

Trapping of optical excitation by two types of acceptors in $\text{La}_{0.72}\text{Pr}_{0.25}\text{Nd}_{0.03}\text{F}_3$

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We have investigated the process of quenching of fluorescence from the 3P_0 state of Pr^{3+} in $\text{La}_{0.72}\text{Pr}_{0.25}\text{Nd}_{0.03}\text{F}_3$ due to cross relaxation to Pr and Nd ions. The fluorescence decay of the ensemble of Pr ions after pulsed excitation is measured as a function of temperature in the (2–70)-K region. Cross relaxation occurs either directly or through a donor-donor transfer within the inhomogeneous line. Knowledge of the dynamics occurring within the inhomogeneous line derived from previous fluorescence line-narrowing experiments is used to analyze the cross-relaxation process from a microscopic viewpoint according to models for fluorescence decay in the presence of traps. In general the decay is consistent with an electric dipole-dipole transfer mechanism. At 2 K the decay can be well described by a direct transfer to Pr and Nd traps without donor-donor transfer. The temperature dependence of the decay at long times can be described for $35 < T < 70$ K by the hopping model. The agreement with theory is much better if the cross relaxation to Nd ions is assumed to occur mainly via the lowest Stark level of the $^4I_{9/2}$ manifold.

I. INTRODUCTION

Energy transfer is one of the oldest problems concerning the luminescence of solids and has been the subject of many recent investigations.^{1,2} In general, two types of ions are involved; we will refer to them as donor ions and acceptor ions. Initially, some fraction of the donors are optically excited. This excitation can migrate among the donors or be transferred to the acceptors. Energy migration within an inhomogeneously broadened system of ions in the absence of traps has been studied experimentally and theoretically and is generally well understood.¹ When acceptor ions, or traps, are randomly distributed around the donors, transfer of energy from the excited donors to the acceptors can occur in addition to energy transfer among the donors. Since there is a random distribution of both donors and acceptors, there is a distribution of donor-acceptor separations and therefore a distribution of donor-acceptor transfer rates. In addition, the temperature dependences of donor-donor (DD) transfer and donor-acceptor (DA) transfer are generally different. Thus, the decay of an excited set of donor ions is rather complex.

In this paper we continue the recent studies of energy transfer in LaF_3 doped with Pr and Nd ions. Previous investigations on $\text{LaF}_3:20$ at. % Pr (Ref. 3) and $\text{PrF}_3:5$ at. % Nd (Ref. 4) have provided estimates of the various microscopic transfer parameters in this system, and have enabled the theoretical predictions and limitations of various models to be tested. In all of this work, the 3P_0 level of the Pr (donor) ions was resonantly excited, and the subsequent decay of the 3P_0 -level population was monitored via the nonresonant 3P_0 - 3H_6 transition. Trapping can take place, either directly or indirectly, following migration among the donors. We now consider a general case in which the donors and acceptors are unlike ions, and both systems are disordered. (This is the usual situation in

transfer studies in glasses.) For this study we chose the system $\text{La}_{0.72}\text{Pr}_{0.25}\text{Nd}_{0.03}\text{F}_3$. Here, we have Pr-Pr intraline transfer, Pr-Nd transfer, as well as the additional complication of Pr-Pr cross relaxation. However, by varying the temperature the relative importance of the various transfer mechanisms can be altered.

This work is organized as follows: Section II of this paper outlines some of the theoretical details and background relevant to this study. Section III describes the experimental procedure. In Sec. IV we present the experimental results and interpret them with the aid of theoretical models. Finally, in Sec. V we comment on the results and conclusions which may be drawn from this work.

II. BACKGROUND REVIEW

We will principally be concerned with the behavior of the 3P_0 system of $\text{LaF}_3:\text{Pr}^{3+}$ with additional Nd^{3+} doping. LaF_3 is, of course, an ideal host for energy-transfer studies since it can be doped with Pr and Nd over a wide range of concentrations. A sequence of studies have been conducted on a number of the transfer properties in $\text{La}_{1-x}\text{Pr}_x\text{F}_3$ and $\text{La}_{1-x-y}\text{Pr}_x\text{Nd}_y\text{F}_3$, which serve as the departure of this study. We summarize the various relevant results of previous studies below.

