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Energy transfer within a regular distribution of donors and acceptors: Application to the upconversion dynamics of Er^{3+}:$YAlO_3$ and Er^{3+}:YAG

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Based on the assumption of a regular distribution of the donors and acceptors, an energy transfer model is built for the three-dimensional and two-dimensional interaction cases. From this model the transfer parameter has a functional activator concentration dependence, e.g., for the two-dimensional interaction case the transfer parameter is proportional to the product of the donor and acceptor concentrations, and for the three-dimensional interaction case the transfer parameter is proportional to the square root of the product of the donor and acceptor concentrations. A satisfactory simulation of the upconversion dynamics of Er^{3+} in $YAlO_3$ and in YAG subsequent to pumping with short (15 ns) pulses at 1.55 μm is obtained when the two-dimensional interaction transfer parameter is included in a rate equation treatment.

INTRODUCTION

The central role of energy transfer in the dynamics of energy upconversion by rare-earth ions was recognized in 1966.[1,2] Nearly all theoretical treatments to date have been based on a random distribution of donors and acceptors among the lattice points of the crystal.[3-5] A very thorough discussion of the rate equation treatment of energy transfer is given by Grant.[6] He points out that a quadratic dependence of the transfer parameter on concentration is very commonly observed, and powers up to three are not unusual. He also shows that for a random distribution of donors and acceptors the transition probability is determined by the number of interacting particles and not the spatial dependence of the interaction. Thus, for a random distribution a Q-particle process should be characterized by an n^Q dependence in the rate equations (n^{Q-2} dependence of the transfer parameter). In the usual case of two-body energy transfer (one donor and one acceptor) this would lead to terms like $n_D n_A$ in the rate equations, and a concentration-independent transfer parameter. This was the approach used to analyze data on the upconversion dynamics of Er^{3+}:$YalO_3$ after excitation with a 1.55-μm pulse.[7] In that work not only the energy transfer parameters but also the decay rates were required to be adjustable parameters to obtain a satisfactory fit to the Er^{3+}:$YalO_3$ data. However, attempts to fit similar data acquired for Er^{3+}:YAG, were unsuccessful for any set of parameters we could find. The present work was motivated primarily by this difficulty.

In this work we develop an energy transfer model based on a regular distribution of donor and acceptor ions, rather than the usual random distribution. This particular distribution, it turns out, gives a quadratic dependence of the transfer parameter on activator concentration when the transfer occurs primarily within a plane. Using this transfer parameter in the rate equations leads to a satisfactory fit for both the Er^{3+}:$YAlO_3$ and the Er^{3+}:YAG data, without the need to use the radiative and multiphonon rates as additional adjustable parameters. Since the activator concentration dependence disappears in the steady-state limit, we expect (and do) find good agreement with published values of the steady-state transfer parameters, and with steady-state (continuously pumped) data. In addition, this model offers an explanation for the previously reported quadratic dependence of the transfer parameter on the total activator (Er^{3+} ion) concentration and for the deviations from this behavior found at low ($<3\%$) and high ($>60\%$) Er^{3+} concentrations.

EXPERIMENTAL DETAILS

Measurements were made at room temperature using a single crystal of YAG containing 3 at. % Er^{3+}. The experimental arrangement used to acquire the YAG data was identical to that described previously for the $YAlO_3$ study. The $YAlO_3$ data included in the present work is the same data presented previously.

ENERGY TRANSFER IN A REGULAR DISTRIBUTION OF DONORS AND ACCEPTORS

We consider a system consisting of two particles, a donor and an acceptor, in the dipole-dipole approximation, neglecting the exchange term the energy transfer rate is given by[8-12]

$$\gamma_{DA} = \frac{C}{R_{DA}^6} , \tag{1}$$

where C is the dipole-dipole transfer microparameter and R_{DA} is the distance between the donor and acceptor ions. In a system consisting of N_D donors and N_A acceptors distributed among the lattice points of the crystal the general form[13-15] of the rate equation for the donors can be written as

