Emission dynamics of the $^4F_{3/2}$ level of Nd^{3+} in YAG at low pump intensities

V. Lupei and A. Lupei

Institute of Atomic Physics, Bucharest, R 76900, Romania

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The room-temperature high-resolution luminescence decay investigation of YAG crystals doped with Nd^{3+} in concentrations up to 1.5 at.% shows that under nonselective weak 532-nm pump, which prevents the up conversion, the emission dynamics of $^4F_{3/2}$ level is influenced by a cross relaxation inside the system of Nd^{3+} ions, dominated by superexchange ($R_0 = 5.43$ Å, $L = 0.54$ Å) for the nearest-neighbor Nd^{3+} ion pair and by dipolar coupling ($C_{DA} = 1.85 \times 10^{-40}$ cm^6 s^{-1}) for all other pairs. These parameters are in strong contradiction with other recent reports. The energy-transfer parameters are verified in the quasiselectively excited decay of the first-, second-, and third-order Nd^{3+} ion pairs by using a proper adaptation of the theory of energy transfer for discrete, equiprobable, and random placement of Nd^{3+} ions in the crystalline lattice. They give also a very good description of the data on quantum efficiency and fractional thermal load for YAG:Nd^{3+} samples of various concentrations. The absence of the quadrupolar interaction in the mechanism of transfer is consistent with the restrictions imposed by the selection rules for the transitions involved in cross relaxation.

I. INTRODUCTION

Spectroscopic properties of Nd^{3+} in YAG, the most important laser active crystal, continue to raise interest: recent important advances have been noted in the description of energy level diagrams and transition probabilities.[1–5] On the other hand, the flow of excitation inside the system of Nd^{3+} ions and its effect on the emission dynamics of the $^4F_{3/2}$ level is currently being investigated owing to its crucial role in determining the laser characteristics of this crystal.[6–12] Due to its concentration dependence, this dynamics could be also a significant test of the various models of energy transfer. The radiative lifetime of $^4F_{3/2}$ Nd^{3+} level in YAG was estimated[13] to about 259 ± 25 μsec. At low temperatures and very small Nd^{3+} concentrations, the measured lifetime lies in the range of 265 to 270 μsec, while at room temperature[14] it is ~ 260 μsec. Thus the intrinsic quantum efficiency is very large, of about 0.98. However, the investigation of the luminescence kinetics[14–20] at low pump intensities shows that for Nd^{3+} concentrations ($C_{Nd^{3+}}$), practical for laser emission, the luminescence kinetics of this level manifests departures from an exponential decay. These nonexponentialities are evident[14,18] at very low concentrations and increase systematically with $C_{Nd^{3+}}$. At the same time the measurements of quantum efficiency[16,22–31] show very large differences, from 0.47 to 1, for about 1 at.% Nd^{3+}. The studies on YAG:Nd^{3+} samples of different concentrations and provenience are sometimes contradictory: while some studies[16,31] evidence a systematic dependence of the quantum efficiency on $C_{Nd^{3+}}$, other reports[30] show a large spread of data and claim that no clear connection between the quantum efficiency and luminescence decay characteristics exists. Various models were proposed to account for these effects; they can be grouped in models based on energy transfer inside the system of Nd^{3+} ions[6,14,15,18–21] or as an effect of OH$^-$ impurities localized in the neighborhood of the Nd^{3+} ions.[17,30] It was assumed that such anionic impurities, with large vibrational energies, localized in the neighborhood of

the Nd^{3+} ion, could induce a very fast electron-phonon relaxation of excitation from the pump levels placed above $^4F_{3/2}$ to the ground state. Since the absorbed energy in these centers does not reach the metastable level $^4F_{3/2}$ they were called ''dead sites.'' The ir measurements show that the concentration of OH$^-$ impurities vary from sample to sample and this could be consistent with the large spread of quantum efficiency data. However, the very large differences in the quantum efficiency values reported for given samples by different methods cannot be explained in this way. Since the ''dead sites'' cannot produce departures from exponential for the global Nd^{3+} emission the most likely explanation for the observed effect is the quenching of emission by energy transfer inside the system of Nd^{3+} ions. Thus YAG:Nd^{3+} is a typical case of a self-quenching system. Previous studies of emission decay[14–21] function on $C_{Nd^{3+}}$ show that up to about 1.5 at.% Nd^{3+} the energy transfer is dominated by direct (static) donor-acceptor processes and the migration on donors is negligible, but above this value it plays an increased role, as shown by the measurements[15,19] on samples with $C_{Nd^{3+}}$ in the range 2.5–2.7 at.% Nd^{3+}. The dramatic decrease of $^4F_{3/2}$ lifetime in YAG films grown by liquid-phase epitaxy[32] with up to 15 % Nd^{3+} can be also explained by the combined effect of the static transfer and migration.

The low-temperature optical-absorption spectra of Nd^{3+} in YAG show satellites that indicate the presence of various structural centers.[6,14,17–19,30,33–35] Some studies[17,18,30,33] based on selective pumping in $^4G_{5/2}$ level suggested intercenter migration at low temperatures and low $C_{Nd^{3+}}$. Subsequent high-resolution spectroscopic measurements,[6] at low temperatures, with pumping in the much better resolved $^4I_{9/2} \rightarrow {}^4F_{9/2}$ line allowed the observation of selective emission of almost all centers without intercenter migration. This limits the possibilities of transfer, at low pump intensities, to a down-conversion cross relaxation on intermediate levels between an excited Nd^{3+} ion and any other Nd^{3+} ions in the ground state; the most probable cross relaxation at the room

temperature is $(^4F_{3/2}, ^4I_{9/2}) \rightarrow (^4I_{15/2}, ^4I_{15/2})$ and can be an intra- as well as an interstructural center process. The excitation reaching $^4I_{15/2}$ level is lost by multiphonon relaxation and transformed into heat. The luminescence decay of $^4F_{3/2}$ under short pulse (10 ns) excitation, measured[14,18] with low resolution (~ 1 μsec) equipment that did not allow the registration of the beginning of decay, has an unusual shape. The subsequent analysis of this decay on the available temporal range has shown[19–21] that it can be consistently explained only by assuming that the interaction responsible for transfer inside the first nearest neighbor NN Nd^{3+}-ion pair is dominated by a strong short-range interaction (most probably superexchange) that determines a very fast initial drop of emission, not observed in the low-resolution measurements, while the transfer to all other Nd^{3+} ions is dominated by a dipole-dipole (d-d) mechanism with unique transfer microparameter C_{DA}^{dd} for all the donor-acceptor pairs. The analysis of the observed decay was facilitated by the use of the theory of energy transfer to discrete and random arrays of acceptors[36–39] that can occupy with equal probabilities the available sites in the crystalline lattices, that was adapted to account for the presence of a multiple interaction picture.[19–21] These experiments were performed under low pumping and the fraction of excited Nd^{3+} ions was estimated to be about 1%, this being considered the initial concentration of donors; all other Nd^{3+} ions, nonexcited by pump, can therefore act as acceptors. The high pumping determine changes that shall be discussed later.

The main conclusion of these studies,[14,18–21] the presence of the multiple interaction picture, is confirmed by the high-resolution measurements of emission under selective excitation[6] of various samples with different Nd^{3+} concentrations. The main satellites in the optical spectra of Nd^{3+} in YAG are[6] satellites P_i connected with the nonstoichiometric Y^{3+} ions that replace part of the octahedral Al^{3+} ions in the melt-grown YAG crystals and satellites M_i connected to pairs of Nd^{3+} ions from the first-, second-, and third-coordination sphere. No satellite connected with the presence of OH^- in the near neighborhood of Nd^{3+} ions was identified to sustain the model[30] of quenching.