A. Experimental background

1. DD transfer within the 3P_0 state of $\text{LaF}_3:\text{Pr}^{3+}$

In earlier work on $\text{La}_{1-x}\text{Pr}_x\text{F}_3$ (Refs. 5 and 6) the DD transfer mechanism between Pr ions has been characterized through fluorescence line-narrowing measurements and was found to be of the electric dipole-dipole character with a characteristic dependence on separation with a characteristic dependence on separation $W_{on}^{\text{DD}} = \beta/R_{on}^6$ where W_{on}^{DD} is the DD transfer rate between ions at site o and n , and β is the DD transfer parameter. R_{on} is the separation of sites o and n . The tem-

perature dependence of the transfer is included in the parameter β , which contains the matrix elements of the interaction. For x up to 0.2, β is found to have a T^3 dependence on temperature.

2. Pr-Pr self-quenching

Because of the complexity of the Pr^{3+} energy levels, Pr ions themselves can serve as quenching centers for the 3P_0 excitation. Thus, nonradiative cross relaxation between Pr ions also occurs in which the intermediate states of the cross-relaxing pair of ions, i.e., 3H_6 and 1D_2 play the role of optical traps.³ The transfer rate for this process is independent of temperature for $T < 30$ K. The decay of the 3P_0 level for intermediate concentration of Pr (e.g., 20 at. %) is nonexponential at low temperatures. It becomes faster with increasing temperature until, for $T > 30$ K, the decay becomes a single exponential. From results alluded to in Sec. IIA 1 above, at 2 K, the DD transfer rate is much smaller than the cross-relaxation (DA) rate and by fitting the decay data to the Inokuti-Hirayama model,⁷ appropriate to this situation, the interaction mechanism can be identified. In $\text{LaF}_3:\text{Pr}$, the Pr-Pr cross-relaxation rate is governed by a dipole-dipole interaction, scaling again as $X_{on}^B = \alpha_B / R_{on}^6$, where α_B is the transfer parameter. X_{00}^B , the nearest-neighbor transfer rate, was estimated to be $8.9 \times 10^4 \text{ s}^{-1}$ at low temperatures, and extrapolating to PrF_3 , the observed decay rate was successfully predicted. Owing to cross relaxation, the lifetime of the 3P_0 state drops from 50 μs to 700 ns as the concentration of Pr is increased, for example, from the dilute limit to 100 at. %.

3. Trapping of 3P_0 excitation

Additional de-excitation channels may be introduced by adding other impurities to $\text{LaF}_3:\text{Pr}^{3+}$.⁴ For example, whereas in pure PrF_3 the 3P_0 level decays exponentially at 2 K, the decay is nonexponential when small amounts of Nd are added. The decay also becomes faster with increasing temperature, being fully exponential at 20 K and temperature independent above ~ 40 K. By contrast, the decay in pure PrF_3 remains constant in this temperature range. The nonexponential decay is again ascribed to transfer to the traps (in this case Nd ions) and the low-temperature data again yield a dipole-dipole mechanism for the transfer with a rate of $X_{on}^A = \alpha_A / R_{on}^6$, where α_A is the Pr-Nd cross-relaxation parameter.⁴ The exponential decay at higher temperature in $\text{PrF}_3:\text{Nd}$ and in $\text{LaF}_3:\text{Pr}$ occurs because β , by virtue of its strong temperature dependence, rapidly becomes much larger than α_A (or α_B). In this situation, the Pr excitation can sample all of the environments before reaching a trap site, and the transfer to traps is limited only by the Pr-trap step in the transfer chain.

4. Alternate transfer mechanisms

Finally, a different interpretation of the transfer in $\text{LaF}_3:\text{Pr}$, in which a short-range exchange interaction was suggested as the transfer mechanism, has been proposed by Vial and Buisson.⁸ Transfer to only two groups of near-neighbor ions (rather than the much larger set impli-

cit in the long-range dipole-dipole model) is considered in their scheme. The rates of transfer to these ions were determined in dilute samples by measuring the decay times of certain satellite transitions of the $^3P_0 \rightarrow ^3H_4$ transition in weakly doped LaF_3 . With the use of these rates, the nonexponential decay of $\text{LaF}_3:20 \text{ at. \% Pr}$ at 2 K could be accurately predicted. The assumption that a small fraction ($\sim 10 \text{ at. \%}$) of the Pr ions did not transfer to traps, which was required to explain the data in Ref. 3, was not necessary in this case.