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$$\frac{d}{dt}\rho_i^D(t) = -\rho_i^D(t)/\tau_D - \sum_j \gamma_{ij}\rho_i^D(t)\rho_j^{A(t)} + \cdots \,, \tag{2}$$

where $1/\tau_D$ is the decay rate of the donor, and $\rho_i^D(t)$ is the probability that the ith lattice point is occupied by a donor and $\rho_j^A(t)$ is the probability that the jth lattice point is occupied by an acceptor at time t. When both the donors and acceptors are erbium ions (possibly in different excited states), distributed among the available lattice sites in the crystal, Eq. (2) becomes

$$\frac{d\rho_i^D(t)}{dt} = -\frac{1}{\tau_D}\rho_i^D(t) - \sum_{j=1}^{N_T} \gamma_{ij}\rho_i^{\mathrm{Er}}\rho_{\mathrm{Er}}^D(t)\rho_j^{\mathrm{Er}}\rho_{\mathrm{Er}}^A(t) + \cdots \,, \tag{3}$$

where $\rho_i^D(t) = \rho_i^{\mathrm{Er}}\rho_{\mathrm{Er}}^D(t)$ and $\rho_j^A(t) = \rho_j^{\mathrm{Er}}\rho_{\mathrm{Er}}^A(t)$; ρ_i^{Er} is the probability that the ith lattice point is occupied by an Er^{3+} ion and ρ_j^{Er} is the probability that the jth lattice point is occupied by an Er^{3+} ion separately; $\rho_{\mathrm{Er}}^D(t)$ is the probability that the Er^{3+} ion which occupies the ith point is occupied by a donor and $\rho_{\mathrm{Er}}^A(t)$ is the probability that the Er^{3+} ion which occupies the jth lattice point is occupied by an acceptor separately; N_T is the total number of lattice points. To consider the average probability density, we should sum over all the lattice points in the total interaction volume V_T and divide both sides of Eq. (3) by this volume (for three dimensions) or carry the sum over all the lattice points in the total interaction area S_T and then divide by this area (for two dimensions). Substituting Eq. (1) into Eq. (3), we obtain the following expression for the rate equation:

$$\frac{dn_D^{(y)}(t)}{dt} = -\frac{1}{\tau_D}n_D^{(Y)}(t) - \frac{1}{L_T^y}\sum_{i=1}^{N_T}\sum_{j=1}^{N_T}\frac{1}{R_{ij}^6}\rho_i^{\mathrm{Er}}\rho_{\mathrm{Er}}^D(t)\rho_j^{\mathrm{Er}}\rho_{\mathrm{Er}}^A(t) + \cdots \,. \tag{4}$$

In the above equation we use L_T^y (L_T is the dimension of the interaction volume or area, $y=3$ or 2) to express V_T or S_T, and

$$n_D^{(y)}(t) = \frac{1}{L_T^y}\sum_{i=1}^{N_T}\rho_i^D(t) = \frac{N_D(t)}{L_T^y} \tag{5}$$

is the concentration of the donors, where $N_D(t)$ is the total number of donors in the region L_T^y. For convenience in the following discussion, we use $n^{(y)}(t)$ to express the y- ($y=3$ or 2) dimensional concentration which has units of L^{-y}, where L is the unit length. From the same considerations we get the rate equation for the acceptors

$$\frac{dn_A{}^{(y)}(t)}{dt} = -\frac{1}{\tau_A}n_A{}^{(y)}(t) - \frac{1}{L_T^y}\sum_{i=1}^{N_T}\sum_{j=1}^{N_T}\frac{1}{R_{ij}^6}\rho_i^{\mathrm{Er}}\rho_{\mathrm{Er}}^D(t)\rho_j^{\mathrm{Er}}\rho_{\mathrm{Er}}^A(t) + \cdots \,, \tag{6}$$

and for any state M at which the donor or acceptor arrives after the energy transfer process

$$\frac{dn_M{}^{(y)}(t)}{dt} = -\frac{1}{\tau_M}n_M{}^{(y)}(t) + \frac{1}{L_T^y}\sum_{i=1}^{N_T}\sum_{j=1}^{N_T}\frac{1}{R_{ij}^6}\rho_i^{\mathrm{Er}}\rho_{\mathrm{Er}}^D(t)\rho_j^{\mathrm{Er}}\rho_{\mathrm{Er}}^A(t) + \cdots \,. \tag{7}$$