The measurements of emission kinetics under very strong pump, that produces a high population of $^4F_{3/2}$ level, accompanied by a considerable depletion of the ground state, evidenced[7,8,12] the presence of up conversion by the interaction between two Nd^{3+} ions excited in the $^4F_{3/2}$ state. Thus in case of strong pump the emission kinetics of $^4F_{3/2}$ becomes very complex and dependent on excitation intensity and concentration. The physical model used in these papers was simplified: no difference between the static and migration-assisted up conversion was considered and a unique up-conversion rate was assumed regardless of the distance between the excited ions. Moreover, in most cases the effect of down-conversion cross relaxation in presence of up conversion was either neglected or accounted improperly together with the intrinsic deexcitation. The up conversion can affect the laser properties of diode-pumped highly concentrated YAG: Nd^{3+} crystals and of Q-switched lasers. For diluted systems and low pump (such as with gas-discharge lamps) as well as for the low threshold cw lasers, the concentration-dependent deexcitation is dominated by down-conversion cross relaxation. The importance of this process

in determining the quantum efficiency and the heat effects was discussed recently by several authors,[9,10,31] without a clear mathematical connection between characteristic parameters.

A recent work[11] puts back the question of the interactions governing the down-conversion energy transfer, by using a Monte Carlo approach to describe the emission decay of $^4F_{3/2}Nd^{3+}$ level in YAG under 532-nm (2nd harmonic of a YAG:Nd laser) pumping. This work claims that the Nd^{3+} ions are coupled by four types of interactions: three multipolar interactions (dipole-dipole d-d, dipole-quadrupole d-q, and quadrupole-quadrupole q-q) and superexchange. However, some assertions of this paper, such as a concentration of donors larger by an order of magnitude than that of the acceptors as well as the extremely large interaction microparameters resulting from the analysis are in disagreement with the observed luminescence decay characteristics. This leads to an apparent contradiction between the Monte Carlo and analytical statistics description of the energy-transfer processes.

The aim of this paper is to give a clear identification of the mechanisms of the self-quenching by down conversion in this system, based on experimental data and a reanalysis of the luminescence decay of $^4F_{3/2}$ level of Nd^{3+} in YAG at low pump intensities, and to relate the characteristic parameters of these mechanisms to the quantum efficiency of the metastable level $^4F_{3/2}$. The paper is organized as follows: after a brief description of the experimental technique, the physical model of self-quenching of $^4F_{3/2}$ emission is discussed, together with the theoretical description of the effect of down-conversion energy transfer on the luminescence decay by considering a model of discrete random and equiprobable occupation of the crystalline sites in two important cases: (i) homogeneous systems, when all the dopant ions have identical spectroscopic properties, and (ii) inhomogeneous systems composed of homogeneous subsystems. This theory is used to compare the data obtained from the high temporal resolution decay of the Nd^{3+} global emission under nonselective pump with those obtained from the selective emission of the various spectrally resolved subassemblies of Nd^{3+} ions (isolated ions and pairs of the various orders) under selective or nonselective pump. The validity of the energy-transfer parameters will be further checked by comparing the calculated quantum efficiency of $^4F_{3/2}$ level at low pump intensities with the existing data on YAG:Nd^{3+} samples of various concentrations. The analysis of emission in presence of up conversion is under study.

II. EXPERIMENTAL METHODS

The samples under investigation are Czochralski-grown YAG ($Y_3Al_5O_{12}$) crystals doped with Nd^{3+} in concentrations from 0.1 to 1.5 at.%. The growth was performed under induction heating and pulling along the $\langle 111 \rangle$ direction. Several other samples, grown by horizontal gradient, Stepanov, or flux methods, were also measured. The measurements involve the high-resolution absorption and emission spectra and emission decay under nonselective pump at 532 nm or quasiselective excitation of the various Nd^{3+} centers. The luminescence spectra and decays were excited by 2nd harmonic of YAG:Nd^{3+} (532 nm) or tunable dye laser pulses of

~10 ns and detection was made by photon counting (20-ns resolution) techniques. The transmission spectra were measured with a high-resolution (~0.5 cm^{-1}) system.

III. PHYSICAL MODEL OF SELF-QUENCHING OF $^4F_{3/2}$ EMISSION IN Nd^{3+}:YAG

We assume that all the Nd^{3+} ions have similar pump absorption cross sections, regardless of the structural center and the pump regime, and that a fraction $r(0)$ of the total Nd^{3+} ions are excited at random in the metastable level at the end of the exciting pulse. Since the $C_{Nd^{3+}}$ are less than 1.5 at.%, the migration of energy on $^4F_{3/2}$ can be neglected and the energy transfers from this level are direct donor-acceptor (D-A) processes. The excited Nd^{3+} ions can participate in various processes: they can be either donors in the down-conversion cross relaxation on intermediate levels and in the up conversion or they can be acceptors in up conversion. According to Nd^{3+} energy-level diagram, from $^4F_{3/2}$ three up-conversion processes are possible: ($^4F_{3/2}$, $^4F_{3/2}$) $\rightarrow$ ($^4G_{5/2}$, $^4I_{15/2}$) or ($^4G_{7/2}$, $^4I_{13/2}$) or [$^2G(1)_{9/2}$, $^4I_{11/2}$]. In all these cases the up-converted excitation relaxes rapidly to $^4F_{3/2}$ and the residual excitation from the terminal level of the donor act relaxes nonradiatively to the ground state. The final effect of all these up-conversion processes combined with the multiphonon relaxation of $^4F_{3/2}$ population is similar and they can be accounted for together; they modify the state of the donor, but not that of the acceptor.

Both down conversion and up conversion are cross-relaxation energy-transfer processes, the only difference being the initial state of the acceptors. Though the bases of the energy transfer between ions in crystals are known,[40,41] in order to make more clear the interpretation of our decay data a review of some significant aspects of this theory shall be presented. In absence of migration, the nonradiative energy transfer from a donor D to an acceptor A is governed by a transfer rate W_{DA} that depends on the nature of the interaction Hamiltonian H_{DA} responsible for transfer according to the golden rule $W_{DA} = 2\pi/h|\langle ab|H_{DA}|a'b'\rangle|^2 S$, where a,a' and b,b' are, respectively, the initial and final states of the D and A ions, and S is the superposition integral of D emission and A absorption. The energy transfer reduces the survival probability of excited donor by a factor equal to $\exp(-W_{DA}t)$.

The D and A ions can interact by multipolar and exchange processes. In the case of multipolar interactions between two rare-earth ions (which result from the series development of the electrostatic interaction $H_{DA} = e^2/|\vec{r}_D - \vec{r}_A|$ that induces transfer between the energy levels SLJ of the ground state configuration $4f^n$) the energy-transfer rate can be written as a sum[41–44] $W_{DA} = W_{DA}^{dd} + W_{DA}^{dq} + W_{DA}^{qq} = \Sigma_s W_{DA}^{(s)}$ with $s=6$, 8, or 10 for d-d, d-q, and q-q interactions, respectively. The presence of these interaction mechanisms is governed by selection rules similar to those for the radiative transitions between the states involved in transfer. Thus the quadrupolar interactions are allowed between states of the ground configuration, while the dipolar interactions are induced by configuration (Judd-Ofelt) mixing: The energy-transfer rates can be written in the simple form $C_{DA}^{(s)} R_{DA}^{-s}$, where R_{DA} is the D-A distance and the transfer microparameter $C_{DA}^{(s)}$ is pro-

portional to the superposition integral $S^{(s)}$ and the product of matrix elements of the unitary tensorial operator of rank λ (with $\lambda = 2$, 4, or 6) $|\langle SLJ|U^{(\lambda)}|SL'J'\rangle|^2$ between the initial and final states of the D and A part of the transfer, respectively.[43,44] In case of the dipolar transitions the rates are proportional to the Judd-Ofelt parameters, while for the quadrupolar transitions only operators of rank $\lambda = 2$ are taken into consideration. The matrix element $\langle SLJ|U^{(\lambda)}|SL'J'\rangle$ is proportional to the product between the 6-j symbols

$$\begin{Bmatrix} J & J' & \lambda \\ L' & L & S \end{Bmatrix}$$

and the reduced matrix elements $\langle SL||U^{(\lambda)}||SL'\rangle$ whose values could be found in tables;[45,46] they impose selection rules on the possible interactions involved in transfer. For the quadrupolar interactions only transitions with $|J-J'| \leq 2$ are allowed. Thus the multipole energy-transfer rates for each pair of D and A ions are determined the distance between ions, by the spectroscopic properties of the transitions and by the matrix elements of the unitary operators $U^{(\lambda)}$; the possible J-mixing effects must be also considered in actual cases.