Despite the preceding comments, a broad range of experimental results in the Pr^{3+} system have been satisfactorily explained by assuming a dipole-dipole interaction for the various transfer mechanisms. By summarizing previous studies, it has been found that $\alpha_A = 5.46 \times 10^{-38} \text{ cm}^6 \text{ s}^{-1}$,⁴ and $\alpha_B = 3 \times 10^{-40} \text{ cm}^6 \text{ s}^{-1}$ below 30 K; the former increases by a factor of 5 at 70 K.³ β varies with temperature as T^3 below 30 K and has the value $18.8 \times 10^{-40} \text{ cm}^6 \text{ s}^{-1}$ at 14 K.⁶

B. Theoretical background

Theoretical treatments of the dynamics of donor fluorescence usually begins with a set of coupled rate equations for the donors. Their solution yields an expression for the fluorescence intensity $I(t)$ at time t after pulsed excitation in the form⁹

$$I(t) = I(0)e^{-\gamma_R t} f(t), \quad (1)$$

where γ_R is the intrinsic decay rate and $f(t)$ denotes the fraction of excited donors which would be present at time t if the excited state had an infinite radiative lifetime. When there is no donor-donor transfer and there are two distinct types of acceptors, $f(t)$ is given exactly by the expression^{7,10,11}

$$f(t) = \prod_n [1 - C_A - C_B + C_A \exp(-X_{on}^A t) + C_B \exp(-X_{on}^B t)], \quad (2)$$

where C_A, C_B are the relative concentrations of the acceptors of type A, B , respectively, and $X_{on}^{A,B}$ denotes the transfer rate from a donor on the site o to an acceptor (type A or B) at site n . Assuming that there is a random distribution of acceptors in the lattice sites, C_A and C_B represent the probability that a lattice site is occupied by an acceptor of type A or B . Therefore, the product in Eq. (2) contributes a factor of $\exp(-X_{on}^A t)$ or $\exp(-X_{on}^B t)$ to $f(t)$ for every site occupied by an acceptor of type A or B , respectively, and the factor unity for every site which does not contain an acceptor. When the transfer occurs via the dipole-dipole interaction, Eq. (1) may be written as

$$I(t) = I_0 e^{-\gamma_R t} \prod_n \left\{ 1 - C_A \left[1 - \exp\left(-\frac{\alpha_A t}{R_{on}^6}\right) \right] - C_B \left[1 - \exp\left(-\frac{\alpha_B t}{R_{on}^6}\right) \right] \right\}. \quad (3)$$

It can easily be verified that even when $\alpha_B / \alpha_A \ll 1$, but $C_A < C_B \ll 1$, the effect of B -type acceptors can be significant.

An exact calculation of $f(t)$ can also be made when the DD transfer is infinitely rapid. In this rapid migration limit it is assumed that all donors are in contact with one another and that the DD transfer takes place so quickly that for $t > 0$ all donors have an equal probability of being excited. In this case $f(t)$ is an exponential,⁹

$$f(t) = \exp \left[- \left(C_A \sum_n X_{on}^A + C_B \sum_n X_{on}^B \right) t \right], \quad (4)$$

and the total decay rate is only the sum of the transfer rates to all the lattice sites, weighted by the probability of occupation by an A or B ion. We caution here that in applying these relations it is necessary that the transfer be incoherent, i.e., that no phase information is transferred. In our case, this allows the Pr donor-to-donor and the Pr→Pr donor-to-acceptor quenching process to be decoupled, each process being incoherent and each having its own transfer rate. Under these conditions, the Pr ions participating in the DA transfer act as "traps" in a manner analogous to the physically distinct Nd centers.

The behavior of $f(t)$ in the regime between these two limits is extremely complicated and the theories which have been developed for $f(t)$ are based on models or approximations. In one extreme, when $\beta > \alpha_A, \alpha_B$, and $C_A, C_B \ll 1$, the hopping model¹² of Burshtein may be used to describe the excitation transfer. At the other extreme, when $\beta < \alpha$, a diffusion model¹³ is appropriate. However, both models predict that the decay of the donor population will initially be nonexponential but should approach an exponential behavior at long times.⁹

We note that there are no models in existence which are addressed to the most general case, i.e., a solution of the population dynamics regardless of the relative values of α_A , α_B , and β . It is understood that this general case poses a formidable theoretical problem which still awaits a solution.