The general rate equations take the form

$$\frac{dn_x^{(y)}(t)}{dt} = -\frac{1}{\tau_x}n_x^{(y)}(t) \pm \frac{1}{L_T^y}\sum_{j=1}^{N_T}\sum_{i=1}^{N_T}\frac{1}{R_{ij}^6}\rho_i^{\mathrm{Er}}\rho_{\mathrm{Er}}^D(t)\rho_j^{\mathrm{Er}}\rho_{\mathrm{Er}}^A(t) + \cdots \,. \tag{8}$$

In the above equation if $n_x^{(y)}(t)$ is the M state ion concentration the sign proceeding the double sum is positive, if $n_x^{(y)}(t)$ is either the donor or the acceptor concentration the sign in front of the double sum is negative.

We now consider a regular distribution of donors and acceptors within a regular distribution of activator ions, such as that which would exist if the activator ions formed a superlattice structure within the crystal. In such a case every configuration of the donors and acceptors would have the same separation between them, and we can choose only one configuration for discussion. For a given configuration only certain lattice points are occupied by the donors or the acceptors, so in Eq. (8) we can take $\rho_i^{\mathrm{Er}}\rho_{\mathrm{Er}}^D(t) = \rho_i^D(t) = 1$ for those lattice points which are occupied by a donor and $\rho_i^{\mathrm{Er}}\rho_{\mathrm{Er}}^D(t) = \rho_i^D(t) = 0$ for those lattice points which are not occupied by a donor, and treat the acceptors in the same way. Equation (8) can then be rewritten as

$$\frac{dn_x^{(y)}(t)}{dt} = -\frac{1}{\tau_x}n_x^{(y)}(t) \pm \frac{1}{L_T^y}\sum_{i=1}^{N_D(t)}\sum_{j=1}^{N_A(t)}\frac{C}{R_{ij}^6} + \cdots \,, \tag{9}$$

where $N_D(t)$ and $N_A(t)$ are the total number of donors and acceptors, respectively, within the interaction region L_T^y. Note that in Eq. (9) the double summation refers to the transfer from every donor to every acceptor.

For energy transfer in three dimensions Eq. (9) takes the form

$$
\begin{aligned}
\frac{dn_x^{(3)}(t)}{dt} &= -\frac{1}{\tau_x} n_x^{(3)}(t) \pm \frac{1}{V_T} \sum_{i=1}^{N_D(t)} \sum_{j=1}^{N_A(t)} \frac{C}{R_{ij}^6} + \cdots \\
&= -\frac{1}{\tau_x} n_x^{(3)}(t) \pm \frac{1}{V_T} N_D(T) \sum_{i=1}^{N_A(t)} \frac{C}{R_{ij}^6} + \cdots \\
&= -\frac{1}{\tau_x} n_x^{(3)}(t) \pm \frac{1}{V_T} N_D(t) n_A(t) \int\int\int \frac{C}{R^6} dV + \cdots \\
&= -\frac{1}{\tau_x} n_x^{(3)}(t) \pm n_D(t) n_A(t) W^{(3)} + \cdots
\end{aligned}
\tag{10}
$$

where $W^{(3)}$ is the three-dimensional transfer parameter which can be expressed as

$$
\begin{aligned}
W^{(3)} = \int\int\int \frac{C}{R^6} dV &= 4\pi C \int_{d_{\rm NN}}^{d_m} \frac{1}{R^4} dR \\
&\approx 4\pi C \int_{d_{\rm NN}}^{\infty} \frac{1}{R^4} dR = \frac{4\pi}{3} \frac{C}{d_{\rm NN}^3} \ .
\end{aligned}
\tag{11}
$$

