Fluorescence quenching by cross relaxation in $LaF_3:Pr^{3+}$

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We have investigated the process of quenching of fluorescence from the $^3P_0$ excited state of Pr^{3+} in LaF_3 due to cross relaxation among the Pr ions. The fluorescence decay of the ensemble of Pr ions after pulsed excitation is measured as a function of temperature for Pr concentration of 20 mol%. About 12% of the ions are in nonquenching sites and contribute an exponential component to the decay. The remainder of the decay originates from the bulk of the ions in quenching sites. Cross relaxation occurs directly in steps after transfer within the inhomogeneous line. Knowledge of the dynamics occurring within the inhomogeneous line derived from fluorescence line-narrowing experiments is used to analyze the cross-relaxation process from a microscopic viewpoint based on a recent model for fluorescence in the presence of traps. At 2 K the decay is consistent with an electric dipole-dipole transfer mechanism with a nearest-neighbor quenching rate of $8.9\times10^4\ s^{-1}$ which is independent of temperature for $T<32$ K and which successfully predicts the observed decay rate in PrF_3. The temperature dependence of the decay for $8\leq T\leq32$ K is well described by a hopping model for excitation trapping. For $T>35$ K an activation process becomes dominant consistent with the onset of cross relaxation involving the $^1D_2(5)$ and $^3H_6(1)$ states in which a 190-cm^{-1} phonon is created.

I. INTRODUCTION

Recently a resurgence of interest in the trapping of optical excitation from inhomogeneously broadened levels of optically active ions in solids has arisen as a result of the growth of new spectroscopic techniques[1,2] and theoretical developments.[3] In the trapping process a system of ions or donors which are in the excited state relax by a combination of radiative decay and transfer to traps or acceptors which are distributed randomly among the donors. The presence of the donor-acceptor interaction strongly affects the fluorescence yield and quantum efficiency. Of particular significance at the present time is the phenomenon of cross relaxation[4–6] whereby the donors act as their own acceptors. In this case an ion in the excited state interacts with another neighboring ion in the ground state with the result that both ions end up in some intermediate state thereby quenching the fluorescence from the excited states. All donors can now act as trapping centers for the excitation. Since this type of cross relaxation is held responsible for the quenching of fluorescence in many highly concentrated optical systems[4,5] we examine the behavior in LaF_3 doped with 20 mol% Pr^{3+} and compare it to predictions based on the recent theoretical developments.

Section II of this paper outlines some of the theoretical details and background relevant to this study. Section III deals with the experimental procedures. In Sec. IV the experimental data are presented and interpreted on the basis of various models. Finally in Sec. V we comment on the results and discuss the relevance of this type of approach in other systems.

II. BACKGROUND REVIEW

It has been known for a long time that as the concentration of Pr^{3+} is increased in LaF_3 both the quantum efficiency and fluorescence lifetime decrease for most levels fluorescing in the visible region of the spectrum. This concentration quenching has been attributed by Brown *et al.*[7] to nonradiative cross relaxation between the ions. Many schemes have been put forward to account for the cross relaxation in terms of the intermediate levels, but it is difficult to pinpoint the relevant ones because of the large scatter in Stark components within J manifolds which are possible candidates. In addition, the number of intermediate levels involved can be quite large since any mismatch between the initial and final energies of the system can be accounted for by the creation or annihilation of one or more phonons. In this paper we concentrate on the $^3P_0$ level of Pr at 20 930 cm^{-1} above the ground state. The radiative lifetime of this level as observed for very low concentrations is $\approx51\ \mu s$. At a concentration of 20 mol% Pr the strains introduced into the lattice are of considerable magnitude as evidenced by the large inhomogeneous widths of the optical transitions ($\approx10\ cm^{-1}$).