As noted, previous investigations of LaF₃:Pr (Ref. 4) or PrF₃:Nd (Ref. 3) have been concerned with understanding the dynamics of transfer from donor to one-type of acceptor as the DD transfer rate was systematically altered by a variation of the sample temperature. In this study we examine the more complex situation in which, in addition to DD transfer (β), we have transfer to two different types of acceptors with different transfer rates (α_A, α_B). Again, through a variation of the sample temperature, the ratios of DD to DA transfer rates can be varied. Through this variation, the conditions necessary for the application of the different theoretical models can be obtained in a single system.

III. EXPERIMENTAL PROCEDURE

A single crystal with nominal concentration La_{0.75}Pr_{0.20}Nd_{0.05}F₃ was obtained from Optovac, Inc. The concentrations were checked using the electron-microprobe analysis technique¹⁴ with LaF₃, NdF₃, and PrF₃ standards and the actual composition was found to be La_{0.72}Pr_{0.25}Nd_{0.03}F₃. This composition was found to be uniform across the sample, to within the experimental accuracy of the technique (~ 1 at. %), and with a spatial

resolution of $\sim 2 \mu$. The sample was immersed in superfluid helium for the 2-K measurements or on the cold finger of a continuous-flow cryostat for higher temperatures. The temperature was measured using a carbon-glass resistor mounted next to the sample and was varied continuously from 5 to 70 K via a wound heating coil around the cold finger operated by a feedback temperature controller.

A nitrogen-laser-pumped dye laser of the grazing incidence configuration was the optical-excitation source. The laser pulse was ~ 10 ns long and the spectral width was approximately equal to the inhomogeneous width (full width at half maximum) of the ${}^3H_4(1)$ - 3P_0 absorption line. In this way, a representative distribution within the whole inhomogeneous broadened system of Pr ions were excited. The decay of the 3P_0 level population was measured after each excitation pulse by monitoring the nonresonant fluorescence (at 16710 cm^{-1}) of the 3P_0 - ${}^3H_6(1)$ transition. The spectrometer slit was adjusted so that the resolution was equal to the spectral width of the fluorescence, since the theoretical models yield an expression for the intensity integrated over the inhomogeneous linewidth. A Princeton Applied Research 162 boxcar integrator, with a nominal resolution of 5 ns, was used for the decay analysis. Time-resolved fluorescence line-narrowing was conducted within the 3P_0 inhomogeneous line at low temperatures. The results agree with previous studies and, for the sake of consistency, the DD rates used below are as per the literature.⁴⁻⁶

IV. EXPERIMENTAL RESULTS

The results of our experiments consist of decay profiles of the nonresonant luminescence from the 3P_0 level of Pr in La_{0.72}Pr_{0.25}Nd_{0.03}F₃ after pulse excitation. The decay of this fluorescence at 2 K is shown in Fig. 1. At this temperature, with the use of the values obtained for β , α_A , and α_B in previous studies (Sec. II A), β is $\ll \alpha_A, \alpha_B$, and therefore Eq. (3) should provide a good description of the

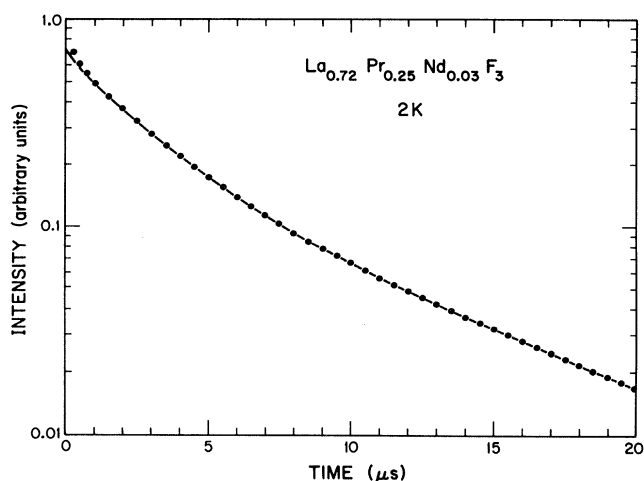


FIG. 1. Plot of the decay of the 3P_0 state of Pr^{3+} in $\text{La}_{0.72}\text{Pr}_{0.25}\text{Nd}_{0.03}\text{F}_3$ at 2 K. The points are the experimental data and the solid curve is the best fit to Eq. (3).

