

Interionic energy transfer by electric multipole interaction in rare-earth pentaphosphates

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(Received 7 August 1980)

We present a thorough investigation of nonradiative energy-transfer processes in various rare-earth (R) pentaphosphates (RP_5O_{14}). Using time-resolved fluorescence spectroscopy, different crystals with high and low concentration of the interacting R^{3+} ions were investigated. It turns out that energy transfer in RP_5O_{14} causes both spatial energy migration of excited states and fluorescence quenching. At high rare-earth concentration the concentration dependence of fluorescence quenching is shown to be governed by fast energy migration. From low-concentration measurements the dominant interionic coupling mechanism could be determined employing a microscopic picture for the energy-transfer process. A particular statistical model is introduced to combine the results obtained in the low- and high-concentration limit. The investigations yield that energy transfer in RP_5O_{14} is due to electric multipole interactions within the entire range of rare-earth concentrations, even at interionic spacings of 5 Å.

I. INTRODUCTION

Neodymium pentaphosphate, NdP_5O_{14} , was the first compound representing the new class of highly concentrated rare-earth laser materials.¹⁻⁴ Since the optically active Nd^{3+} ion is a stoichiometric constituent of the crystal, its high concentration together with a significant fluorescence cross section results in a large optical gain per unit length. Thus these so-called stoichiometric laser materials allow a miniaturization of laser devices which makes them attractive in optical fiber communications.⁴ Whereas the laser properties of these rare-earth compounds have been thoroughly investigated, less is known about the fundamental physical processes involved.

The essential property of these stoichiometric laser materials is that the high concentration of the optically active Nd^{3+} ions does not result in a drastic degradation of the fluorescence efficiency.²⁻⁴ In well studied materials like $Nd:Y_3Al_5O_{12}$, strong fluorescence quenching occurs due to nonradiative energy transfer between the Nd^{3+} ions⁵ which restricts the appropriate Nd concentration in laser crystals to a doping level of about 10^{20} cm⁻³. In NdP_5O_{14} , however, interionic interactions are weak so that efficient laser operation is achieved despite the extremely high Nd^{3+} concentration of 4×10^{21} cm⁻³.¹⁻⁴

Concentration quenching in NdP_5O_{14} was studied^{2-4,6} by replacing the Nd^{3+} ions by optically inactive La^{3+} ions. Quenching processes reduce the quantum efficiency of Nd^{3+} only by a factor of 3. Surprisingly, the decay of luminescence after a short exciting pulse is observed to be pure exponential over a wide range of Nd^{3+} concentrations. Moreover, the decay rate of the excited Nd^{3+} ions

in $Nd_xLa_{1-x}P_5O_{14}$ crystals is found to be a linear function of x . This behavior contradicts simple theories for concentration quenching in rare-earth materials. Although many suggestions have been made in recent papers,^{2,3,6,7} no satisfactory explanation covering all experimental results could be given. In particular, the physical nature of the interionic coupling responsible for the quenching process could not be determined.⁸ Fluorescence quenching in highly concentrated neodymium materials thus presents a problem of practical as well as of theoretical importance. A better understanding of these interionic interactions would be helpful for the development of new laser crystals and, on the other hand, it will provide information about the fundamental physics of rare-earth ions.

In this paper we present new experimental and theoretical results concerning fluorescence quenching by nonradiative energy transfer in rare-earth pentaphosphates. In these compounds interionic interactions cause different types of energy transfer processes: The total excitation energy of a donor ion can be transferred to an identical ion situated nearby. In this donor-donor transfer process, which is commonly called spatial energy migration,² excitation energy is conserved but a delocalization of excitation energy occurs. Another type of energy transfer named cross relaxation² is responsible for fluorescence quenching. Here only part of the excitation energy of the donor ion is transferred to a nearby acceptor ion.

To obtain more general information our investigations are not limited to NdP_5O_{14} . We have studied the dynamics of energy transfer between various rare-earth ions in pentaphosphate crystals using time-resolved fluorescence spectroscopy. Starting with highly concentrated crystals we show

that the concentration dependence of fluorescence quenching is strongly affected by fast energy migration among the donor ions. To explain the experimental results we introduce a specific model which fits the particular situation in highly concentrated compounds. Then we provide new experimental data for low rare-earth concentrations from which the dominant interaction mechanism can be determined using a microscopic picture for the interionic coupling. We will discuss how the behavior in both the low- and high-concentration limits is correlated. From our results it is evident that electric multipole interactions govern the energy-transfer processes in rare-earth pentaphosphates within the entire concentration range, even for rare-earth spacings of only 5 Å.