The experimental data indicate that the use of only multipolar interactions is not sufficient for many systems doped with rare earths and a superexchange interaction via the bridging ligands must be considered. This interaction has a short-range character and is anisotropic and depends both on the distance R between the rare-earth ions, on the levels involved and on the nature, number, and geometrical configuration of the intervening ligands. Several authors[47–50] deduced, in the case of ionic crystals, an exponential decrease of the superexchange for the non-nearest neighbors. We shall use here for the transfer rate a relation similar to that for the case of the isotropic direct exchange:[47]

$$W_{ex}(R) = \frac{1}{\tau_0} \exp\left[\gamma\left(1 - \frac{R}{R_0}\right)\right], \quad (1)$$

where $\gamma = 2R_0 L^{-1}$, with L the effective Bohr radius and R_0 the penetration depth, i.e., the distance at which the transfer rate due to exchange equals the rate due to intrinsic deexcitation lifetime τ_0^{-1}.

In crystals each excited Nd^{3+} ion p can act as a donor and is surrounded by a particular configuration of N_A ions j placed at the $r_{j;p}$ distances, which at a given moment of time can be acceptors either for up conversion or down conversion, depending on their instantaneous energy state ($^4F_{3/2}$ or $^4I_{9/2}$). Up conversion and down conversion compete in the deexcitation of $^4F_{3/2}$, a special circumstance being that a high excitation density in $^4F_{3/2}$ at the beginning of decay, $r(0)C_{Nd^{3+}}$, reduces accordingly the initial concentration [$1 - r(0)]C_{Nd^{3+}}$ of Nd^{3+} ions in the ground state. The fraction r varies in time and modifies the ratio between the instantaneous concentrations of acceptors for up conversion and down conversion. The distance dependence of the transfer rates induces also a modification in time of the geometrical distribution of the excited Nd^{3+} ions. This indicates that even under very strong pump [$r(0)\rightarrow 1$] these processes must be taken into account together. However, if the pump is weak and $r(0)$ is small, of the order of 1%, the problem can

be reduced to a good approximation to the down conversion, by assuming a time-independent concentration of acceptors, practically equal to the Nd^{3+} ions concentration.

IV. DOWN-CONVERSION ENERGY TRANSFER BETWEEN IONS IN CRYSTALS

Each of the acceptors from the particular configuration around donor can contribute independently to the deexcitation of donor by energy transfer and the survival probability in presence of transfer is given by

$$N_p(t) = \prod_{j=1}^{N_A} \exp(-W_{j;p}t) = \exp\left[-\sum_{j=1}^{N_A} W_{j;p}t\right]. \quad (2)$$

Because the individual rates $W_{j;p}$ depend on the type of interaction and on distance, particular multiple interaction pictures are possible for the near-ion pairs.

The temporal dependence of the luminescence intensity of the whole system of donors after a short exciting pulse is then obtained by summing the individual contributions,

$$I(t) = \sum_p I_{op} \exp\left(-\frac{t}{\tau_{Dp}}\right) N_p, \quad (3)$$

where I_{op} is the emission intensity of donor p, given by the product between the integrated spontaneous emission Einstein coefficient A and the energy quantum $h\nu$, while τ_{Dp} is the emission lifetime for donor p in absence of transfer.

The temporal dependence of $I(t)$ is nonexponential. The summation in Eq. (3) is difficult due to the very large number of donors p (usually larger than 10^{17}–10^{18} cm^{-3}) and since the exact configurations of acceptors around each donor is not known. Because of this the response of the whole system is taken as an average on all the possible acceptor configurations, i.e., on the whole sublattice of sites available to the acceptor ions; this averaging depends on the homogeneity of the D and A systems and on the statistical model of distribution of the acceptor ions on the available lattice sites.

A. Energy transfer in homogeneous systems

If all the ions of each D and A systems have identical spectral properties and absorption and emission cross sections (regardless of p, $I_{0p} \equiv I'_0$, and $\tau_{Dp} = \tau_D$) these systems are considered homogeneous and Eq. (3) becomes

$$I(t) = I \exp\left(-\frac{t}{\tau_D}\right) \sum_p I_{op} \exp\left[-\sum_{j=1}^{N_A} W_{j;p}t\right]. \quad (4)$$

According to the discussion of the preceding section, the sum in Eq. (4) can be replaced by the product between the number of donors N_{D0} at the beginning of decay and the average survival probability $N(t)$ over all the possible acceptor configurations:

$$I(t) = I_o \exp\left(-\frac{t}{\tau_D}\right) N(t) = I_o \exp\left(-\frac{t}{\tau_D}\right) \exp[-P(t)], \quad (5)$$

where I_0 is the emission intensity after the laser pulse ($I_0 = Ah\nu N_{D0}$) and the function $P(t)$ is called the transfer function. The average survival probability N and the transfer function P depend on the model used for the statistical distribution of acceptors in crystals. Basically there are two types of distributions: continuous and discrete. In the continuous uniform distribution the density of dopant ions is the same at any geometrical point of the crystal and the transfer function $P(t)$ can be written in a closed form for each multipolar interaction.

When only the down conversion is effective, the transfer function in the continuous distribution model has an explicit dependence[47] on t,

$$P(t,n_A) = \frac{4}{3}\pi n_A \Gamma\left(1 - \frac{3}{s}\right) C_{DA}^{3/s} t^{3/s}, \quad (6)$$

where $\Gamma(x)$ is the Euler function and n_A the absolute acceptors concentration. The temporal evolution of donor emission (5) with the transfer function (6) is nonexponential over the whole temporal range of emission. Equation (6) predicts a very fast decay at early times and its derivative at $t=0$ becomes infinite. Although it enables a direct determination of the multipolarity s by predicting a linear dependence[41,42] of $P(t)$ on $t^{3/s}$, a major shortcoming is its limitation to a single type of multipolar interaction. The theory of energy transfer in the continuous distribution model was recently adapted to accommodate the correlated placement[51] (regions of enhanced or depleted concentration of acceptors around the donor) or the multiple interaction picture;[52] however, the parameters obtained from the fit of the experimental data have not a precise physical meaning.

In case of the discrete distribution models the dopant ions are localized at specific crystallographic sites and the average donor emission can be obtained by specific statistical methods, such as the Monte Carlo simulation or the analytical statistics. In the Monte Carlo simulations[11] particular random configurations of acceptors are generated around each donor by using appropriate averaging functions and cumulative distribution functions for donors and acceptors and the total emission is then obtained as an average of the individual emission of the donors. This method, as other numerical approaches, does not allow a direct discussion of the influence of the various parameters of the system on emission kinetics.