decay. By using $\gamma_R = 2 \times 10^4 \text{ s}^{-1}$ (i.e., radiative lifetime = 50 μs), $C_A = 0.03$, and $C_B = 0.25$, the experimental decay was fitted to Eq. (3) using various values of α_A , α_B , and values of r_{on} calculated from the crystal structure. The first 300 neighbors of an excited ion were included in the calculation. The best agreement with the experimental data was obtained with the values $\alpha_A = 2.5 \times 10^{-38} \text{ cm}^{-6} \text{ s}^{-1}$ and $\alpha_B = 1.5 \times 10^{-40} \text{ cm}^{-6} \text{ s}^{-1}$ for the Pr-Nd and Pr-Pr transfer parameters, respectively. The decay calculated with the use of these values is shown as the solid curve in Fig. 1. The values of α_A and α_B obtained are approximately a factor of 2 smaller than the estimates obtained in previous studies.^{3,4} The calculated curve by using the latter values showed large deviations from the experimental data. Since the trap concentrations were not accurately known in the earlier studies of LaF₃:20 at. % Pr or PrF₃:5 at. % Nd, the agreement with the earlier data can be considered adequate. We should point out that if we neglect the Pr-Pr cross relaxation in this sample, i.e., set $C_B = 0$ in Eq. (3), then the best fit to the 2 K data obtains $\alpha_A = 5.8 \times 10^{-39} \text{ cm}^{-6} \text{ s}^{-1}$ for the Pr-Nd transfer parameter, a factor of 10 smaller than that reported previously. We also attempted to fit the data to Eq. (3) with $\alpha_B = 0$, i.e., no Pr-Pr cross relaxation but assuming instead a short-range interaction between the Pr ions and including additional terms in the product as in Ref. 8. (The appropriate fluorescence quenching rates were taken from Ref. 8.) The best fit, which still showed a 10% discrepancy from the experimental data at early times, gave $\alpha_A = 8.1 \times 10^{-39} \text{ cm}^{-6} \text{ s}^{-1}$, again in total disagreement with the earlier measurement. The values of α_A and α_B obtained from the fit at 2 K were used to interpret the higher-temperature data, as will be discussed later.

At higher temperatures, the decay becomes exponential at long times as predicted by the theoretical models. Figure 2 shows typical decay curves obtained at 40, 50, and

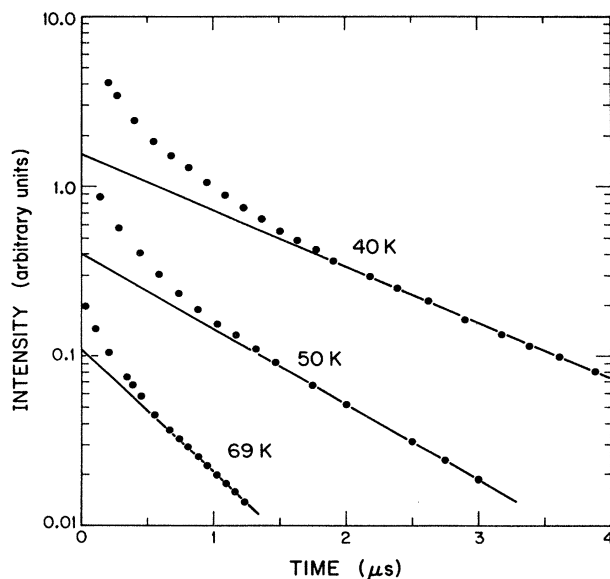


FIG. 2. Plot of the decay of the 3P_0 state of Pr^{3+} at different temperatures. The asymptotic decay at long times is emphasized for clarity.