II. EXPERIMENTAL ARRANGEMENT

We have measured the fluorescence decay of Nd^{3+} ions in various RP_5O_{14} crystals, namely $\text{Nd}_x\text{La}_{1-x}\text{P}_5\text{O}_{14}$, $\text{Nd}_{1-x}\text{Tb}_x\text{P}_5\text{O}_{14}$, $\text{Nd}_{1-x}\text{Eu}_x\text{P}_5\text{O}_{14}$, and $\text{Nd}_{0.001}\text{Gd}_{0.999-x}\text{Tb}_x\text{P}_5\text{O}_{14}$. The crystals were grown from the R oxides dissolved in phosphoric acid as described elsewhere.⁹ The investigated samples were as grown platelets about 1 mm² in area and 0.5-mm thick. The Nd^{3+} fluorescence was excited by the 7525-Å line of a krypton laser. Short excitation pulses (pulse length 3 μsec) were created with the help of an acousto-optical modulator. The fluorescence from the $^4F_{3/2}$ state of Nd^{3+} was analyzed by an 0.5-m Czerny Turner spectrometer and detected with a S1 photomultiplier. The signal was fed through a standard photon counting system and a multichannel analyzer was used for time resolved registration of the fluorescence decay curves.

It is well known² that the rare-earth pentaphosphates crystallize in different phases due to the different ionic radii of the various R^{3+} ions. To check for phase transitions when varying the concentration in, e.g., $\text{Nd}_{1-x}\text{Tb}_x\text{P}_5\text{O}_{14}$, we have measured the Nd^{3+} $^4F_{3/2} \rightarrow ^4I_{9/2}$ emission for each crystal since each phase is correlated with a characteristic line spectrum.¹⁰ All the investigated samples belonged to the monoclinic $P2_1/c$ phase.

III. EXPERIMENTAL RESULTS AND ANALYSIS

A. High concentration

Figures 1 and 2 summarize the concentration dependence of the Nd^{3+} fluorescence decay rate τ^{-1} in $\text{Nd}_x\text{La}_{1-x}\text{P}_5\text{O}_{14}$, $\text{Nd}_{1-x}\text{Tb}_x\text{P}_5\text{O}_{14}$, and $\text{Nd}_{1-x}\text{Eu}_x\text{P}_5\text{O}_{14}$. At all concentrations x , $0.01 \leq x \leq 1$, we observed a pure exponential decay of the Nd^{3+} fluorescence. Thus a well defined lifetime τ of the upper fluorescence state $^4F_{3/2}$ could be easily determined. The

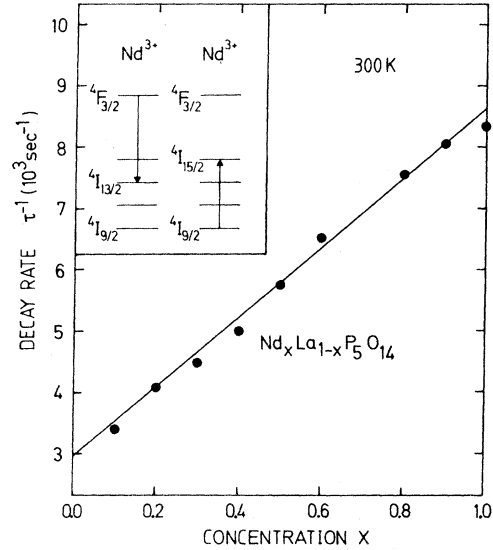


FIG. 1. Inverse lifetime τ^{-1} versus concentration x for $\text{Nd}_x\text{La}_{1-x}\text{P}_5\text{O}_{14}$. The individual nonradiative transitions involved in the cross-relaxation process are shown in the inset.

concentration dependence of the decay rate results from fluorescence quenching by interionic cross relaxation due to nonradiative energy transfer. In such an interaction process a donor ion decays

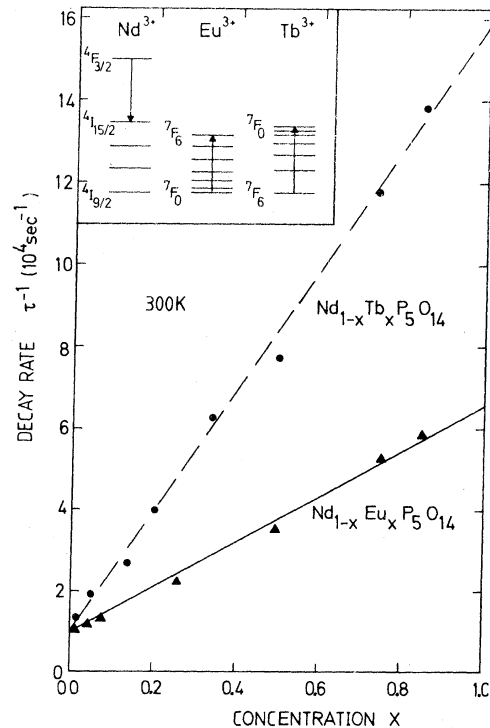


FIG. 2. Inverse lifetime τ^{-1} versus concentration x for $\text{Nd}_{1-x}\text{Tb}_x\text{P}_5\text{O}_{14}$ and $\text{Nd}_{1-x}\text{Eu}_x\text{P}_5\text{O}_{14}$. The cross-relaxation processes are indicated by the arrows in the inset.

nonradiatively from the excited state E_3 to an intermediate level E_2 while, simultaneously, a nearby acceptor ion is excited from its ground state E'_g to an intermediate state E'_2 . This process is illustrated in the right part of Fig. 3. The individual energy levels involved are indicated in the insets of Figs. 1 and 2. Any energy mismatch between the two transitions is accounted for by the emission of phonons.