The cross-relaxation behavior is most directly measured by examining the fluorescence decay after pulsed excitation. In the special case of PrF_3 where

the Pr ions form a regular array, each Pr ion is surrounded by the same environment of other ions, the probability of decaying by cross relaxation is identical for each ion with the net result that the ensemble decay is exponential at all times. At lower concentrations, however, the Pr ions form a disordered system, a broad range of interion separations occur and the cross-relaxation rate depends on the particular site occupied by the excited ion. In certain cases the observed decay resulting from an ensemble average over all configurations is nonexponential. The decay pattern in this case depends strongly on whether there is any concomitant "resonant" transfer among the ions. In this type of process an excitation can be transferred from one ion to a neighboring ion such that the second ion ends up in the same excited state.[8] We attach the label donor-donor (D-D) transfer to this in order to distinguish it from the cross-relaxation transfer (D-A). The movement of the excitation over the donors changes the trapping efficiency strongly since all excitations including those which are initially remote from any trap can now move to ions which have traps as near neighbors. The general problem of fluorescence in the presence of traps has been treated theoretically in detail by Huber[3] and examined by Hegarty *et al.*[2] in the system PrF_3 doped with Nd traps. The usefulness of these studies stems from the fact that it is possible to measure directly the donor-donor transfer using the technique of time-resolved fluorescent line narrowing (TRFLN).[9–11] In this technique spectral diffusion between ions within an inhomogeneous line is measured as a function of temperature and position leading to an understanding of the interaction strengths and phonon mechanisms involved.[12,13] Truly resonant coherent transfer is also possible but cannot be probed by this technique. At the present time it is believed, however, that spatial coherent migration is weak in the LaF_3 system at all Pr concentrations for all accessible temperatures.

The donor-donor dynamics in LaF_3 doped with 20 mol% Pr have been investigated in detail[14] and theoretical modelling of the microscopics of the transfer has aided in the interpretation of the data.[12] The nearest-neighbor transfer rate at 14 K has been measured to be $0.37\times10^6\ s^{-1}$ with a T^3 dependence consistent with a one-phonon second-order process. With this knowledge we can now also approach the problem of trapping by cross relaxation from a microscopic viewpoint. We can write the D-D transfer rate, W_{0n}^{DD}, and D-A (cross-relaxation) transfer rates, W_{0n}^{DA}, between two ions at sites 0 and n, separated by a distance R_{0n} as

$$W_{0n}^{DD}=\frac{\beta}{R_{0n}^{s}},\quad W_{0n}^{DA}=\frac{\alpha}{R_{0n}^{s}}\ , \tag{1}$$

where s is 6, 8, or 10 appropriate, respectively, to electric dipole-electric dipole, electric dipole-electric quadrupole or electric quadrupole-electric quadrupole interaction. The factors α and β contain the matrix elements of the interaction and have a temperature dependence associated with the particular type of phonon mechanism coming into play. Since in the cross-relaxation process high-energy phonons are likely involved we expect α to be only weakly dependent on temperature at low temperatures. β, on the other hand, varies as T^3 at low temperatures so that by changing the temperature we can span the range $\beta \ll \alpha$ to $\beta > \alpha$. The dynamics of decay for this type of situation has been treated by Huber[3] and contact was made with earlier phenomenological diffusion[15,16] and hopping[17] models. These phenomenological models have been reasonably successful in the past in explaining the transfer of electronic excitation between two species of ions in disordered systems. They were limited in scope, however, since the donor-donor dynamics were unknown and could only be indirectly inferred. In the diffusion approach the donor excitation was treated as flowing down an excitation density gradient created by a trapping center, eventually ending up on the trap. For this approach to be valid the sphere of influence of the trap must include many donors. Such a condition can be satisfied if the average transfer time between donors is much greater than the donor-acceptor transfer time so that the excitation on average remains for a sufficiently long time on each donor to effectively feel the influence of the trap, i.e., if $\beta \ll \alpha$. At the other extreme were the D-D transfer time is on the order of or less than the D-A time, i.e., $\beta \gtrsim \alpha$ the sphere of influence of the trap is much smaller, and the motion of the excitation has been treated as a hopping process. Both of these models predict that the decay of the donor ions be nonexponential at first but should approach an exponential behavior in the asymptotic time limit. In the case where β becomes extremely small the decay behavior for a disordered system of donors approaches that described by the model of Inokuti and Hirayama.[18] We compare the cross-relaxation behavior in LaF_3:20 mol% Pr with predictions of these models.