In the analytical statistics treatment[36–39] the survival probability is given by the average value of the donor emission over all the possible acceptor configurations, which thus encompass the whole sublattice available to the acceptors. The averaging could be made either on the various structural subassemblies i of this sublattice and the survival probability for the whole system is obtained subsequently by multiplying these partial average values, or it can be made directly for the whole sublattice. The averaging inside of each subassembly i takes into ccount the various possibilities k, each occurring with the weighed probability ρ_{ki} and corresponding to a survival probability $n_{ki}(t)$:

$$\bar{N}_i(t) = \sum_k \rho_{ki} n_{ki}(t). \quad (7)$$

The most simple subassembly of the sublattice available to acceptors is each crystallographic site of this sublattice. In the case of a unique energy-transfer process, down conver-

sion, and one type of acceptors, for each site i there are only two possibilities: it is occupied with the probability p_i [$\rho_{1i} = p_i$ and $n_{1i} = \exp(-W_i t)$] or it is not occupied ($\rho_{2i} = 1 - p_i, n_{2i} = 1$). Thus

$$\bar{N}_i(t) = (1-p_i) + p_i \exp(-W_i t) \qquad (8)$$

and

$$N(t) = \prod_{i=1}^{N_t} \bar{N}_i(t)$$

$$= \prod_{i=1}^{N_t} [(1-p_i) + p_i \exp(-W_i t)] = \exp[-P(t)], \qquad (9)$$

where N_t denotes the total number of sites for the sublattice available to the acceptors and $P(t)$ is called the transfer function. In case of random discrete occupation with equal probability of the sites of this sublattice, the occupation probability p_i sites equals the relative acceptor concentration C_A:

$$P(t) = -\sum_{i=1}^{N_t} \ln[(1-C_A) + C_A \exp(-W_i t)]. \qquad (10)$$

The functions $N(t)$ and $P(t)$ can be calculated if the individual transfer rates to acceptors at any lattice sites i are known. Thus the discrete distribution model enables one to take into account the multiple interaction pictures or any factor that could modify the probability of occupation or the characteristics of transfer from site to site, such as the charge or dimensional correlations. If the structure of the crystalline lattice allows the definition of coordination spheres for acceptors around the donors, each containing m_l available sites and if the transfer rates depend only on distance, the transfer function can be written as

$$P(t) = -\sum_{l=1}^{N_t} m_l \ln[(1-C_A) + C_A \exp(-W_l t)]. \qquad (11)$$

Though the transfer functions $P(t)$, Eqs. (10) and (11), are valid over the whole temporal range of emission kinetics, over definite temporal ranges they can be approximated by simple functions of time and concentration. Unlike the case of the continuous uniform distribution, the derivative of function $P(t)$, Eq. (10), is finite at $t=0$ and equal to $W_{st} = C_A \Sigma_i W_i$. At low acceptor concentrations the beginning of decay (over several to tens of μsec, determined mainly by the inverse of the transfer rate to the acceptors from the first sphere accounted for in sum) can be approximated by a linear function of time, $P(t) = W_{st} t$, while at large t for a multipolar interaction it can be approximated by Eq. (6).

The theory of the static energy transfer in the random discrete distribution model for homogeneous systems met considerable success in describing the luminescence decay governed by down conversion at low pump intensity for various doped crystals. However, in many cases[6,14,35,53–56] the high-resolution spectra show an appreciable structural and hence spectral disordering of the systems of dopant ions due to the mutual crystal-field perturbations inside the statistical ensembles of dopant ions in near lattice sites. Owing to the discreteness of the crystalline lattice a chain of discrete perturbations, corresponding to the various near ion ensembles can be produced, leading to the apparition of spectral satellites whose number and relative intensities depend on the structure of the crystalline lattice and on the concentrations of the dopant ions. These perturbations could also modify the optical transition probabilities and the radiative lifetimes. All these spectral and dynamic effects of perturbation transform the systems of dopant ions in nonhomogeneous systems, composed of homogeneous subsystems of ions with identical spectroscopic (wavelength, intensity, lifetime) properties. These subsystems can be linked with the resolved spectral satellites (''perturbed'' subsystems), a special subsystem corresponding to the weakly perturbed ions (''isolated'' ions). The homogeneous subsystems are also particularized[55,56] by a selective manifestation of the energy-transfer processes, since the type of acceptor configurations around the donor will be different for each of the perturbed subsystems (there is always an acceptor in one of the nearest coordination spheres), while for the subsystem of ''isolated'' ions the donor is surrounded only by distant acceptors. The averaging of the donor decay can be then made for each of these subsystems and the decay of the whole system of donors under a uniform, nonselective excitation can be obtained by simply adding the individual contributions of the subsystems, weighted by the corresponding occurrence probabilities. The selective excitation of each subsystem enables a direct determination of the transfer rates corresponding to various near acceptors and thus provides a check of the transfer parameters inferred from the global response of the sample under nonselective excitation.

B. Energy transfer in inhomogeneous systems

We consider a crystal with a small concentration of donors and with a larger concentration of acceptors and assume that only the nearest acceptor ion from one of the first k acceptor coordination spheres around the donor could produce resolved crystal-field perturbations at the donor site, i.e., induce satellites in the donor optical spectra. In order to make the problem more clear we assume that the acceptor concentration is not so high as to have more than one acceptor ion placed on only one of the coordination spheres of order smaller than or equal to k: thus the number of homogeneous subsystems equals $(k+1)$, the first k being perturbed subsystems. The energy-transfer functions for these subsystems can be calculated by a proper averaging on the specific acceptor configurations or by the particularization of Eqs. (10) and (11) to the structure of each of these subsystems: this specificity is determined by the occupation of sites in the nearest spheres (up to the sphere k), the remainder of the acceptor system being considered identical for all subsystems. Thus in case of the perturbed donor subsystems the energy-transfer process can be considered as composed of two parts, a fast transfer to the nearest (perturbing) acceptor companion and a slow transfer to the system of distant acceptors, outside of the coordination sphere k, while in case of the isolated donor ions subsystem only the second part is active.

Thus for the perturbed systems with only down conversion and under low pump intensity, if the perturbing acceptor is placed on the sphere j,

$$P_j(t) = W_{DAj}(r_j)t + P_{DA}^{(d)}(t) \qquad (12)$$

with the distant transfer contribution

$$P_{DA}^{(d)} = -\sum_{l>N_k} m_l \ln[1 - C_A + C_A \exp(-W_l t)], \qquad (13)$$

where $N_k = \Sigma_{j=1}^{k} m_j$, while for the system of isolated donor ions $P(t) \equiv P^{(d)}(t)$. Thus the sum in Eq. (13) is truncated as compared to Eq. (11), by excluding the contribution of the first k spheres. With these particularized transfer functions a specific temporal evolution can be obtained for each subsystem. As shown by Eqs. (12) and (13), the luminescence decay for the D-A near pairs is not purely exponential and independent on C_A, as largely accepted, but it is modulated by the distant transfer which is nonexponential and depends on the acceptor concentration.