In the above expression d_m is the maximum D-A distance which is equal to L_T, the size of the total interaction volume, and $d_{\rm NN}$ is the average nearest-neighbor distance between the donors and acceptors. Since $d_m \gg d_{\rm NN}$, we may take $d_m = \infty$ from now on. Within such a regular distribution of donors and acceptors the average D-A nearest-neighbor distance must depend on the donor and acceptor concentrations. We can obtain the relationship for this dependence from the following considerations. If the system consisted only of donors distributed as above, for a given donor concentration the nearest D-D neighbor distances are all equal. In this case we can treat each donor as a sphere which occupies a volume of $V_D(t) = V_T / N_D(t)$, and the donor-donor nearest-neighbor distance is the diameter of this sphere. Similar considerations for a system consisting only of acceptors leads to the acceptor-acceptor nearest-neighbor distance being given by the diameter of a sphere with volume $V_A(t) = V_T / N_A(t)$. Thus, for a system consisting of both donors and acceptors we can define a sphere which has the average volume of sphere D and sphere A:

$$
\begin{aligned}
\bar{V}(t) &= [V_D(t) V_A(t)]^{1/2} \\
&= \left[\frac{V_T}{N_D(t)} \frac{V_T}{N_A(t)} \right]^{1/2} \\
&= [n_D^{(3)}(t) n_A^{(3)}(t)]^{-1/2}
\end{aligned}
\tag{12}
$$

and

$$
\bar{V}(t) = \frac{4\pi}{3} R_{\rm NN}^3 = \frac{\pi}{6} d_{\rm NN}^3 \ . \tag{13}
$$

From Eqs. (12) and (13) we get

$$
\frac{1}{d_{\rm NN}^3} = \frac{\pi}{6} [n_D^{(3)}(t) n_A^{(3)}(t)]^{1/2} \ . \tag{14}
$$

Equations (11) and (14) lead to the following expression of the energy transfer parameter:

$$
W^{(3)} = \frac{2\pi^2}{9} C [n_D^{(3)}(t) n_A^{(3)}(t)]^{1/2} \ . \tag{15}
$$

If, for any reason, the energy transfer is constrained to be planar, with no transfer between planes, the rate equation (9) takes the form

$$
\begin{aligned}
\frac{dn_x^{(2)}(t)}{dt} &= -\frac{1}{\tau_x} n_x^{(2)}(t) \pm \frac{1}{S_T} \sum_{i=1}^{N_D(t)} \sum_{j=1}^{N_A(t)} \frac{C}{R_{ij}^6} + \cdots \\
&= -\frac{1}{\tau_x} n_x^{(2)}(t) \pm \frac{1}{S_T} N_D(t) \sum_{j=1}^{N_A(t)} \frac{C}{R_{ij}^6} + \cdots \\
&= -\frac{1}{\tau_x} n_x^{(2)}(t) \pm \frac{1}{S_T} N_D(t) n_A{}^{(2)}(t) \int\int \frac{C}{R^6} dS + \cdots \\
&= -\frac{1}{\tau_x} n_x^{(2)}(t) \pm n_D^{(2)}(t) n_A^{(2)}(t) W^{(2)} + \cdots \ ,
\end{aligned}
\tag{16}
$$

where $W^{(2)}$ is the two-dimensional transfer parameter which can be written as

$$
W^{(2)} = \int\int \frac{C}{R^6} dS = 2\pi C \int_{d_{\rm NN}}^{\infty} \frac{1}{R^5} dR = \frac{\pi}{2} \frac{C}{d_{\rm NN}^4} \ . \tag{17}
$$

As in the three-dimensional case, $d_{\rm NN}$ is the average nearest-neighbor distance between the donor and acceptor which varies with the donor and acceptor concentrations. We can obtain this relationship from the same considerations as for the three-dimensional interaction case, but treating circles of area $S_{\rm D,A}$ for donor or acceptor, respectively. Thus we define a circle with the average area of circle D and circle A,

$$\begin{aligned}\bar{S}(t)&=[S_D(t)S_A(t)]^{1/2}\\&=\left[\frac{S_T}{N_D(t)}\frac{S_T}{N_A(t)}\right]^{1/2}\\&=[n_D^{(2)}(t)n_A{}^{(2)}(t)]^{-1/2}\end{aligned}\qquad(18)$$

and take

$$\bar{S}(t)=\pi R_{\mathrm{NN}}^2=\frac{\pi}{4}d_{\mathrm{NN}}^2 \ . \qquad(19)$$