III. EXPERIMENTAL

A single crystal of LaF_3 doped with 20 mol% Pr was grown by Optovac, Inc. No evidence of the presence of other rare-earth ions could be detected in this sample. For measurements at 2 K the sample was immersed in a bath of liquid helium pumped below its λ point. For other temperatures the sample with dimensions $1\times1\times5\ mm^3$ was carefully attached to the cold finger of a continuous flow helium cryostat. The temperature was measured with a carbon glass resistor in contact with the sample and controlled with a feedback temperature controller employing a

wire-wound heater coil on the cold finger. The excitation source was a nitrogen laser-pumped dye laser system of the grazing incidence type[19] with a pulse length of ~ 5 ns. Since in the experiment all of the donor ions are treated as a unit the linewidth of the laser was adjusted to be approximately twice the inhomogeneous width of the $^3H_4(1)$-$^3P_0$ absorption line. In this way a representative distribution of ions were excited. The population of the $^3P_0$ state after pulsed excitation was measured by monitoring the strong nonresonant $^3P_0$-$^3H_6(1)$ transition at 16 710 cm^{-1} with a spex 1402 double monochromator. The slit width was again adjusted so that the resolution was on the order of the inhomogeneous width of the fluorescence line. Care was taken, however, that fluorescence from spurious sites not included in the main line was not collected which would complicate the analysis.

The time evolution of the fluorescence was analyzed with a PAR 162 boxcar integrator with a nominal time resolution of 5 ns. Since local heating of the crystal[20] and nonlinear effects such as stimulated emission[21] are possible at high Pr concentrations under tight focussing and high pump power the peak intensity was reduced to less than 10 kW/cm^2 by defocussing and by use of neutral density filters. The signal from the boxcar was finally normalized to the laser intensity and transmitted to an X-Y recorder.

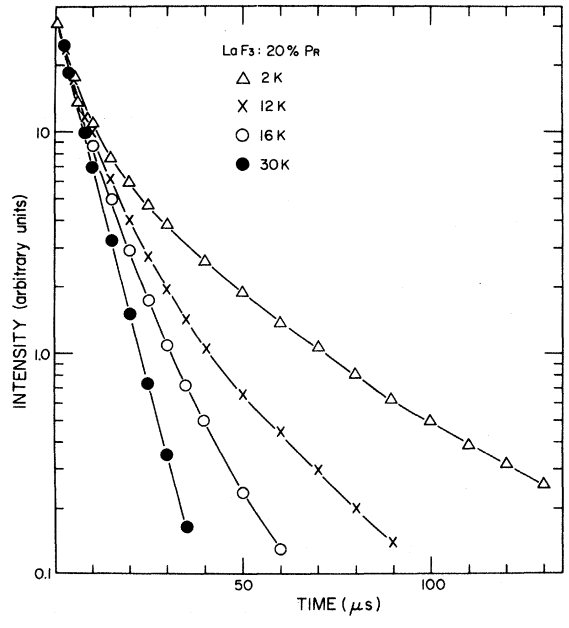

FIG. 1. Plot of the decay of the $^3P_0$ state of Pr^{3+} in $La_{0.8}Pr_{0.2}F_3$ at different temperatures. The decays are normalized at $t=0$.

IV. EXPERIMENTAL RESULTS

The decay of the $^3P_0$ state of Pr is shown as a semilog plot in Fig. 1 for several temperatures. At the lowest temperature of 2 K the decay is strongly nonexponential. As the temperature is raised above 2 K the decay becomes faster, for $T > 30$ K the decay follows a simple exponential behavior at all times. In the region 8–20 K the decay changes rapidly but then approaches a saturating value in the 20–35-K region. For $T > 40$ K the decay rate begins to increase rapidly again and does not reach a maximum value. To understand this behavior we treat the different temperature regions separately. We can rule out any role played by reabsorption in this system because of the reduced overall quantum efficiency and because the branching ratio for a transition to the $^3H_4(1)$ ground state is much less than 1%.