In the case of $\text{Nd}_x\text{La}_{1-x}\text{P}_5\text{O}_{14}$, the Nd^{3+} ions act as donor ions as well as acceptor ions, which is commonly denoted as a self-quenching system,² La^{3+} being inert in this context. The concentration dependence of the measured Nd^{3+} decay rate $\tau^{-1}(x)$ originates from a concentration-dependent quenching rate $q(x)$ as expressed by Eq. (1):

$$\tau^{-1}(x) = \tau_0^{-1} + q(x), \quad (1)$$

where τ_0^{-1} is the intrinsic decay rate of an isolated Nd^{3+} ion. The intrinsic decay rate is primarily due to radiative transitions although a considerable portion may arise from multiphonon nonradiative processes.¹¹ However, this does not affect any of our conclusions.

From Fig. 2 it is evident that Tb^{3+} and Eu^{3+} acting as acceptor ions in an energy-transfer process are efficient quenchers of the Nd^{3+} fluorescence. Therefore increasing the acceptor concentration x results in an increase of the donor-acceptor quenching and a decrease in donor-donor quenching. For the overall quenching we must write

$$q(x) = q_D(x) + q_A(x). \quad (2)$$

From Figs. 1 and 2 it follows that all quenching rates $q_D(x)$ and $q_A(x)$ depend linearly on x within the full concentration range.

In a recent paper Flaherty and Powell⁷ have reported the Nd^{3+} self-quenching in $\text{Nd}_x\text{Y}_{1-x}\text{P}_5\text{O}_{14}$ to vary approximately as $x^{3/2}$ for $0.1 \leq x \leq 1$. However, they apparently were not aware that a phase transition occurs in this system at $x = 0.17$, which is correlated with a steplike change of the decay rate $\tau^{-1}(x)$.¹⁰ From a detailed investigation¹⁰ of the fluorescence behavior near the critical concentration $x = 0.17$, it turns out that on both sides of $x = 0.17$ the inverse lifetime $\tau^{-1}(x)$ and the quenching rate $q(x)$ depend linearly on the Nd^{3+} concentration x .

The linear concentration dependence of the Nd^{3+} self-quenching in $\text{Nd}_x\text{La}_{1-x}\text{P}_5\text{O}_{14}$ crystals has been observed by several authors.^{2-4,6,8} It has often been assumed that one could draw conclusions regarding the nature of the quenching mechanism from this behavior. However, no satisfactory explanation covering all experimental results could be given. The new experimental data presented in Fig. 2 show that the linear concentration depend-

ence of the quenching rate is not restricted to Nd^{3+} self-quenching but is also valid for $\text{Nd}_{1-x}\text{Tb}_x\text{P}_5\text{O}_{14}$ and $\text{Nd}_{1-x}\text{Eu}_x\text{P}_5\text{O}_{14}$. In the following section we will discuss a theoretical model which explains the observed concentration dependence of the fluorescence quenching in highly concentrated neodymium pentaphosphates.

Compounds like $\text{Nd}_{1-x}\text{Tb}_x\text{P}_5\text{O}_{14}$ represent donor-acceptor systems where both the donor and the acceptor concentration are fairly high for a wide range of x . This opens the way for fast energy migration among the donor ions. The excitation probability $P_D(i, E_3)$ for an individual donor i is affected by all deexcitation channels as illustrated in Fig. 3. Besides the pure radiative decay rate τ_0^{-1} and the transition rate $W_q(R_{ij})$ for a quenching process by acceptor j in distance R_{ij} , there is a transition probability $W_d(R_{ik})$ for energy migration to donor k . In the materials under consideration, fast energy migration has been observed by several authors,^{4,8,12,13} who reported this Nd-Nd transfer occurring on a 10-nsec time scale. It is reasonable that the excitation migration within the donor system is much faster than cross-relaxation quenching (compare Figs. 1 and 2). The process giving rise to migration is in exact energy resonance² while the quenching event by donor-acceptor transfer requires the participation of phonons for conservation of energy, which drastically reduces the transfer probability.^{14,15}

In order to describe the dynamics of fluorescence quenching by donor-acceptor cross relaxation we have included energy migration in the rate equation for the time-dependent probability $P_D(i, E_3)$ that donor i is in excited state E_3 . In a previous paper¹⁶ we have discussed the general theory and solved the rate equations in the fast migration limit. In the following we focus on the essential parts of the model which are necessary for the interpretation of the new results presented below.

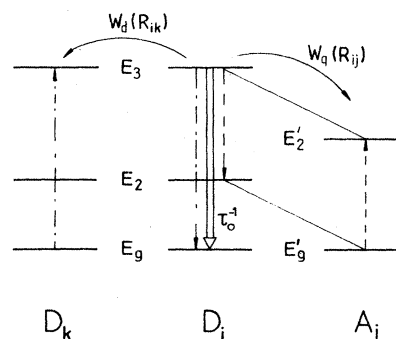


FIG. 3. Schematic illustration of donor-acceptor cross relaxation and donor-donor energy migration. See text for further explanation.