From Eqs. (17)–(19) we obtain the following expression of the two-dimensional energy transfer parameter:

$$W^{(2)}=\frac{\pi^3}{32}Cn_D^{(2)}(t)n_A^{(2)}(t) \ . \qquad(20)$$

For purposes of comparison it is necessary to transform the two-dimensional rate equations (16) into a three-dimensional form. This can be accomplished by transforming the transfer parameter $W^{(2)}$ as follows:

$$W^{(2)}=\frac{\pi^3}{32}CL^2n_D^{(3)}(t)n_A{}^{(3)}(t) \ , \qquad(21)$$

where L is the distance between two adjacent interaction planes, which is determined by total concentration of the doped Er^{3+} ions n_{TE}:

$$\left[\frac{4\pi}{3}\right]\left[\frac{L}{2}\right]^3=\frac{1}{n_{\mathrm{TE}}{}^{(3)}} \ . \qquad(22)$$

By dividing both sides of equation (16) by L we obtain

$$\begin{aligned}\frac{dn_x^{(3)}(t)}{dt}&=-\frac{1}{\tau_x}n_x^{(3)}(t)\pm W^{(2)}Ln_D{}^{(3)}(t)n_A^{(3)}(t)+\cdots\\&=-\frac{1}{\tau_x}n_x^{(3)}(t)\pm W^{(3)}n_D^{(3)}(t)n_A^{(3)}(t)+\cdots \ ,\end{aligned}\qquad(23)$$

where

$$W^{(3)}=W^{(2)}L=\frac{\pi^3}{32}CL^3n_D^{(3)}(t)n_A{}^{(3)}(t) \ , \qquad(24)$$

which gives the two-dimensional interaction transfer parameters in the three-dimensional form.

RESULTS AND DISCUSSION

Figure 1 shows the energy levels and various decay and energy transfer processes which we consider in treating the upconversion dynamics of Er^{3+} in both YAlO_3 and YAG. The decay rates A_{ij} indicate the rate from state i to state j, by either radiative or nonradiative (multiphonon) processes. The energy transfer parameters are indicated as $W(ij)$, where i and j refer to the transfer occurring from an ion in state i to another ion in state j. To simplify the scheme as much as possible, we have considered the ${}^4I_{11/2}$ and the ${}^4I_{9/2}$ levels as one level.[16,17] This leads to the following set of rate equations:

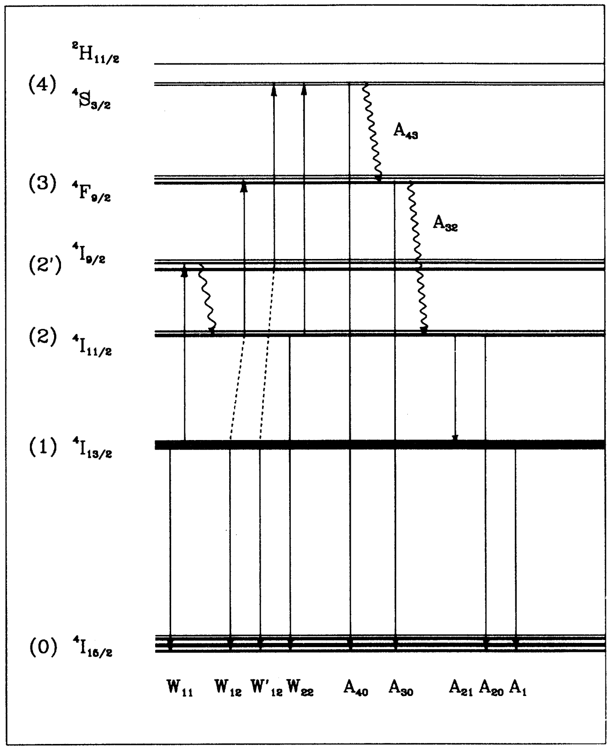

FIG. 1. Energy level scheme of Er^{3+} showing the energy transfer and decay processes considered in the rate equations.