V. EXPERIMENTAL RESULTS AND DISCUSSION

The previous high-resolution absorption and emission studies[6] on Nd^{3+} in YAG have shown a variety of satellites around the main lines connected either with the presence in the vicinity of Nd^{3+} ions of nonstoichiometric defects—satellites P_i, or with Nd^{3+} ion pairs: satellite M_1 corresponding to the first-order (NN) pair, satellite M_2—second-order (NNN) pair, and satellite M_3—third-order pair. In the optical transition ${}^4I_{9/2}(1) \rightarrow {}^4F_{3/2}(1)$ the M_i satellites are placed, respectively, at -5, $+1$, and -0.8 cm^{-1} from the main line N (11 425.5 cm^{-1}) corresponding to the isolated ions. Only the satellite M_1 is well resolved while M_2 and M_3 are observed as shoulders of the N line, satellite M_3 is also very close (0.5 cm^{-1}) to satellite P_3. The best resolution of these satellites was obtained in the absorption spectrum ${}^4I_{9/2}(1) \rightarrow {}^4F_{9/2}(1)$ whose N line lies at 14 621 cm^{-1}. Several other much weaker satellites of uncertain origin (ensembles of higher order than pairs, accidental impurities) were also observed. The high-temperature grown crystals show also the presence of the spectrum A which was tentatively assigned[6] to a small fraction of Nd^{3+} ions in octahedral a sites. According to these studies, 532-nm excitation is almost resonant, at very low temperatures, with a sharp absorption in the ${}^4G_{7/2}$ level of center A, but with increasing the temperature the absorption in this region is dominated by a wing of the hot band transition ${}^4I_{9/2}(3) \rightarrow {}^4G_{7/2}(4)$ of the main center N and of the associated satellites. At room temperature it can be considered that 532 nm excites nonselectively the centers N, P_i, and M_i. Thus if a sufficiently large pass width is used for detection, the emission of the whole ensemble of Nd^{3+} isolated ions and pairs is observed. This nonselective room-temperature 532-nm excitation was used to investigate the luminescence decay of the ensemble of Nd^{3+} ions and the low-temperature selective excitation in ${}^4F_{9/2}$ to check the conclusions resulted from the global emission. In order to avoid the effects of up conversion in all these cases the excitation was weak and promoted less than 1% of the Nd^{3+} ions to the metastable level ${}^4F_{3/2}$.
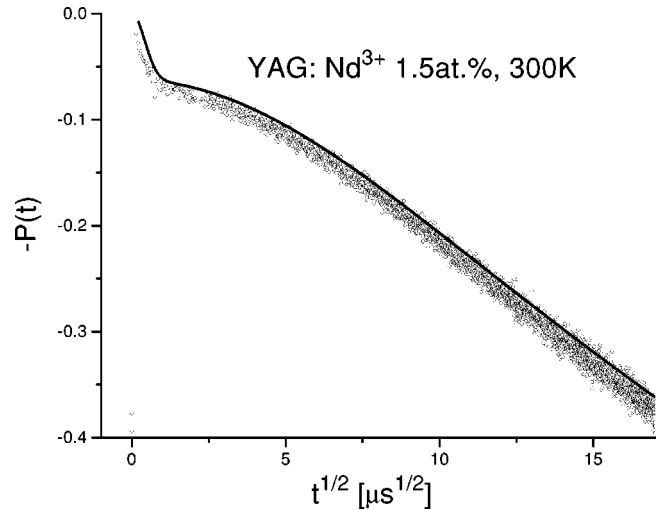

FIG. 1. Experimental $P(t)$ function versus $t^{1/2}$ for ${}^4F_{3/2}$ emission of Nd^{3+} (1.5 at.%) in YAG at 300 K and theoretical fitting with Eq. (11). The experimental points are shifted uniformly downward in order to evidence more clearly the quality of the fit.

A. Emission decay under 532-nm low intensity excitation

The high-resolution room-temperature luminescence decays of YAG:Nd^{3+} with concentrations of 0.1 to 2.5 at.% Nd^{3+} show a concentration-dependent nonexponential decay which up to 1.5 at.% Nd is dominated by a static D-A transfer regime, while at larger concentrations, such as 2.5 at.% Nd, a clear evidence of migration is observed. In this study we focus on crystals with less than 1.5 at.% Nd by using a high time resolution measurement ($\sim$20 ns).

The energy-transfer effects are analyzed by studying the temporal and concentration dependence of the transfer function $P(t,C_A) = -[\ln(I/Io) + t/\tau_D]$, with $\tau_D = 260$ μsec. An illustration is given in Fig. 1 for a sample with $\sim$1.5 at.% Nd where $P(t)$ is presented as a function of $t^{1/2}$ (dots represent the experimental points). The experimental data reveal three time-dependence regions. At long times the decays are well described by $t^{1/2}$ (d-d mechanism), at intermediate times $\sim$5–40 μsec (Fig. 2) the transfer function shows a quasilinear temporal dependence, while the beginning of the decay
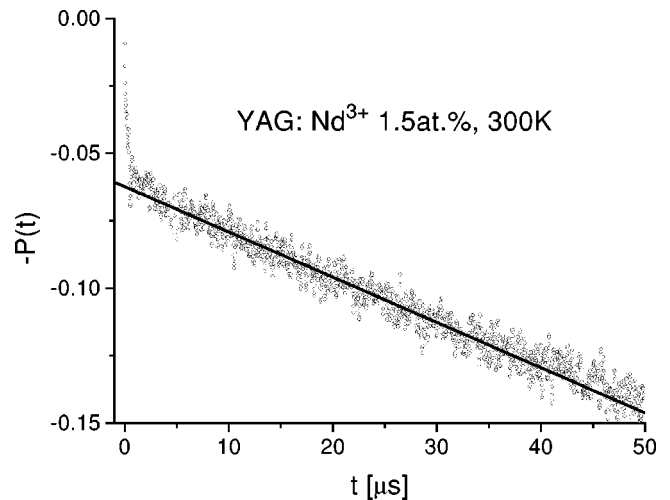

FIG. 2. Emission decay at early times for ${}^4F_{3/2}$ level of Nd^{3+} (1.5 at.%) in YAG at 300 K with 532-nm excitation.

TABLE I. Static energy-transfer parameters for self-quenching of $^4F_{3/2}$ emission of Nd^{3+} in YAG at 300 K estimated in the present work and in Ref. 11.

Multipolar microparameters			Superexchange parameters		References
$C_{DA}^{(6)}(cm^6\ s^{-1})$	$C_{DA}^{(8)}(cm^8\ s^{-1})$	$C_{DA}^{(10)}(cm^{10}\ s^{-1})$	$R_o(\text{Å})$	$L(\text{Å})$	
1.85×10^{-40}	0	0	5.43	0.54	This work
1.148×10^{-38}	9.87×10^{-53}	9.53×10^{-67}	10.75	0.1	Ref. 11

($t < 2$ μsec) is much faster. For $t > 2$ μsec the decays are similar to those observed earlier[14,18,19] in the low temporal resolution measurements.

The complex shape of this decay can be explained by assuming that the transfer rate W_1 to the nearest acceptors ($l = 1$) is much larger than to the others. In this case Eq. (11) can be written as

$$P(t) = -m_1 \ln[1 - C_A + C_A \exp(-W_1 t)]$$
$$- \sum_{l>1}^{N_i} m_l \ln[(1 - C_A) + C_A \exp(-W_l t)]$$
$$= P_1(t) + P_2(t). \qquad (14)$$

For very low acceptor concentrations (of ~ 1 at.%) the first term $P_1(t)$ of Eq. (14) reaches a value of about $m_1 C_A$ at the time $t'_1 \approx m_1 W_1^{-1}$. For high W_1 rates, t'_1 could be outside the experimental temporal resolution; in this case $P_1(t)$ can be approximated by $m_1 C_A$, and corresponds to a sudden drop of $P(t)$ at the beginning of decay. The second term $P_2(t)$, is similar in form to Eq. (11) but the sum is truncated at $l = 1$, i.e., it excludes the NN acceptors considered by $P_1(t)$. For early times $P_2(t)$ can be approximated by a linear function of time-static ordered regime, with a slope $C_A \sum_{l>1} m_l W_l$; the temporal range of quasilinearity in this case is rather long due to the exclusion of $l = 1$ term from the sum. If we assume that for $l > 1$ the transfer is dominated by a d-d interaction ($W_l = C_{DA}^{dd} R_l^{-6}$), for long times and low acceptor concentration the function $P_2(t)$ can be approximated by Eq. (6) for continuous distribution[40,41,47] with $s = 6$ or by a correlated distribution function which excludes a volume from the acceptor distribution around donor.[54] The $t^{1/2}$ dependence (Fig. 1) and the fit of experimental data with Eq. (6) gives the d-d microparameter $C_{DA}^{dd} \sim 1.85 \times 10^{-40}$ cm^6 s^{-1}. A slightly larger microparameter $C_{DA}^{dd} \sim 1.9 \times 10^{-40}$ cm^6 s^{-1} is estimated from the slope $C_A \sum_{l>1} m_l C_{DA}^{dd} R_l^{-6}$ of $P_2(t)$ in the static ordered regime. The small difference between these two C_{DA}^{dd} values could be explained by the residual influence in the transfer to the acceptor from the second and third coordination spheres of the strong short-range interaction which determines the quenching inside the NN Nd-ion pairs.