The total number $N_D(E_3)$ of excited donor ions is governed by the following rate equation:

$$\begin{aligned} \dot{N}_D(E_3) &= \sum_{i=1}^{N_D} \dot{P}_D(i, E_3) \\ &= \sum_{i=1}^{N_D} \left(-\frac{P_D(i, E_3)}{\tau_0} - P_D(i, E_3) \sum_{j=1}^{N_A} W_q(R_{ij}) \right). \end{aligned} \quad (3)$$

Energy migration leads to a spatial delocalization of excited states but not *per se* to a quenching of excitation energy. Thus the migration rate does not occur explicitly when the total number of donors is considered (compare Ref. 16). This, of course, does not mean that $N_D(E_3)$ is not affected by the migration process as will become evident in the following.

The sum over j in Eq. (3) is over the acceptors and denotes the overall quenching probability q_i for donor i surrounded by a specific environment of acceptor ions j . To good approximation the probability $P_A(j, E'_g)$ that the acceptor ions are in their ground state E'_g was assumed to be 1. The excitation density used in our experiments was sufficiently low and the intermediate states excited in the cross relaxation processes decay quickly by multiphonon emission.¹⁵ At this point we make use of the fact that the energy migration is very rapid in the systems of interest. Therefore to good approximation $P_D(i, E_3)$ is independent of i . This is expressed by spatial equilibrium with respect to the donor excitation in level E_3 , i.e., $P_D(i, E_3) = N_D(E_3)/N_D$, where N_D gives the total number of donor ions. The fast energy migration effectively averages over the various individual donor environments so that the quenching rate q_i is the same for all donors. Thus in Eq. (3) the sum over acceptor ions can be replaced by a sum over sites, each site being weighted with the probability x that it is occupied by an acceptor. Now we can write

$$q_i = \sum_{j=1}^{N_A} W_q(R_{ij}) = \sum_{j=1}^{N_s} W_q(R_{ij})x = \langle W_q \rangle x. \quad (4)$$

Equation (4) can be shown to be an exact result of a general configuration average.¹⁷ From crystallographic arguments each site sees the same surrounding of other sites, so that $\langle W_q \rangle$ is independent of i . That the averaged quenching rate is independent of the reference site is plausible because, in the fast diffusion limit, the excitation probability for each donor must decay at the same rate.

Finally it follows that

$$\dot{N}_D(E_3) = -\frac{N_D(E_3)}{\tau}, \quad (5)$$

where

$$1/\tau = 1/\tau_0 + \langle W_q \rangle x.$$

Thus we have obtained a unique macroscopic decay rate τ^{-1} for the whole crystal which determines a pure exponential deexcitation law. The overall quenching rate derived in our model depends linearly on the acceptor concentration x , as observed experimentally (Figs. 1 and 2). In the investigated rare-earth pentaphosphates the linear concentration dependence of fluorescence quenching is a simple result of a statistical averaging process by fast energy migration and is not connected with the form of the interionic interaction.

One might argue that our model fails when the donor concentration is reduced to the point where energy migration decreases. In a self-quenching system like $\text{Nd}_x\text{La}_{1-x}\text{P}_5\text{O}_{14}$ the ratio of the transfer rates for migration and cross relaxation is maintained as constant whatever the concentration because the Nd^{3+} ions act as donors as well as acceptors. In the more general system $\text{Nd}_{1-x}\text{Tb}_x\text{P}_5\text{O}_{14}$, decreasing donor concentration necessarily results in increasing the acceptor concentration. From statistical considerations it is reasonable that for high acceptor concentration each donor sees a nearly full acceptor environment; a relatively small number of donor-donor hoppings are necessary to average over the slightly different donor surroundings.

We should mention here that recently the implications of "supermigration" on the concentration dependence of Nd^{3+} self-quenching have been suggested.^{8,18} While these theories are similar to ours, we have given a detailed and rigorous derivation of Eq. (5),^{16,17} together with a clear physical discussion. We emphasize that we have made no assumptions concerning the spatial form of the interionic interaction during the development of our model. It turns out, in fact, that no information about the physical nature of interionic cross relaxation can be obtained from the linear concentration dependence of the macroscopic decay rate. The physics of the ion-ion interaction, which is hidden in $\langle W_q \rangle$ can, however, be elucidated by the low-concentration measurements which will be discussed in the next subsection. In Ref. 8 the result that the electric dipole-dipole coupling is apparently responsible for the cross relaxation in NdF_3 (Ref. 18) was simply taken over for the special case of $\text{NdP}_5\text{O}_{14}$. Assuming that energy transfer between Nd^{3+} ions *generally* occurs via dipole-dipole interaction is a very questionable procedure. Each host material exhibits a specific

environment with specific interionic spacings which, in principle, leaves the way open for different interionic coupling mechanisms.