69 K. However, the interpretation of the data at higher temperatures is complicated since the ratios β/α_A and β/α_B are such that different theoretical models are required to describe the transfer from the donor population to the two types of acceptors. For example, at 14 K, $\beta/\alpha_A = 0.08$ suggests that a diffusion model is appropriate for the Pr-Nd transfer, while $\beta/\alpha_B = 13$ indicates that the hopping model is appropriate for the Pr-Pr transfer. The corresponding ratios in the (35–70)-K range are 1.17–9.4 and 176–1808, respectively. Thus the hopping model, valid when $\beta \geq \alpha$, should apply to the Pr-Nd transfer; the rapid-migration model, valid when $\beta \gg \alpha$, should apply to the Pr-Pr transfer. In this temperature range we attempt a quantitative comparison between the experimental measured asymptotic decay rates and the values predicted by these models. For the hopping model, a general expression for the asymptotic decay rate W_{as} has been derived by Huber,⁹ and for the case of an electric dipole-dipole interaction, the asymptotic decay rate due to transfer to the Nd acceptors can be written as

$$W_{as} = \frac{4}{9} \pi^{7/2} n_D n_A (\alpha_A \beta)^{1/2} \times \left[1 - \frac{2}{\pi} \tan^{-1} [3.71 r_c^3 n_D (\beta/\alpha_A)^{1/2}] \right], \quad (5)$$

where the factor in large parentheses ensures that W_{as} has the correct behavior in the rapid-migration limit. This will be the case when r_c is chosen such that

$$\frac{4}{3} \pi \frac{n_A}{r_c^3} = C_A \sum_{n \neq 0} \frac{1}{R_{on}^6} \quad (6)$$

and n_D , and n_A are the density of donors and the Nd acceptors, respectively. Calculating r_c from Eq. (6) yields $r_c = 3.06 \text{ \AA}$, which represents the effective shortest donor-acceptor separation in the continuum limit.⁹ The rate of Pr-Pr cross relaxation can be calculated by using the rapid-migration model ($\beta \gg \alpha_B$), and its contribution to the total decay is simply the donor-acceptor energy-transfer rate. Therefore, we expect that the total asymptotic decay according to Ref. 9 (using dipole-dipole interactions) will be given by

$$W_H = \gamma_R + W_{as} + C_B \alpha_B \sum_{n \neq 0} R_{on}^{-6}, \quad (7)$$

where γ_R is the intrinsic decay rate without any transfer to acceptors. In a slightly different treatment of the hopping model,^{15,16} Sakun and co-workers arrive at an alternative expression for the term, W_{as} , in Eq. (7). According to these authors, the total decay rate in the (35–70)-K range is given by

$$W_S = \gamma_R + \pi \left[\frac{2\pi}{3} \right]^{5/2} n_D n_A (\alpha_A \beta P_0)^{1/2} + C_B \alpha_B \sum_{n \neq 0} R_{on}^{-6}, \quad (8)$$

where P_0 is the probability that during a random walk of the donor excitation in the lattice the excitation will never return to the starting point. From the simplest three-dimensional random walk, $P_0 = 0.66$,¹⁶ and we have used

this value in our calculation.¹⁶ It should be noted that, strictly speaking, the second term in Eq. (8) is only applicable in the region where the expression in large parentheses in Eq. (5) is close to unity. In this regime, the ratio of W_{as} calculated from Eq. (6) to the third term in Eq. (8) is approximately equal to 1.5.

Before attempting to compare these predictions with the experimental data there are some corrections which must be taken into account. First, we note that in the present experiment not all of the donor ions can be excited by the dye-laser pulse. It is only those ions in the lowest Stark level of the 3H_4 manifold which can be excited. The fraction of Pr ions in the ground state varies from 0.92 at 30 K to 0.62 at 70 K.¹⁷ Second, the effective density of acceptors which can participate in the cross relaxation depends on the transfer processes. If we assume cross-relaxation processes of type $^3P_0, ^3H_4(1) \rightarrow ^1G_4(m), ^4F_{3/2}(1)$ for the Pr-Nd relaxation (the number in parentheses refers to the Stark components within the J manifold), then the effective acceptor ions are those which are in the lowest Stark level of the ground state, and n_A and C_B in Eqs. (7) and (8) refer to the concentration of these ions only. However, the detailed relaxation process is not clear yet and there is a possibility that cross-relaxation processes in this system may occur via excited Stark levels. These processes will actually introduce new parameters α'_A and α'_B which may be larger or smaller than α_A and α_B depending on the appropriate matrix elements and on the phonon energies which are relevant to these high-temperature cross-relaxation channels. This difficulty can be partly avoided by using the experimental values of the temperature-dependent transfer rate, $C_B \alpha_B \sum_{n \neq 0} R_{on}^{-6}$, obtained for LaF₃:20 at. % Pr in this temperature range.³ Taking into account that in the present system the effective relative concentration of the Pr ions C_B is 1.25 times the concentration of Ref. 3 and that the temperature-independent part of α_B obtained from the fit at 2 K is half that of Ref. 3, we can obtain the desired value for the Pr-Pr cross-relaxation rate at any temperature in the (35–70)-K range. The rate obtained in this way is given by

$$C_B \alpha_B \sum_{n \neq 0} \frac{1}{R_{on}^6} = (0.93 + 400e^{-288/T}) \times 10^5 \text{ s}^{-1}. \quad (9)$$