$$\begin{aligned}\dot{n}(4)&=-[A_{43}+A_{40}]n(4)+W(22)n(2)^2\\&\quad+W'(12)n(1)n(2) \ ,\\\dot{n}(3)&=A_{43}n(4)-A_3n(3)+W(12)n(1)n(2) \ ,\\\dot{n}(2)&=A_{32}n(3)-A_2n(2)+W(11)n(1)^2\\&\quad-2W(22)n(2)^2-[W(12)+W'(12)]n(1)n,(2)\\\dot{n}(1)&=A_{21}n(2)-A_1n(1)-2W(11)n(1)^2\\&\quad-[W(12)+W'(12)]n(1)n(2) \ ,\\\dot{n}(0)&=A_{40}n(4)+A_{30}n(3)+A_{20}n(2)+A_1n(1)\\&\quad+W(11)n(1)^2+W(22)n(2)^2\\&\quad+[W(12)+W'(12)]n(1)n(2) \ .\end{aligned}\qquad(25)$$

Using the above equations to treat the energy transfer processes, the same ion in different energy levels is either the donor or acceptor. Since this kinetic scheme includes five levels, there can be as many as four different donors and four different acceptors. Considering donor-acceptor energy matching we have included only the above four energy transfer processes.

If the energy transfer occurs in three dimensions, the transfer parameters in Eq. (25) are given by

$$\begin{aligned}W(11)&=\alpha C_{11}n(1) \ ,\\W(12)&=\alpha C_{12}[n(1)n(2)]^{1/2} \ ,\\W'(12)&=\alpha C'_{12}[n(1)n(2)]^{1/2} \ ,\\W(22)&=\alpha C_{22}n(2) \ ,\end{aligned}\qquad(26)$$

where $\alpha=2\pi^2/9$. If, on the other hand, the transfer is limited to only two dimensions the energy transfer parameters in Eq. (25) take the form

$$\begin{aligned} W(11)&=\beta C_{11}n(1)^2\ ,\\ W(12)&=\beta C_{12}n(1)n(2)\ ,\\ W'(12)&=\beta C'_{12}n(1)n(2)\ ,\\ W(22)&=\beta C_{22}n(2)^2\ , \end{aligned} \tag{27}$$

where $\beta=(\pi^3/32)L^3$ is a constant with units of cm^3 and C_{ij} is the dipole-dipole microparameters of Eq. (1).

Satisfactory fits to the data could only be obtained using the rate equations that result from planar (two-dimensional) energy transfer. The experimental data are fit using available experimental values for the decay rates[18,19] noting that A_i refers to the total decay rate, or the summation over j of A_{ij}. Only the initial population of level 1, and the parameters βC_{ij} are allowed to vary to obtain the best fit to the experimental data. Fits of acceptable quality are obtained for both the Er^{3+}:YAlO$_3$ and the Er^{3+}:YAG experimental data, and are shown in Figs. 2 and 3. The values of the parameters found from this procedure are given in Table I.

The fitted values of the parameters βC_{ij} are used to calculate the transfer microparameters C_{ij} which are given in Table II. These values, which range from 5.34×10^{-36} to 8.36×10^{-33} cm^6 s^{-1} are consistent with published values for the systems of this sort.[20,21]