B. Low concentration

From the model worked out in the preceding section it is evident that energy migration among donor ions has to be avoided if one wants to determine the interaction mechanism responsible for fluorescence quenching by donor-acceptor cross relaxation in rare-earth pentaphosphates. To accomplish this we have employed the system $\text{Nd}_{0.001}\text{Tb}_x\text{Gd}_{0.999-x}\text{P}_5\text{O}_{14}$ with an extremely diluted donor concentration. The quenching of the Nd-fluorescence by $\text{Nd}^{3+} \rightarrow \text{Tb}^{3+}$ energy transfer is strong enough so that it could be easily observed with time-resolved fluorescence spectroscopy for acceptor concentrations $0.02 \leq x \leq 0.12$. Gd^{3+} is inert with respect to the Nd^{3+} fluorescence. The small variation of the Tb^{3+} to Gd^{3+} ratio in the investigated interval of the Tb^{3+} concentration x does not alter the crystallographic phase of the crystals because the ionic radii of Gd^{3+} and Tb^{3+} differ only slightly. The monoclinic phase $P2_1/c$ was confirmed for each sample by fluorescence measurements as described above.

The intrinsic lifetime $\tau_0 = 285 \mu\text{sec}$ for the Nd^{3+} state ${}^4F_{3/2}$ was determined from the fluorescence decay in a $\text{Nd}_{0.001}\text{Gd}_{0.999}\text{P}_5\text{O}_{14}$ crystal. The $\text{Nd}_{0.001}\text{Tb}_x\text{Gd}_{0.999-x}\text{P}_5\text{O}_{14}$ crystals exhibit a statistical distribution of Nd^{3+} and Tb^{3+} ions. Each Nd^{3+} donor ion is surrounded by an individual environment of Tb^{3+} acceptors. As there is no longer energy migration within the diluted donor system, the various Nd^{3+} surroundings give different, individual contributions to the macroscopic fluorescence decay. Thus the measured fluorescence decay deviates from pure exponential curves. For this type of donor-acceptor system the fluorescence decay has been studied theoretically by Inokuti and Hirayama¹⁹ under the assumption that the energy-transfer processes result from electric multipole interactions.²⁰ According to the Inokuti-Hirayama model¹⁹ the normalized decay curves can be expressed by

$$\phi(t) = \exp\left[-\frac{t}{\tau_0} - \Gamma\left(1 - \frac{3}{s}\right) \frac{C}{C_0} \left(\frac{t}{\tau_0}\right)^{3/s}\right], \quad (6)$$

with $s = 6, 8$ and 10 , respectively, for electric dipole-dipole, dipole-quadrupole, and quadrupole-quadrupole interactions. C is the acceptor concentration. Energy transfer is assumed to occur within a single donor-acceptor pair. Neglect of higher-order interaction processes involving more than two ions is reasonable for the low concentrations under consideration.²¹ Then the energy-transfer probability $n(R)$ for interionic multipole

coupling depends isotropically on the donor-acceptor distance R

$$n(R) = \left(\frac{R_0}{R}\right)^s \frac{1}{\tau_0}, \quad (7)$$

where the so-called critical interionic spacing R_0 is defined by $n(R_0) = 1/\tau_0$. R_0 corresponds to a critical concentration $C_0 = 3/4\pi R_0^3$ in Eq. (6).¹⁹

To determine the appropriate multipole interaction one has to analyze the measured decay curves with respect to Eq. (6). This can easily be done by plotting $\ln[-\ln\phi(t) - t/\tau_0]$ versus $\ln t/\tau_0$. From Eq. (6) one expects a straight line with the characteristic slope $3/s$. Figure 4 contains such double logarithmic plots for five different Tb^{3+} concentrations x . For $0.02 \leq x \leq 0.08$ the resulting straight lines have slopes in the range $0.51-0.53$ while the curve for $x = 0.12$ has slope 0.59 . From these values it is evident that the electric dipole-dipole interaction ($s = 6$) is the dominant interionic coupling mechanism. Dipole-quadrupole and quadrupole-quadrupole interactions would yield slopes of $\frac{3}{8} = 0.375$ and $\frac{3}{10} = 0.3$, respectively. The slight deviation of the slope value for $x = 0.12$ may be an indication that the Inokuti-Hirayama theory¹⁹ already begins to fail at this Tb^{3+} concentration. We emphasize that the statistics introduced in the model are valid only at low-acceptor concentrations.^{15,19}

The critical Nd^{3+} - Tb^{3+} distance R_0 for the dipole-dipole energy-transfer probability can now be derived from each of the measured decay curves. Using $s = 6$ and $\phi(t)$ evaluated at $t = \tau_0$ from Eq. (6) we have calculated R_0 for each of the five curves in Fig. 4. The average value is $R_0 = 8.06 \text{ \AA}$ with $\pm 3\%$ variation in the individual values. Since $s = 6$ was inserted in Eq. (6) the good agreement of the five values obtained for R_0 confirms the electric dipole-dipole interaction for the Nd^{3+} - Tb^{3+} cross relaxation.