As shown by the data (Fig. 2), the fast initial decay determined by $P_1(t)$ extends practically to ~ 2 μsec after the excitation pulse and induces a drop in emission proportional to the Nd^{3+} concentration. This can be explained with a rate W_1 of the order of 2.5×10^6 s^{-1} with an error of 20%. Since the estimated dipolar contribution to W_1 is of $\sim 7.5 \times 10^4$ s^{-1}, the transfer rate W_1 contains a dominant strong short-range interaction contribution. If we assume that this inter-

action is superexchange, from W_1 and the possible small effect discussed above in the transfer to the acceptors from second sphere the characteristic parameters entering in Eq. (1) could be estimated: $L \sim 0.54$ Å and $R_0 \sim 5.43$ Å, values that are affected by the experimental errors in W_1. These two parameters together with the d-d interaction microparameter $C_{DA}^{dd} = 1.85 \times 10^{-40}$ cm^6 s^{-1} enable the calculation of the transfer rates $W_i = W_i^{dd} + W_i^{ex}$ for each site i and the transfer function (10) describes well the observed decay under weak pump over the entire temporal range starting now from 20 nsec (continuous line in Fig. 1). These data confirm our previous low-resolution measurements where the fast drop was not observed, but its presence was inferred from the analysis of the shape of $P(t)$ on the available time range ($t > 2$ μsec) and explained in a mixed interaction picture consisting of a short-range interaction that manifests within the first 2 μsec and a d-d interaction in a cross-relaxation process and the inadequacy of the d-d continuous distribution model ($t^{1/2}$ dependence) to describe the energy-transfer processes at early times. The present analysis suggests the extension of the influence of the superexchange interaction to at least the second and third coordination spheres.

A fast initial decay was also reported[11] recently, but a completely different set of energy-transfer parameters for $^4F_{3/2}Nd^{3+}$ level in YAG were inferred from a Monte Carlo description. It was assumed that a complex four-type interaction picture (three multipolar interactions and exchange) takes place with the parameters given in Table I that includes for comparison also the parameters determined in the present work. The parameters[11] were deduced by assuming that for a sample of 1.1 at.% Nd (i.e., a concentration of 1.523×10^{20} cm^{-3}) the donors concentration was 1.320×10^{20} cm^{-3} and that of the acceptors 0.144×10^{20} cm^{-3}—one order of magnitude smaller; the role of remaining Nd ions was not specified. It is not clear how such a high donor concentration was achieved by exciting with 532 nm. On the other hand, one would expect a very strong manifestation of up conversion, making the model of analysis only by down conversion improper. Apparently the model[11] was based on the assumption that only part of the Nd^{3+} ions can act as acceptors, namely those corresponding to the perturbed centers. No justification of this unusual choice and no clear identification of these centers was provided; apparently they refer to Nd^{3+} pairs, although the value given for the acceptor concentration was lower than the global concentrations of the first- and second-order Nd^{3+} pairs. All the other Nd^{3+} ions are considered as donors. Physically this eliminate the largest part of Nd^{3+} ions, including the majority of isolated (nonperturbed) centers N, from acting as acceptors and the Nd^{3+} ions of NN and NNN pairs from acting as donors. This in turn excludes any trans-

fer inside these pairs and leaves as the only possible transfer that from isolated Nd^{3+} ions to the ions from NN and NNN pairs, i.e., a selected type of distant transfer. The model[11] and its implications are in evident contradiction with the actual physical picture of the energy transfer inside the system of Nd^{3+} ions in YAG. It is not clear if only this choice of concentrations determines the huge energy-transfer parameters reported in Ref. 11. The multipolar contributions to the energy-transfer rates calculated with these parameters for the various near Nd^{3+} ion pairs are $W_1 = 2.45 \times 10^8$ s^{-1}, $W_2 = 4.43 \times 10^6$ s^{-1}, and $W_3 = 2.4 \times 10^6$ s^{-1} for the first-, second-, and third-order pairs, respectively, and the calculated q-q and d-q rates dominate the d-d contribution up to 9.545 and 9.272 Å, i.e., beyond the eighth-order pair. At the same time the superexchange rates $W_l^{(ex)}$ calculated with Eq. (1) and with the parameters[11] amount to 1.1×10^{65} s^{-1} and 1.633×10^{48} s^{-1} for the first two Nd^{3+} pairs; even for the ninth-order pair (at 10.181 Å), $W_9^{(ex)}$ still amounts to 3.367×10^8 s^{-1}. With these parameters the energy transfer between the Nd^{3+} ions in YAG is dominated up to large distances above 10 Å by superexchange. According to the above discussion, all the pairs with such high transfer rates would induce a fast drop of emission at the beginning of decay: all the emission inside the pairs up to the tenth order should vanish in a few nsec, while the emission of the first two pairs would disappear practically at the end of the excitation pulse.

Such enormous energy-transfer rates as predicted by the transfer parameters[11] are very unlikely, for systems such as Nd:YAG where the superposition integral S of the donor emission and acceptor absorption for the down-conversion cross relaxation that quenches the $^4F_{3/2}$ emission is very small. In fact, these rates exceed by far any other data on energy-transfer processes in Nd^{3+} doped systems and are in strong contradiction to those determined in the present paper for Nd^{3+}:YAG. A criterion for the selection of the most appropriate energy-transfer parameters is to check their effect in other experiments such as the selective emission of $^4F_{3/2}$ level under quasiselective excitation of various Nd^{3+} pairs (that enables the direct estimation of the transfer rates inside the various near ion pairs) and the circuit of excitation after cross relaxation. Since the excitation of the terminal level of cross relaxation, $^4I_{15/2}$, is completely lost by multiphonon relaxation, the influence of the energy-transfer parameters in populating this level and the subsequent flow of excitation can be investigated by quantum efficiency and fractional heat effect measurements.

B. Emission decay of $^4F_{3/2}$ under quasiselective low intensity excitation

The absorption spectrum of $^4I_{9/2}(1) \rightarrow {}^4F_{9/2}(1)$ transition shows a better spectral resolution than other transitions used to pump the $^4F_{3/2}$ emission. However, due to the large variety of structural centers and to the partial superposition of their absorption or emission spectra, or the selectivity of experimental setup, the resolution of the emission of the various centers is not perfect. The luminescence decays of the quasiselectively excited centers N and M_i, detected in the $^4F_{3/2} \rightarrow I_{9/2}$ transitions with a temporal resolution of 20 ns show very large differences. The emission decays of the pair

lines M_i depend on the Nd^{3+} concentration and show slight departures from exponential. The emission of M_1 center has a very fast component that disappears practically within 2μsec, followed by a much slower weak tail; the fast part of M_1 decay rate, at low Nd^{3+} concentration, is of the order estimated from the global emission (2.5×10^6 s^{-1}) while the weak long tail is due to the accidentally excited long-lived centers, in agreement with the time-resolved spectra that show some nonselectivity in emission. The emission decay of the M_2 satellite shows an obvious concentration dependence: for the sample of 0.5 at.% Nd^{3+} the effective decay time ($1/e$ time) is $\sim 90 \mu$sec, while for 1 at.% Nd it becomes $\sim 85 \mu$sec. For M_3 this effective lifetime is around 130 μsec at 0.5 at.% Nd^{3+}. Thus for all the pair centers the effective lifetime is much shorter than for center N, which shows at the beginning of decay a quasilinear temporal dependence with the lifetime of about 245 μsec for 0.5 at.% Nd^{3+} and 235 μsec for 1 at.% Nd^{3+}. At the same time, the lifetime at the beginning of decay for center N is larger than that corresponding to the measured low-temporal resolution W_{st} values for the global response of samples under nonselective 532-nm pump (230 and 205 μsec, respectively).