A. $T=2$ K

At this temperature the nearest-neighbor donor-donor transfer rate observed in TRFLN[12] is extrapolated to be 1000 s^{-1} and hence is negligible on the time scale of our measurements. Consequently we expect that the Inokuti-Hirayama model[18] of D-A transfer in the absence of any backtransfer from the acceptors should describe the behavior. Since in cross relaxation the interacting ions end up in energy levels many thousands of wave numbers below the $^3P_0$ state the effect of any backtransfer to the $^3P_0$ level is negligible at low temperatures. The fluorescence intensity I as a function of time after the laser pulse can be written in the special form of the Inokuti-Hirayama equation[12]

$$\ln I + \frac{t}{\tau_0} \simeq \ln I_0 - \frac{4\pi}{3} n_A R_{\min}^3 (W_0^{DA} t)^{3/s} \Gamma(1-3/s) \ , \tag{2}$$

where τ_0 is the radiative lifetime of the $^3P_0$ state, I_0 is the intensity at $t=0$, n_A is the number of acceptor ions per unit volume, which is equal to the number of Pr ions per unit volume in this case, $R_{\min}$ is the minimum (nearest-neighbor) separation between the Pr ions, W_0^{DA} is the cross-relaxation rate for nearest neighbors and Γ is the gamma function. Hence a plot of $\ln I + t/\tau_0$ against $t^{3/s}$ should give a straight line for the correct choice of s. An attempt to fit the data, however, failed for all values of s, the fit being worse the smaller the s value. For $s=10$ the fit was good at early times but at late times the deviation became large. A close examination of the decay showed an unexpectedly strong late-time fluorescence decaying with the radiative decay rate suggesting that some of the ions are either in very isolated sites or else the cross relaxation between them is not allowed. If the exponential tail is extrapolated to $t=0$ as

showed in Fig. 2 and subtracted from the data the remainder $I'(t)$ is also seen to be nonexponential. $I'(t)$ fits the Inokuti-Hirayama equation very well, however, for $s=6$ as shown in Fig. 3. Also shown in this figure is a similar plot but for $s=10$. The fit in this case is not as good. The deviation at early times from the straight-line behavior is due to the fact that the Inokuti-Hirayama model is based on a continuum and does not take into account the discrete nature of the lattice at short distances. The ratio of the extrapolated exponential component to the total intensity at $t=0$ in Fig. 2 indicates that 12% of the total number of Pr ions are in nonquenching sites. If we assume that the remainder are distributed normally with an effective concentration of 17.5 mol% we can derive a value for W_0^{DA}, the nearest-neighbor quenching rate. In LaF_3, $R_{\min}=4.138$ Å and from the crystal structure n_A can be calculated to be $3.\times10^{21}$ ions/cm^3 corresponding to a fractional concentration $c_A=0.175$. We found

$$W_0^{DA}=8.9\times10^4\ \mathrm{s}^{-1}\ .$$

It is possible to predict the cross-relaxation behavior for all other concentrations using this value of W_0^{DA}. In particular, for the case of PrF_3 where each Pr ion sees the same environment the total cross-relaxation rate will be exponential and given by[12]

$$W^{DA}=\sum_{n\neq0} W_{0n}^{DA}\ , \tag{3}$$

where W_{0n}^{DA} is the cross-relaxation rate for two ions in sites 0 and n and the summation is over all crystal sites. W_{0n}^{DA} is related to W_0^{DA} by

$$W_{0n}^{DA}=\frac{R_{\min}^6}{R_{0n}^6}W_0^{DA} \tag{4}$$

for $s=6$. $R_{\min}$ in PrF_3 is 4.085 Å, smaller than in LaF_3. Adjusting W_0^{DA} upwards to account for this change, a simple computer calculation gives $W^{DA}=1.21\times10^6\ \mathrm{s}^{-1}$. If the radiative rate, $2\times10^4\ \mathrm{s}^{-1}$, is included a net decay time of 830 ns results. The decay time observed is 750 ns. We repeated this process using instead $s=10$ and the slope given by the early time uncorrected data [$I(t)$ in Fig. 2] where as mentioned earlier a reasonable fit was possible for this value of s at short times. The value predicted for the total decay time in PrF_3 in this case, however, was 269 ns, in total disagreement with the measured value. Hence we conclude that the dominant mechanism responsible for quenching in the Pr system is the dipole-dipole interaction.