As both the donor and the acceptor concentrations are low in the systems investigated above, it makes sense to define an average donor-acceptor distance \bar{R} by $\bar{R} = (3/4\pi C)^{1/3}$. The Inokuti-Hirayama model¹⁹ then enables one to determine the energy-transfer probability $n(\bar{R})$ for a Nd^{3+} - Tb^{3+} pair with spacing \bar{R} . Using the lifetime τ_e given by $\phi(\tau_e) = (1/e)\phi(0) = 1/e$, Eqs. (6) and (7) yield the following expression for $n(\bar{R})$ (Ref. 22):

$$n(\bar{R}) = \left[\Gamma\left(1 - \frac{3}{s}\right)\right]^{-s/3} \frac{1}{\tau_e} \left(1 - \frac{\tau_e}{\tau_0}\right)^{s/3}. \quad (8)$$

Using $s = 6$ and the measured values for τ_e and τ_0 we have evaluated $n(\bar{R})$ for the \bar{R} 's corresponding to the concentrations studied. The results are plotted semilogarithmically in Fig. 5. The slope of the resulting straight line corresponds to a

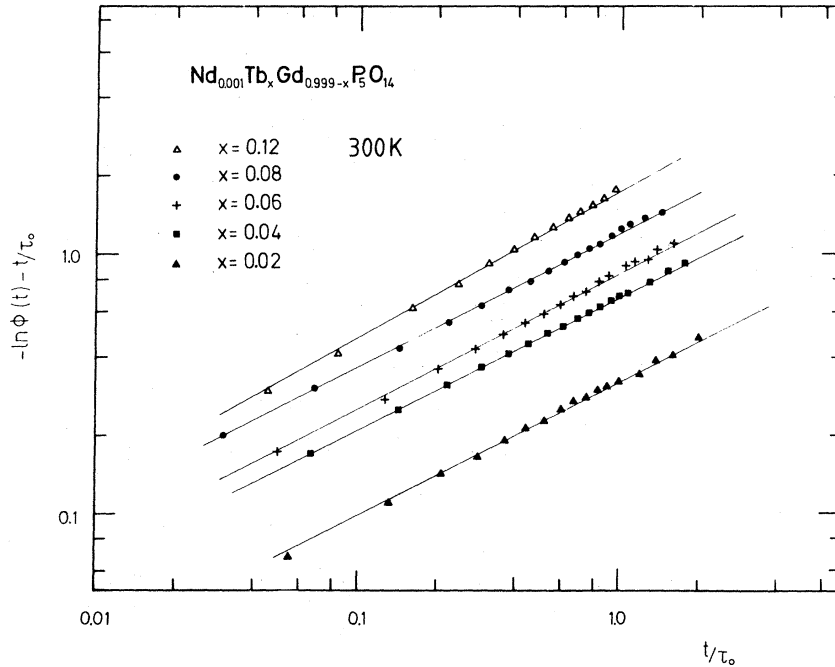


FIG. 4. Luminescence decay of the ${}^4F_{3/2}$ state of Nd^{3+} in $\text{Nd}_{0.001}\text{Tb}_x\text{Gd}_{0.999-x}\text{P}_5\text{O}_{14}$. $[-\ln \phi(t) - t/\tau_0]$ as derived from measured fluorescence decay curves $\phi(t)$ vs t/τ_0 for five different Tb^{3+} concentrations x .

$R^{-5.8}$ power law. Thus Fig. 5 is an illustration of the R^{-6} dependence²⁰ of the energy-transfer rate with interionic dipole-dipole coupling. Furthermore, it is indeed a confirmation of the uniqueness of our determination of $s=6$ since substituting a value of s other than 6 in Eq. (8) does not lead to a power law $n(\bar{R}) \sim \bar{R}^{-s}$ with the same s , i.e., the determination of the transfer rate is only self-consistent for $s=6$.

IV. DISCUSSION

In Sec. III A we have studied the macroscopic behavior of fluorescence quenching by cross relaxation in highly concentrated rare-earth pentaphosphates. Each of the systems we investigated can be characterized by an overall quenching rate $q(x) = \langle W_q \rangle x$ which depends linearly on the concentration of the quenching ions. For the low-concentrated donor-acceptor system employed in Sec. III B we have found the cross-relaxation process to be caused by electric dipole-dipole interaction. The microscopic picture of interionic interaction used for these investigations enables us to evaluate the averaged quenching parameter $\langle W_q \rangle$ characterizing the fluorescence quenching in highly concentrated materials. Equations (4) and (7) lead to the following expression for $\langle W_q \rangle$ where the summation is over all rare-earth sites:

$$\langle W_q \rangle = \sum_{j=1}^{N_s} W_q(R_{ij}) = \sum_{j=1}^{N_s} \frac{1}{\tau_0} \left(\frac{R_0}{R_{ij}} \right)^s. \quad (9)$$

Thus $\langle W_q \rangle$ denotes the total quenching rate of a donor ion i embedded within a complete acceptor environment: $\langle W_q \rangle$ is given by summing the contributions of all individual acceptors located at distances R_{ij} . The parameter $\langle W_q \rangle$ is actually realized as quenching rate $q(x=1) = \langle W_q \rangle \times 1$ in the system $\text{Nd}_{1-x}\text{Tb}_x\text{P}_5\text{O}_{14}$ for $x \rightarrow 1$ where it describes the overall strength of fluorescence quenching by $\text{Nd}^{3+} \rightarrow \text{Tb}^{3+}$ energy transfer. For the $\text{Nd}^{3+} - \text{Tb}^{3+}$ interaction, τ_0 , R_0 , and s have been determined in Sec. III B. The spacings R_j follow from the lattice geometry known from crystallographic data.²³ Thus we can calculate $\langle W_q \rangle$ for $\text{Nd}_{1-x}\text{Tb}_x\text{P}_5\text{O}_{14}$ from Eq. (9).