These decays can be explained by Eqs. (12) and (13) for the energy transfer in case of the inhomogeneous systems of dopant ions. Thus for the isolated Nd^{3+} ions only the distant transfer $P^{(d)}(t)$ to acceptors placed outside the third coordination sphere is effective: the long ($\sim 100 \mu$sec) linear portion of the transfer function at the beginning of decay and its slope are consistent with the dipolar mechanism of interaction, with the microparameter C_{DA}^{dd} determined from the global emission decay and the sum in Eq. (11) excludes the first three coordination spheres. For the pair centers M_i the luminescence decays are well described by assuming a fast transfer $W_i = W_i^{ex} + W_i^{dd}$ from donor to the perturbing acceptor companion (the first term on the right side of Eq. (13), modulated by the concentration-dependent transfer to distant donors $P^{(d)}(t)$. Thus the rate W_1 is equal to $\sim 2.5 \times 10^6$ s^{-1} and is dominated by superexchange with a weak contribution from d-d interaction, for rate W_2 of 7.9×10^3 s^{-1}, the situation is reversed, with d-d dominating, while W_3, of 4.3×10^3 s^{-1} is almost completely determined by this interaction. Up to ($1/e$) drop of emission $P^{(d)}$ is nearly linear in time, with a slight deviation for M_3, but it introduces a nearly linear concentration-dependent contribution to decay. The total decay rates for these pairs, including the intrinsic de-excitation (τ_D), the fast and the distant transfer, calculated with the transfer parameters determined in this work from the global emission decay are in a good agreement with those determined experimentally for ($1/e$) drop of emission. For longer times $P^{(d)}$ induces slight departures from exponential. The observation of the individual emission of all these pairs, extending (except of M_1) over a quite long time, contradicts the enormous energy-transfer rates calculated with parameters of Ref. 11 and the dynamics of emission of the selectively excited individual centers N and M_i rule out completely the physical model used in that paper.

C. Energy transfer and quantum efficiency of $^4F_{3/2}$ emission

The energy-transfer processes reduce the global quantum efficiency η of the emitting $^4F_{3/2}$ donor level. This effi-

ciency can be regarded as a product between the intrinsic quantum efficiency η_i, which takes into account the effect of the intracenter nonradiative processes (such as the multiphonon relaxation) on the lifetime of the center and the quantum efficiency η_t which reflects the effect of the energy transfer in the reduction of the intrinsic lifetime $\eta = \eta_i \times \eta_t$. Since the multiphonon relaxation does not change the exponential decay, the intrinsic efficiency is expressed by the ratio between the measured lifetime τ_D of the level at very low concentrations and the radiative lifetime; as discussed above for $^4F_{3/2}$Nd^{3+} level in YAG $\eta_i \sim 0.98$. On the other hand, the extrinsic quantum efficiency is determined by the area under the decay curve

$$\eta_t(C_{Nd}) = \frac{1}{\tau_D} \int_0^\infty \exp\left(-\frac{1}{\tau_D}\right) \exp[-P(t)]dt. \quad (15)$$

By using the energy-transfer function $P(t)$ given by Eqs. (10) and (11) the extrinsic quantum efficiency can be approximated by a simple exponential dependence on the acceptor concentration

$$\eta_t = \exp(-bC_A), \quad (16)$$

where the parameter b can be related to the individual transfer rates,

$$b = \sum_i \frac{W_i}{\tau_D^{-1} + W_i} = \sum_l m_l \frac{W_l}{\tau_D^{-1} + W_l}. \quad (17)$$

With the down-conversion transfer parameters measured in this work and summing over 120 coordination spheres (2740 lattice sites) available to acceptors around a donor site, for the $^4F_{3/2}$ level of Nd^{3+} in YAG we obtain $b \sim 20$. Equation (16) is more accurate than the relation $\eta_t = 1 - 18.2C_A$ used previously,[19,20] which is a linearization of this equation around $C_A = 0.01$.

The quantum efficiency for YAG:Nd^{3+} was measured by a large variety of methods.[16,22–31] These include the measurement of the $^4F_{3/2}$ emission decay, of the emitted power or of heating effects, such as the rise of temperature of the sample, thermally induced stress or optical distortion. The luminescence decay method assumes an exponential form, regardless of Nd^{3+} concentration, and takes as emission lifetime the time necessary for an e drop on a selected portion of decay that excludes the beginning, i.e., precisely the portion where the transfer to the nearest spheres of acceptors contributes to the loss in emission. Thus, for ~ 1 at.% Nd this effective lifetime lies in the range of 230 to 235 μsec, which suggests η_t in the range of 0.9. However, Eq. (16) predicts for 1 at.% Nd a value of $\eta_t \sim 0.819$, i.e., $\eta \sim 0.8$. Thus a more realistic effective lifetime of the decay at a given Nd^{3+} concentration would be $\tau_{rad}\eta(C_{Nd}) = \tau_D \eta_t(C_{Nd})$, i.e., ~ 213 μsec for 1 at.% Nd.

Unfortunately, most of the reported data on η refer to a unique sample, usually of about 1 at.% Nd, and they vary in the range of 0.47–1. However, several works report data on samples of various Nd^{3+} concentrations: η obtained by interferometric calorimetry on three YAG:Nd samples of various concentrations[16] or the fractional thermal load for other three samples, measured[31] by monitoring the temperature
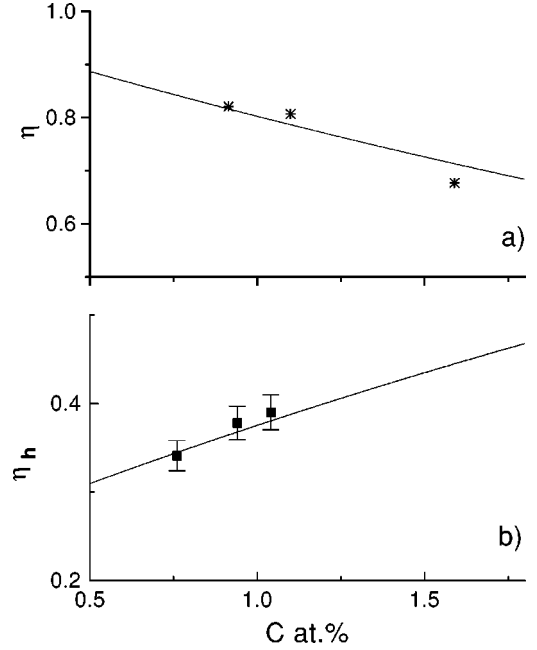

FIG. 3. (a) Calculated room-temperature emission quantum efficiency for $^4F_{3/2}$Nd^{3+} level in YAG at low pump intensity (continuous line) and (*) experimental data (Ref. 16); (b) calculated fractional thermal load for $^4F_{3/2}$Nd^{3+} level in YAG at low pump intensity at 808 nm (continuous line). The squares indicate experimental data (Ref. 31).

rise of the sample. The fractional thermal load is defined as the fraction of the absorbed pump power that is transformed into heat. By considering that the pump is made in a level E_p from which all the excitation relaxes nonradiatively on the emitting level E_m and that the average photon energy of the radiative spontaneous processes from E_m is E, the fractional thermal load in absence of laser emission, can be written as

$$\eta_h = 1 - \eta \frac{E}{E_p} = 1 - \eta_i \exp(-bC_A)\frac{E}{E_p}. \quad (18)$$

The values of the measured quantum efficiency of $^4F_{3/2}$ emission and of fractional thermal load for YAG:Nd at low pump intensities are compared with those calculated with Eqs. (16) and (18) in Fig. 3 by assuming $C_A = C_{Nd}$; for the last of these the pump was made at 808 nm with a diode laser and the average emitted photon E was 9635 cm^{-1}, hence $\eta_h = 1 - 0.763 \times \exp(-20C_{Nd})$. As these figures show, the energy transfer parameters determined in this work describe very well some of the existing systematic data on the quantum efficiency and thermal load effects for Nd^{3+} in YAG. The very slight disagreement for the sample of 1.589 at.% Nd [Fig. 3(a)] can be explained by the onset of energy migration which accelerates the deexcitation of the $^4F_{3/2}$ level.