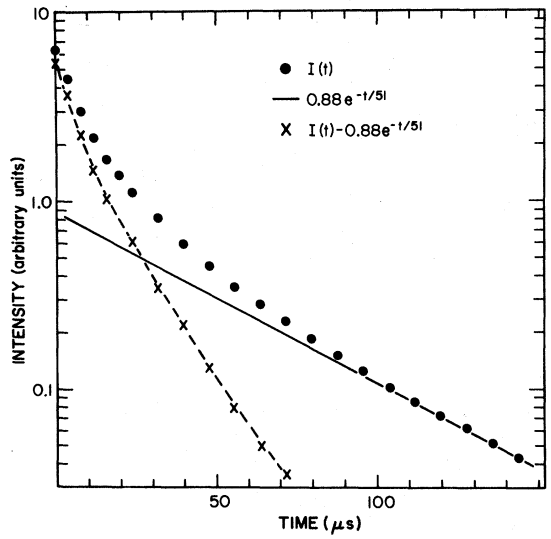

FIG. 2. Plot of the fluorescence intensity against time at 2 K. The corrected intensity is obtained by subtracting an exponential term with slope equal to the radiative decay rate from the observed decay. The ratio at $t=0$ of the slow component intensity to total intensity is 0.125.

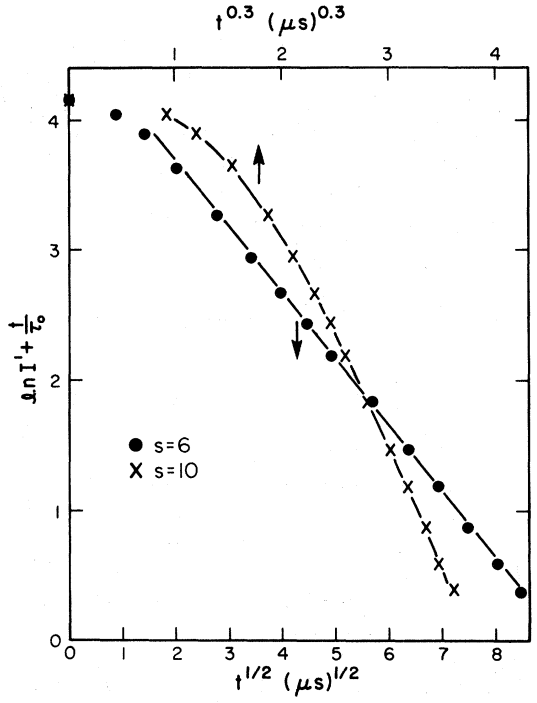

FIG. 3. Plot of $\ln I+t/\tau_0$ against $t^{3/s}$ for $s=6$ and 10 corresponding to electric dipole-electric dipole and electric quadrupole-electric quadrupole mechanisms, respectively.

B. 8–32-K temperature region

As the temperature is increased in this region the decay of the $^3P_0$ state increases rapidly at first and approaches a constant value at about 32 K. The decay

is nonexponential except at the highest temperatures. After subtracting out the radiative rate at 32 K a saturating rate of $\simeq 1.5 \times 10^5$ s^{-1} is obtained. The presence of saturation and exponential decay is indicative of the fact[3] that by 30 K the donor-donor rate is much faster than the cross-relaxation rate, that is, the probability of decay by cross relaxation becomes site independent. In this case the decay rate, W^{DA}, due to cross relaxation is given by

$$W^{DA} = c_A \sum_{n \neq 0} W_{0n}^{DA} = c_A W_0^{DA} \sum_{n \neq 0} \left(\frac{R_{\min}}{R_{0n}} \right)^6 . \quad (5)$$

For $c_A \simeq 0.175$ a value of 5.9×10^4 s^{-1} is calculated for W_0^{DA}. This differs from the low-temperature estimate of 8.9×10^4 s^{-1} by about 30%. This discrepancy can be explained in part by the transfer of the population in the $^3H_4(1)$ ground state to the $^3H_4(2)$ state at 50 cm^{-1} as the temperature is raised. At 30 K the $^3H_4(1)$ population is reduced by about 10% from its low-temperature value thereby reducing the cross-relaxation rate involving the $^3H_4(1)$ states. As shown in Sec. IV C new processes become prominent at temperatures above 32 K so that the measured value of W_0^{DA} should be regarded as a lower limit. An approximate value for α in Eq. (1) is calculated from the value of W_0^{DA} to be $\simeq 3 \times 10^{-40}$ cm^6 s^{-1}.