In $\text{Nd}_{1-x}\text{Tb}_x\text{P}_5\text{O}_{14}$ for the concentration limit $x \rightarrow 1$ each Nd^{3+} ion has eight nearest Tb^{3+} neighbors located at $5.2 \text{ \AA} \leq R_j \leq 7.7 \text{ \AA}$.²³ The main contributions to $\langle W_q \rangle$ come from this nearest-neighbor shell and these contributions will be added individually. The contributions of all other acceptors can be approximated by assuming a uniform distribution and integrating. Thus we write

$$\langle W_q \rangle = \frac{R_0^6}{\tau_0} \left(\sum_{j=1}^8 R_j^{-6} + N_0 \int_{\bar{R}} r^{-6} 4\pi r^2 dr \right). \quad (10)$$

N_0 denotes the concentration of R^{3+} sites, i.e., the maximum R^{3+} concentration in RP_5O_{14} , $N_0 = 4 \times 10^{21}$

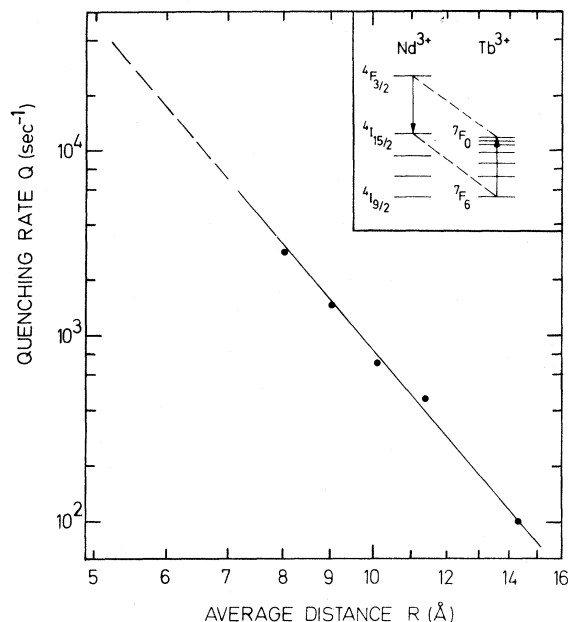


FIG. 5. Quenching rate $P(R)$ calculated from Eq. (8) as function of the average $\text{Nd}^{3+} - \text{Tb}^{3+}$ distance \bar{R} in $\text{Nd}_{0.001}\text{Tb}_x\text{Gd}_{0.999-x}\text{P}_5\text{O}_{14}$. \bar{R} is related to the actual Tb^{3+} concentration C by $\bar{R} = (3/4\pi C)^{1/3}$. The inset illustrates the $\text{Nd}^{3+} - \text{Tb}^{3+}$ fluorescence quenching process.

cm^{-3} .² Taking the individual distances R_i from Ref. 23 and assuming $\bar{R} = 9 \text{ \AA}$ we obtain $\langle W_q \rangle = 1.38 \times 10^5 \text{ sec}^{-1}$. This calculation is based on the assumption of cross relaxation by dipole-dipole interaction which so far has only been determined for low concentrations of Nd^{3+} and Tb^{3+} ions. However, $\langle W_q \rangle$ can also be directly obtained from the decay measurements at high concentration. The slope of the straight line observed for the concentration dependence of $q(x)$ in Fig. 2 yields $\langle W_q \rangle = 1.54 \times 10^5 \text{ sec}^{-1}$. This value is in fairly good agreement with the calculation above. This result indicates that no additional interionic coupling mechanisms other than the dipole-dipole interaction need be assumed at high Nd^{3+} and Tb^{3+} concentrations. The fluorescence quenching of Nd^{3+} ions by Tb^{3+} ions in rare-earth pentaphosphate crystals can be consistently described by electric dipole-dipole energy transfer throughout the full concentration range.

The calculation of $\langle W_q \rangle$ also shows that for acceptor concentration $x \rightarrow 1$, about 50% of the overall quenching is due to the two nearest neighbors which are located at 5.2 and 5.9 \AA .²³ The other six neighbors in the first R^{3+} coordination sphere contribute 34% and the remaining environment contributes 16%, which is by no means negligible.

The thorough investigation of $\text{Nd}_{1-x}\text{Tb}_x\text{P}_5\text{O}_{14}$ and $\text{Nd}_{0.001}\text{Tb}_x\text{Gd}_{0.999-x}\text{P}_5\text{O}_{14}$ has yielded a determination of the physical nature of the $\text{Nd}^{3+} - \text{Tb}^{3+}$ interaction.