These results show that the energy transfer is a basically limiting process for the emission efficiency of $^4F_{3/2}$Nd^{3+} level in YAG and suggest that the very large values of quantum efficiency reported by several authors are unrealistic; at the same time, the lower values reported in other papers can be determined either by an experimental error or by the accidental presence of other quenching centers in the crystals. However, the presence of such centers must be considered

with caution: sometimes their presence was inferred as a result of the use of some improper energy-transfer parameters. Thus in Ref. 31 a quantum efficiency of 0.9 for 1 at.% Nd was used for interpretation of data, which induced to an obvious disagreement between the experimental and calculated values of fractional thermal load; this difference was attributed to the presence of "dead sites"[30] (about 10% of the total Nd ions) where the Nd^{3+} excitation is completely quenched in a electron-phonon process that is independent of the energy-transfer self-quenching. However, our results show that the data reported in Ref. 31 correspond exactly to the extent of self-quenching by down-conversion cross relaxation if proper energy-transfer parameters are used. A further check of the validity of Eq. (16) is the value of η inferred from the effects of the thermal processes in YAG:Nd^{3+} rods on the parameters of laser emission[57] (~ 0.8 for 1 at.% Nd).

Thus for low pump intensity the global emission luminescence decay under nonselective pump, the quasiselective emission decay of the various of near ion ensembles (pairs), the quantum efficiency and the fractional thermal load measurements at various Nd^{3+} concentrations (up to 1.5 at.%) as well as the effect of self-quenching on global laser emission efficiency of YAG:Nd^{3+} rods can be explained consistently by a unique set of static down-conversion energy-transfer parameters. According to this model the energy transfer that quenches the $^4F_{3/2}$ emission of Nd^{3+} in YAG in this concentration range is a cross relaxation on intermediate levels determined by mixed superexchange-dipolar interactions in which the first dominates for the NN pairs and the second for the other pairs; a good fit of the data was obtained by assuming an exponential distance dependence of superexchange.[48-50] The presence of superexchange for the NN pairs could be a likely explanation for the larger width of the M_1 satellite at low temperatures as compared to the lines of all the other centers from the system. At the same time, these decay data cannot be explained by the physical model and by the energy-transfer parameters reported in Ref. 11. Thus the selective emission of Nd ion pairs of first, second, and third order is a crucial test for our model.

The limitation of the multipolar interactions to dipole-dipole interaction can be explained as a result of the selection rules that govern the transfer rates for these processes. As discussed earlier the quadrupolar interactions impose a selection rule $|J - J'| \leqslant 2$ for the pairs of levels involved in the donor and acceptor act of the cross relaxation: none of the pairs involved in the cross relaxation $(^4F_{3/2}, {}^4I_{9/2}) \rightarrow (^4I_{15/2}, {}^4I_{15/2})$ responsible for self-quenching satisfy this condition. Apparently, in case of YAG:Nd the J-mixing effects for the levels involved in down-conversion cross relaxation are too weak to induce sizeable contributions to these parameters so as to make the quadrupolar transfer allowed. This is in agreement with the studies of optical transition probabilities on this system which show that the electric-dipole process is really dominant[1-5,13] and with the calculations for aqueous Nd ions.[58] A similar situation was also remarked in the study of other Nd^{3+} doped systems, such as fluorides[59,60] where the quadrupolar contribution is absent in the down-conversion cross relaxation of $^4F_{3/2}$, but it has an important role in the deexcitation of the level $^4G_{5/2}$ by the process $(^4G_{5/2}, {}^4I_{9/2}) \rightarrow (^4F_{9/2}, {}^4I_{13/2})$.

The analysis presented here can be extended to take into account cases with a higher Nd concentration or with a high pump intensity which induces a large $r(o)$ fraction. These cases impose the consideration of the up conversion together with down conversion as well as of the migration assistance of cross relaxation; such a study is now in progress.

VI. CONCLUSION

The high temporal resolution (20 ns) emission decay of $^4F_{3/2}$ Nd^{3+} level in YAG (for concentrations up to ~ 1.5 at.%) under nonselective weak pump, which precludes the up conversion, shows a complex, concentration-dependent behavior due to the self-quenching of emission by cross relaxation on intermediate levels; no clear evidence of migration in this concentrations range is observed. The experimental data are analyzed by the theory of direct donor-acceptor energy transfer for discrete, equiprobable, and random placement of the dopant ions at the available lattice sites.

The emission decay shows an initial very fast portion, which was not observed in the earlier low-resolution (1 μsec) experiments although its presence was predicted from the analysis of decay which concluded that the transfer inside the NN pairs is dominated by a short-range interaction (most probably superexchange) while for all other D-A pairs the transfer is determined by a d-d interaction. The present data confirm this model and enable a more accurate evaluation of the transfer parameters; the influence of superexchange interaction beyond the first coordination sphere is also assumed with an exponential dependence[55-57] on the distance between the Nd^{3+} ions. The limitation of the multipolar interaction responsible for self-quenching of $^4F_{3/2}$ emission to the d-d contribution inferred from the present work is supported by the microscopic theory of the transfer rates: none of the transitions involved in cross relaxation obeys the selection rules for the quadupolar interactions and the J mixing is too weak to induce a sizable violation of these rules. This conclusion is supported also by the existing reports on other systems, such as various fluoride crystals.

The theory of energy transfer for discrete, equiprobable, and random placement of dopant ions was adapted here to take into account the effects of the spectral disordering introduced by the mutual crystal-field perturbations inside the statistical ensembles of ions in near crystalline sites: for the Nd^{3+} concentrations used in this work the most important ensembles are Nd^{3+} ion pairs of various orders. These effects are manifested in the spectra by the presence of the satellites M_i ($i = 1, 2, 3$) corresponding to various pairs and they justify the division of the system of Nd^{3+} ions in several spectrally homogeneous subsystems corresponding to these pairs, a special subsystem being that of "isolated" ions. A selective manifestation of the energy transfer in these subsystems is observed. For the perturbed subsystems the energy transfer contains a very fast transfer to the nearest acceptor companion and a slow transfer to the other acceptors, while in case of the isolated Nd^{3+} ions only the last transfer takes place. The observation of the emission decay for these subsystems enables a direct estimation of the transfer rates to near acceptors. The emission of these subsystems can be further linked to the global emission of the system by using proper weighting coefficients. The luminescence de-

cays of M_i Nd^{3+} centers in YAG under quasiselective dye laser pump confirm the characteristics of the energy transfer inferred from the global decay.

The validity of the energy-transfer parameters given in this work is further confirmed by the very good agreement with the measured values of emission quantum efficiency[16] and fractional thermal load[31] for YAG:Nd^{3+} samples of various concentrations. It is evident that the self-quenching by cross relaxation inside the system of Nd^{3+} ions in YAG imposes an upper limit, C_{Nd} dependent, of the emission quantum efficiency and that a proper account of these processes could avoid in most cases a costly and timeconsuming search for other, nonexisting, quenching processes.

The data presented here invalidate the Monte-Carlo analysis of decay[11] for YAG:Nd, based on a mixed interaction picture containing superexchange and three multipolar interactions (d-d, d-q, and q-q) with an assumed concentration of donors much larger than that of acceptors, for several reasons: (a) the energy-transfer microparameters are too large for the very poor superposition of the donor emission and acceptor absorption and the quadrupolar interactions are severely forbidden; (b) the enormous transfer rates induced by these parameters for the near Nd^{3+} ion pairs are invalidated by the decay of the selectively excited emission of Nd^{3+} pairs of first, second, and third order; and (c) the very high donor concentration assumed in Ref. 11 would normally lead to strong up conversion processes making the analysis of decay only by down conversion inappropriate.

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