Since the high- and low-temperature behavior are qualitatively consistent we can now attempt to explain the behavior at intermediate temperatures, where the donor-donor transfer rate is comparable to the cross-relaxation rate. The low-temperature (2 K) behavior indicates that Pr ions occupy at least two distinct types of site in the crystal. The ions in one type of site do not cross relax but decay radiatively. Since as the temperature is raised from 2 K the overall decay becomes faster the non-cross-relaxing component also becomes faster. If we assume that this component remains exponential at all temperatures and approximate it by a tangent to the latest part of the decay then we show in Sec. V that its temperature dependence is consistent with a two-phonon assisted spectral transfer out of the inhomogeneous line. The remainder of the decay, obtained at each temperature by subtracting off the exponential part, describes the cross-relaxing population. This decay also approaches an exponential at late times down to the lowest temperature of 8 K and a plot of this rate against temperature is shown in Fig. 4.

In the temperature regime $8 \lesssim T \lesssim 32$ K the decay of the cross-relaxing ions is a result of competing D-D and D-A transfer processes. At 8 K the extrapolated value of β is 1.88×10^{-39} cm^{6}s^{-1} so that the condition $\beta >> \alpha$ is satisfied at all temperatures > 8 K. From the criterion outlined in Sec. II for the diffusion and hopping models we might expect the hopping model to be a reasonable description of the behavior. In accordance with the procedure used in

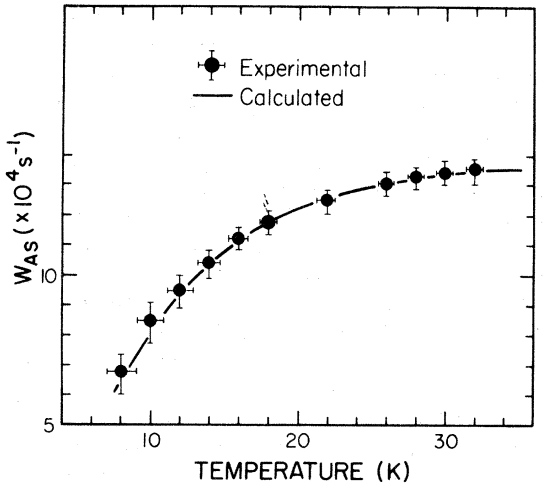

FIG. 4. Plot of the asymptotic decay rate of the fast component fluorescence against temperatures. The points with error bars are the observed rates while the solid line is the behavior predicted by Eq. 6.

Ref. 2 we fit the asymptotic decay rate W_{AS} to the equation[22]

$$W_{AS} = \frac{2\pi^2}{3} n_A \left(\frac{\alpha}{\tau_0} \right)^{1/2} \left[1 - \frac{2}{\pi} \tan^{-1} \left(\frac{r_c^6}{\alpha \tau_0} \right)^{1/2} \right] , \quad (6)$$

where r_c is chosen such that W_{AS} calculated from Eq. (6) at the upper temperature limit is equal to the observed saturating value of 1.5×10^5 s^{-1}.[23] The parameter τ_0 is the average time that an excitation spends on a single donor and is related to the results of TRFLN by the relation[3]

$$\tau_0 = \int_0^\infty R(t)\, dt ,$$

where $R(t)$ is the normalized intensity of the sharp-line fluorescence observed in fluorescent line narrowing. We have calculated τ_0 for all temperatures using the expression for $R(T)$ given by model 2 of Ref. 12 which takes into account backtransfer among the donors. By converting $R(t)$ to an integral τ_0 is given approximately by

$$\tau_0 = \frac{1.389}{W_0^{DD}} ,$$

where W_0^{DD} is the donor-donor transfer rate for nearest neighbors. Insertion of this value of τ_0 into Eq. (6) gives the predicted values of W_{AS} shown as a solid line in Fig. 4. Even though we have used an *ad hoc* procedure in deconvoluting the two parts of the decay curve, the agreement in Fig. 4 shows that the hopping model provides an internally consistent picture of the dynamics of cross relaxation with parameter values in agreeent with the results of independent measurements.