Although no completely rigorous conclusions about the interaction mechanisms in other rare-earth pentaphosphates can be drawn, some arguments concerning the general situation in these compounds can be given. In general, two essentially different interionic couplings are discussed when energy-transfer processes between rare-earth ions are considered,²⁴ i.e., electrostatic multipole interactions and exchange interactions.^{15, 19, 20, 24} Exchange interactions are due to charge cloud overlap of the interacting ions. Thus coupling by exchange depends on the spatial range of the ionic wave functions and the interionic spacing, the latter being given by the lattice structure of rare-earth pentaphosphate. The electronic states under consideration are derived from the $4f$ wave functions of trivalent rare-earth ions. The range of the $4f$ wave functions varies only slightly throughout the series of R^{3+} ions; their radial maximum of about 0.3 \AA is small compared to the nearest-neighbor distance of 5.2 \AA .²⁵ Since no effects of exchange interactions have been observed in the investigations of the $\text{Nd}^{3+} - \text{Tb}^{3+}$ energy transfer it seems reasonable that exchange interactions can be generally ruled out for energy-transfer processes in rare-earth pentaphosphates. From the same arguments this generalization may even be extended to other known rare-earth miniature laser materials^{2, 3, 4} exhibiting similar minimum rare-earth spacings.

However, electric multipole interactions of higher order than the dipole-dipole type may give nonvanishing contributions to energy-transfer processes between rare-earth ions other than Nd^{3+} and Tb^{3+} . Which multipole interaction is dominant depends in a complicated manner on the oscillator strength of the individual multipole transitions coupled in the nonradiative energy-transfer process (see Fig. 3) as outlined by Dexter.²⁰ Although electric quadrupole transitions make a negligible contribution to radiative decay probabilities they can be important for the interionic energy transfer.²⁴ In particular cases, e.g., electric dipole-quadrupole interactions may dominate electric dipole-dipole interactions. Nevertheless, we argue that the Nd^{3+} -self quenching in the laser material $\text{Nd}_x\text{La}_{1-x}\text{P}_5\text{O}_{14}$ is due to electric multipole interaction, whatever the dominant multipole term may be.

The relative weakness of cross relaxation in $\text{NdP}_5\text{O}_{14}$ as compared to, e.g., $\text{Nd}:\text{YAG}$ (yttrium aluminum garnet) is usually explained by the different energy-level schemes in these compounds.^{2, 4, 5} The energetic position of the intermediate states involved in the energy-transfer process (compare Fig. 1) allows an energy resonant transfer process in $\text{Nd}:\text{YAG}$.⁵ In $\text{NdP}_5\text{O}_{14}$

there is a slight shift of these states²⁶ so that considerable phonon assistance is required for energy conservation in interionic cross relaxation. Thus the transfer probability is reduced. However, in $K_5NdLi_2F_{10}$ (Ref. 27) the quenching is weak in spite of the energy resonance. Thus, in addition to resonance, other parameters such as transition probabilities, selection rules, and interionic spacings may be important.

V. CONCLUSIONS

We have investigated energy-transfer processes between various rare-earth ions in rare-earth pentaphosphates. Time-resolved fluorescence spectroscopy measurements were performed for high as well as for low concentration of the interacting rare-earth ions. First, examples were given confirming the linear concentration dependence of fluorescence quenching in these compounds. Introducing rapid spatial migration of excited states into the dynamics of the quenching process, we developed a statistical model which describes the observed interaction behavior at high concentrations. It turned out that in crystals like $Nd_{1-x}Tb_xP_5O_{14}$ the fast energy migration among the donor ions results in an efficient averaging process over the different surrounding environments of the excited ions. In such a system the fluorescence quenching by donor-acceptor cross relaxation is thus determined by an averaged quenching rate which causes the overall deexcitation of the crystal to vary linearly with the acceptor concentration x . From our model it is evident that the unusual linear concentration dependence of the fluorescence quenching is a direct result of a

statistical averaging process due to fast energy migration. It does not originate from a specific type of the interionic interaction mechanism as suggested in previous papers.^{2,3,6}

In order to determine explicitly the interionic coupling involved we employed the system $Nd_{0.001}Tb_xGd_{0.999-x}P_5O_{14}$ as a probe. In these crystals the strength of donor-acceptor interaction was varied by altering the Tb^{3+} concentration x while energy migration between the extremely diluted Nd^{3+} ions remained negligible. The observed fluorescence decay curves show a behavior as expected from the Inokuti-Hirayama theory¹⁹ for fluorescence quenching by electric dipole-dipole interaction. Based on these results we presented a model from which the averaged quenching rate for $Nd_{1-x}Tb_xP_5O_{14}$ could be calculated using a microscopic picture for the energy-transfer processes. Since this calculation is in good agreement with the directly measured rate, the electric dipole-dipole interaction is confirmed for the entire range of Nd^{3+} and Tb^{3+} concentrations in rare-earth pentaphosphate. Whereas direct results were obtained for the Nd^{3+} - Tb^{3+} interaction, some straightforward arguments could be given which make it reasonable that energy-transfer processes in other rare-earth pentaphosphates also are due to electrostatic Coulomb interaction.

ACKNOWLEDGMENTS

Fruitful discussions with H. G. Danielmeyer are gratefully acknowledged. We would like to thank F. Lutz for assistance in growing the crystals. One of the authors (W. L.) wishes to thank the Deutsche Forschungsgemeinschaft for support.

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