Here, we are making the reasonable assumption that the same temperature-activated Pr-Pr transfer process that was obtained in LaF₃:20 at. % Pr will be operative in our samples and that its activation energy will also be the same. A cross-relaxation mechanism involving the $^1D_2(5)$ and $^3H_6(1)$ levels has been suggested as a possible explanation for the activation.³

We are now in a position to compare the experimental results with the calculated values by using the value of α_A obtained from the fit at 2 K (which is assumed constant⁴ up to 70 K), $\gamma_R = 2 \times 10^4 \text{ s}^{-1}$ for the radiative decay rate,¹⁸ and by using the expression for $\beta = 6.85 \times 10^{-43} T^3 \text{ cm}^6 \text{ s}^{-1}$ which has been found for La_{0.8}Pr_{0.2}F₃ in the range (5–30)-K and which we assume to be valid up to 70 K. We also make use of Eq. (9) with two possibilities for the variation of n_A with temperature.

(a) n_A is temperature independent and is equal to its

low-temperature value, i.e., we assume that the high-temperature cross-relaxation parameter α_A is equal to α_A .

(b) $n_A = n_{A0}(T)$ where $n_{A0}(T)$ is the population of the lowest Stark level of the $^4I_{9/2}$ manifold,¹⁹ i.e., we assume that no cross relaxation can occur via thermally-excited Nd ions.

The comparison with theory is shown in Fig. 3, which shows that the best agreement with experiment is obtained using the assumption (b). When this is done, Eq. (7) results in a slightly better agreement with the experimental measurements. However, taking into account the many assumptions which have been made, our results do not permit us to distinguish between the theoretical models leading to Eqs. (7) and (8). We should emphasize that our starting point in this calculation was the information on the values of α_A , α_B , and β , which was available from previous studies involving only one type of acceptor. Using improved estimates of α_A , and α_B obtained from the 2-K data, and making reasonable assumptions concerning the temperature dependence of the various parameters, we have identified a temperature region in which the theoretical models should be applicable to our system. It should be noted also that the temperature variation of the Pr-Pr transfer rate indicated by Eq. (9) was used in all cases. Its relative contribution to W_{as} [with the use of the assumption in (b)] varies from ~13% at 35 K to 45% at 70 K and is significant. Considering the complexity of the system, the agreement with theory is good.

Finally, the behavior of W_{as} with temperature in the (18–20)-K region is shown in Fig. 4. If the diffusion model is valid in this temperature region for the Pr-Nd transfer and if this is the major contribution to the

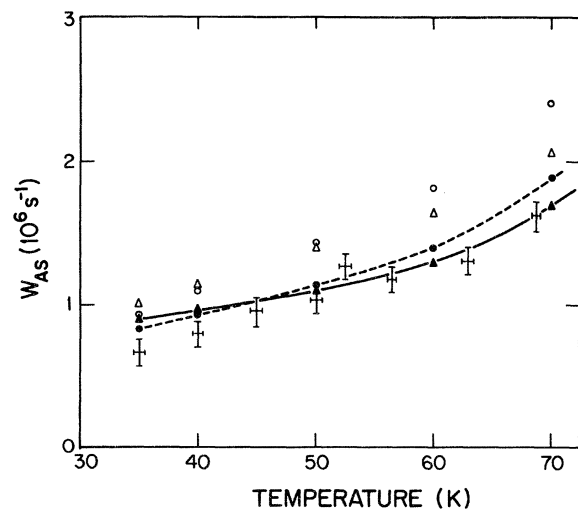


FIG. 3. Temperature dependence of the asymptotic decay rates in the (35–70)-K region. \dagger are the experimental data, Δ is calculated by using Eq. (7) with $n_A = \text{const.}$ \triangle is calculated by using Eq. (7) with $n_A = n_{A0}(T)$. \circ is calculated by using Eq. (8) with $n_A = \text{const.}$ \bullet is calculated by using Eq. (8) with $n_A = n_{A0}(T)$.