The previously observed functional dependence of $W(11)$ and $W(22)$ on the total Er^{3+} ion concentration in Er^{3+}:YAG (Refs. 16 and 19–21) also follows from the preceding treatment. The transfer parameter $W^{(3)}$ is proportional to $n_D^{(3)}(t)n_A^{(3)}(t)$, which under normal circumstances would be proportional to the square of the total Er^{3+} ion concentration $n_{TE}^{(3)}$ and thus the quadratic dependence of $W^{(3)}$ on $n_{TE}^{(3)}$. The deviations from quadratic concentration dependence noted in Refs. 16, 20, and 21 for Er^{3+} concentrations above ca 60% (cf. Fig. 5 of Ref. 16), are also consistent with the model discussed above. At low concentrations (< 3%) the distance between donor and acceptor ions is so large that the energy transfer is effectively three dimensional, which, according to Eq. (15), would result in the observed linear dependence of the transfer parameter on the total Er^{3+} concentration. At high concentrations the reported deviation from quadratic concentration dependence can be accounted for by the onset of randomization. As shown by Grant[6] a random distribution always leads to rate equations in which the transfer parameter is constant, i.e., independent of the activator concentration, unless many-body interactions are included. Thus deviation from regular distribution towards random distribution of the donors and acceptors leads to an intermediate functional dependence of the transfer parameter on total concentration, of the form

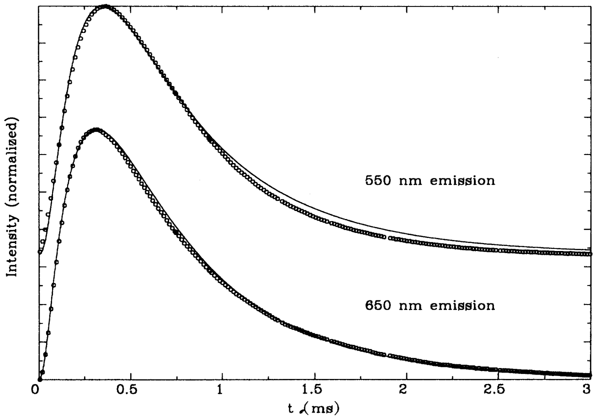

FIG. 2. Time dependence of the upconversion emission at 550 nm ($^4S_{3/2}$) and 650 nm ($^4F_{9/2}$) from Er^{3+}:YAlO$_3$ at room temperature, subsequent to a 15-ns pulse at ca. 1550 nm. Open circles, experimental points; solid lines, calculated from Eqs. (25) using the parameter values in Table I.

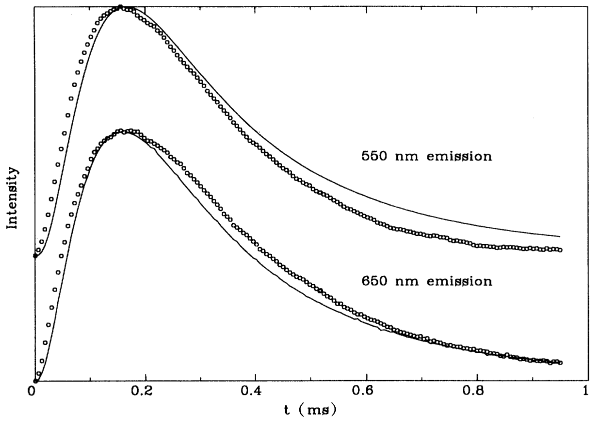

FIG. 3. Time dependence of the upconversion emission at 550 nm ($^4S_{3/2}$) and 650 nm ($^4F_{9/2}$) from Er^{3+}:YAG at room temperature, subsequent to a 15-ns pulse at ca. 1550 nm. Open circles, experimental points; solid lines, calculated from Eqs. (25) using the parameter values in Table I.

TABLE I. Values of the energy transfer parameters obtained from a least-squares fit of the rate equations. Decay rates used are literature values, as indicated, or are deduced from the literature as described in the text.