C. $T > 32$ K

As mentioned in Sec. IV B, above 40 K the decay of the $^3P_0$ state begins to increase rapidly suggesting the onset of an activation process. The decay rate W for an activated process obeys the relation $W = Ae^{-\Delta/kT}$ where Δ is the activation energy and A is a constant. To compare our data with this model we have plotted the measured decay rate in Fig. 5 as a function of $1/T$ for temperatures up to 100 K. The radiative rate has been subtracted from these values. If the saturating low-temperature decay rate predicted by the hopping model and indicated by the broken line is subtracted from the observed rate a straight-line behavior results shown by the solid line in Fig. 5. The slope of this line yields an activation energy of $\simeq 200$ cm^{-1}. This cannot be due to activation to any higher lying energy level of Pr since the $^3P_1$ state is 544 cm^{-1} above the $^3P_0$ state. That the activation is a Pr-Pr effect is evidenced by the fact that at very low concentrations the effect is not observed.[7] An examination of the intermediate level energies shows that a cross relaxation involving the $^1D_2(5)$ and $^3H_6(1)$ levels is a possible explanation as indicated in Fig. 6. Such a mechanism would demand the creation of 190-cm^{-1} phonon, closed to the measured values of

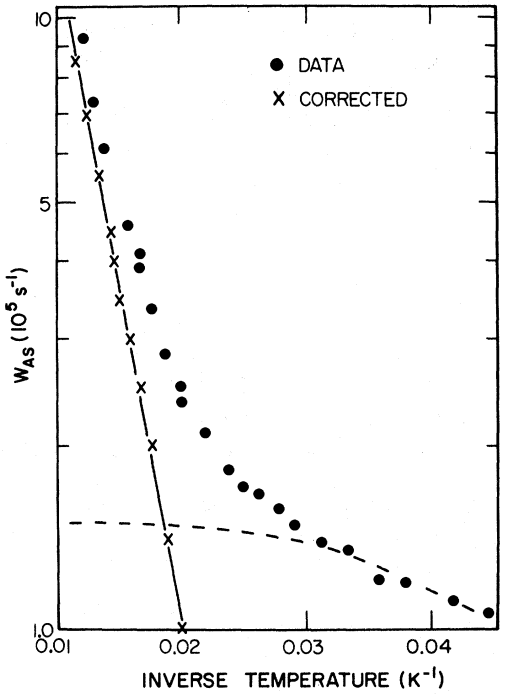

FIG. 5. Plot of $^3P_0$ decay rate as a function of $1/T$ for $20 \leq T \leq 100$ K. The rates given by the hopping model (broken line) are subtracted from the data to give the straight solid line whose slope corresponds to $\Delta = 200$ cm^{-1}.

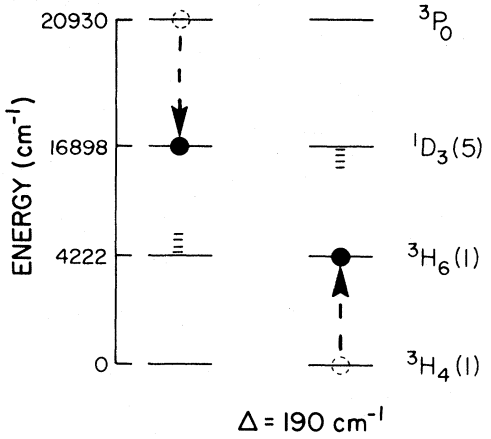

FIG. 6. Schematic outline of the cross-relaxation process responsible for the high-temperature activation behavior. The numbers in brackets refer to the Stark components within the J manifold.

$$E[^1D_2(5)] + E[^3H_6(1)] - E(^3P_0) = 190 \text{ cm}^{-1} .$$

Δ. An attempt to observe fluorescence from the $^1D_2$ level failed, however. This is not unexpected since fluorescence from the $^1D_2$ level state itself is strongly quenched as the Pr concentration is increased.