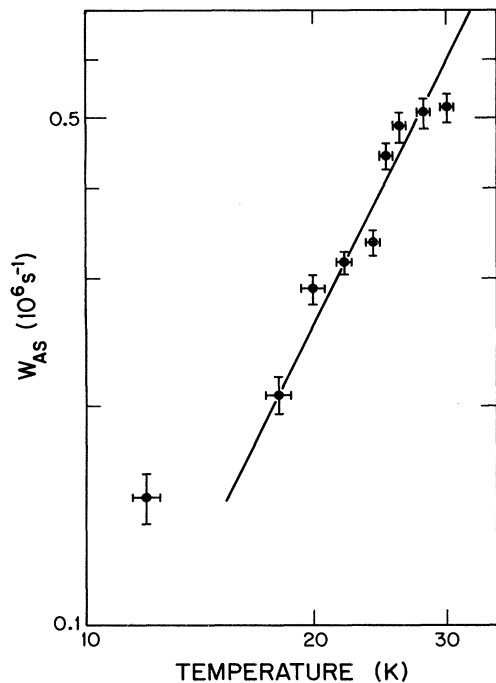


FIG. 4. Temperature dependence of the asymptotic decay rate in the temperature range 18–30 K. Solid line has a slope of 2.06.

asymptotic decay rate, then we would expect a $T^{2.25}$ dependence on temperature in this region. This is a consequence of the T^3 dependence of β and the $\beta^{3/4}$ dependence of W_{as} .^{4,16} Actually, the relations $0.16 < \beta/\alpha_A < 0.74$, $12 < \beta/\alpha_B < 719$ in this region imply the validity of a hopping or rapid-migration model for the Pr-Pr transfer but can not imply the validity of the diffusion model (which is valid when $\beta \ll \alpha$) for the Pr-Nd transfer. The solid line in Fig. 4 has been drawn with a slope of 2.06 but the experimental values of W_{as} differ by about 25 at. % from the calculated values. We believe that in this region, the Pr-Nd system is in an intermediate regime where no model is known to work, and a more general theory is needed.⁹

V. CONCLUSION

In this paper we have examined a complicated system in which donor excitation can be transferred to other

donors as well as to two different types of acceptors. This work and Ref. 16 are as far as we know the only works which present quantitative investigations of such systems at relatively high temperatures. In the system $\text{La}_{0.72}\text{Pr}_{0.25}\text{Nd}_{0.03}\text{F}_3$, the phonon-assisted donor-donor transfer parameter β changes with temperature as T^3 up to 70 K, and by changing the temperature we could span the range of $\beta \ll \alpha_A, \alpha_B$ to $\beta \gg \alpha_B, \beta > \alpha_A$ in a single system. At 2 K, the decay rate of the donor ions due to two kinds of acceptors can be successfully calculated by assuming a dipole-dipole interaction and no donor-donor transfer, and by using a generalized exact $f(t)$ expression for two different acceptors. In the (30–70)-K region the Pr-Pr and Pr-Nd cross-relaxation transfers are governed by the rapid-migration and hopping models, respectively. It is important to realize that the α_A values are such in this region ($\beta/\alpha \approx 1-10$) that the asymptotic decay rate appropriate for the rapid-transfer limit has not been reached, thus it is possible for the donor excitation to trap at a Nd site prior to transferring to another donor. This obviously affects the decay dynamics. The true rapid-migration limit, in other words, requires that $\beta \gg \alpha_i$ for all i , i.e., all relevant trapping processes; in such a case Eq. (4) yields the decay behavior for all t . In the (18–30)-K region the system is governed partly by a hopping or rapid-migration model for the Pr-Pr transfer but is in an intermediate region for the Pr-Nd transfer.

We have shown that even complex luminescent systems can be understood fairly well if the temperature dependence of the different parameters (β , α_A , α_B , etc.) can be measured independently either by using the information obtained from measurements on very similar systems or by using the information obtained from measurements on the same system in different temperature ranges. It is clear, however, that there remain areas where additional theoretical effort is required so that we may obtain a more exact, quantitative understanding of these processes.

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