	Er^{3+}:YAlO$_3$	Er^3:YAG
A_1 (s^{-1})	188 Ref. 18	111 Ref. 19
A_2 (s^{-1})	820 Ref. 18	9.1×10^3 Ref. 19
A_{20} (s^{-1})	227 Ref. 18	7.8×10^3 Ref. 19
A_3 (s^{-1})	5.26×10^4 Ref. 18	8.33×10^5 Ref. 19
A_{30} (s^{-1})	3.57×10^3 Ref. 18	8.24×10^5 Ref. 19
A_4 (s^{-1})	6.25×10^3 Ref. 18	9.52×10^4 Ref. 19
A_{40} (s^{-1})	2.63×10^3 Ref. 18	8.91×10^4 Ref. 19
βc_{11} (s^{-1}cm^9)	7.78×10^{-57}	7.48×10^{-56}
βc_{22} (s^{-1}cm^9)	5.01×10^{-57}	3.68×10^{-53}
βc_{12} (s^{-1}cm^9)	9.40×10^{-57}	2.61×10^{-54}
$\beta c'_{12}$ (s^{-1}cm^9)	3.75×10^{-56}	1.30×10^{-53}
$n(1)/n_T$, $t=0$	0.037	0.040
n_T (cm^{-3})	1.97×10^{21}	4.2×10^{20}

TABLE II. Values of the microparameter C_{DA} derived from the parameters in Table I.

	Er^{3+}:YAlO$_3$	Er^{3+}:YAG
C_{11} ($cm^6 s^{-1}$)	8.29×10^{-38}	1.70×10^{-37}
C_{22} ($cm^6 s^{-1}$)	5.34×10^{-38}	8.36×10^{-35}
C_{12} ($cm^6 s^{-1}$)	1.00×10^{-37}	5.39×10^{-36}
C'_{12} ($cm^6 s^{-1}$)	4.00×10^{-37}	2.97×10^{-35}

$$W^{(2)} \propto [n_D{}^{(3)}(t) n_A^{(3)}(t)]^{\gamma} \propto (n_{\mathrm{Te}}{}^{(3)})^{2\gamma} , \tag{28}$$

where $0<\gamma<1$. At total Er^{3+} concentrations above 50% it is easy to demonstrate that the Er^{3+} ions can no longer be regularly distributed, which causes the donors and acceptors to be irregularly distributed. Thus, according to Eq. (28), the transfer parameter depends on lower power of concentration.

In the interest of comparing these results with those of other workers, we examined the steady-state limit of Eqs. (25). In the steady state, the concentration dependence becomes constant, permitting such comparison. The only values available in the literature for Er^{3+}:YAG are for the transfer parameters corresponding to $W(11)$ and $W(22)$ in our scheme. For 3% Er^{3+}:YAG, Ref. 16 gives $W(11)=1.6\times10^{-17}$ $cm^3 s^{-1}$ in good agreement with our value of 1.57×10^{-17} $cm^3 s^{-1}$ for 40 W cm^{-2}. To compare our results (for 3% Er^{3+}) of $W(22)=3.84\times10^{-18}$ $cm^3 s^{-1}$ with those of Ref. 19 we corrected their value of $W(22)=5.1\times10^{-17}$ $cm^3 s^{-1}$ (for 10% Er^{3+}) to our concentration, by using the quadratic concentration dependence reported by those authors, which gives 4.6×10^{-18} $cm^3 s^{-1}$, in reasonable agreement with our result of 3.84×10^{-18} $cm^3 s^{-1}$.

CONCLUSIONS

We have shown that the energy transfer parameter can have a functional dependence on the donor and acceptor concentrations when the donors and acceptors are not randomly distributed, but rather are distributed in a regular arrangement, such as in a superlattice structure. This is in contrast to the results for a random distribution, which regardless of the spatial arrangement, always requires the interaction of more than two donors and/or acceptors to arrive at such a dependence.[6]

The inclusion of these results in a rate equation treatment of the upconversion dynamics of Er^{3+} in YAlO$_3$ and YAG successfully reproduced the experimental upconversion dynamics over the entire time scale, but only when the energy transfer was restricted to planar (two-dimensional) interactions. While it may be possible to speculate that the energy transfer is indeed largely constrained to two dimensions because of a combination of polarization and dipole emission geometric effects, there is no supporting evidence for any long-range superlattice structure in these materials. It will be interesting to see if these materials indeed have a superlattice structure, and if the results obtained in this work can be broadly applied to energy transfer in materials which are known to have a superlattice structure.

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