol fractions.

In general, we have found that several authors<sup>9,10</sup> have

used an empirical concentration law to explain the experimental results from untrue average arguments, leading to wrong interpretations.

In view of this, the proposed method of investigation contributes in a decisive way for the investigation of the nature of rare-earth (3+) interactions in solids. Also, it is very appropriate for analyzing the nonradiative energy transfer processes between rare-earth ions in solids. The applied model has the advantage of being general and applicable to any donor-acceptor transfer case.

#### ACKNOWLEDGMENTS

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