V. COMMENTS

There are several points to be noted in regard to the above results. Firstly the behavior of the decay of the Pr ion system is consistent with trapping due to cross relaxation. The agreement of the low-temperature data to the Inokuti-Hirayama model and of the higher-temperature data with the hopping model demonstrates this. Furthermore the quenching rates derived from the decay in the case of 20 mol% Pr gives a reasonable prediction of the observed decay in PrF_3. Our assumption that the parameter α is independent of temperature up to about 35 K is valid since the observed decay rate in PrF_3 remains constant up to this temperature.[2] Secondly since the data can be explained on the basis of incoherent transfer of localized excitations, there is no evidence for any coherent spatial migration at low temperatures.

The decay of $^3P_0$ state seems to contain two components, the slow component corresponding to ions in sites which do not partake in the quenching process. It is not clear at present what the origin of these sites are. One possibility is that at such high concentrations of Pr, domains are formed within which the ions are distributed with a larger than normal interion separation thus ruling out the possibility of effective cross relaxation. An attempt to selectively excite only those ions, using a laser linewidth of

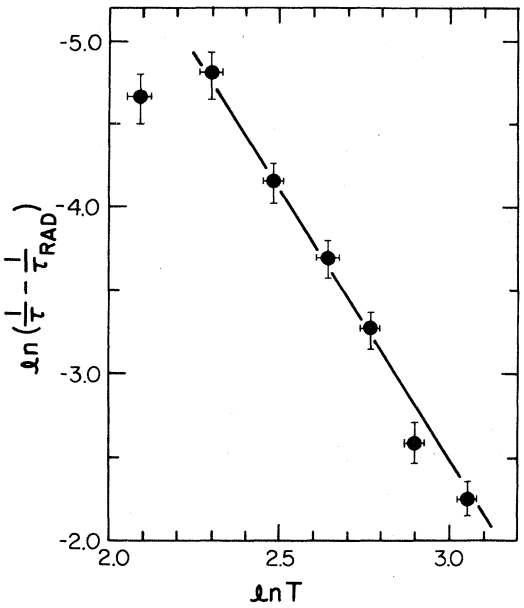

FIG. 7. Plot of the decay rate of the slow component fluorescence against temperature on a log-log scale. The units for τ and T are μs and K, respectively. A $T^{3.5}$ dependence is suggested for the temperature region 10–22 K.

$\simeq 1$ GHz failed; their absorption energies are spread out over the whole inhomogeneous line of the regular ions. As the temperature was raised the long-lived component decayed at an increasingly faster rate. Activation was ruled out as a possible explanation for this since a plot of the rate against $1/T$ deviated considerably from a straight-line behavior. The data could, however, be fitted to a simple power dependence on T in the range 10–22 K, with a power of $\simeq 3.5$ as shown in Fig. 7. Since this is close to the observed temperature dependence of the D-D transfer rate it is possible that these ions can transfer their excitation to other dissimilar sites not contained within the main inhomogeneous distribution. It is to be noted also that the dominant mechanism in the quenching process is of the electric dipole-electric dipole type. It has been proposed[7,24] that because of the forced electric dipole nature of optical transitions in rare earths, cross relaxation should be dominated by the quadrupole-quadrupole mechanism. This does not seem to be the case in this system.

The role played by the donor-donor dynamics in the case of Pr in LaF_3 together with better theoretical tools has enabled the process of cross relaxation to be understood better and to be interpreted successfully in terms of a hopping model. Cross relaxation is of particular importance in the design of potential laser systems since any type of fluorescence quenching reduces the efficiency. The relative roles played by D-D transfer and transfer to trapping centers remains a controversial subject in many other systems.[5,6] An analysis along the lines presented in this paper should offer a valid contribution to the further understanding of these problems.

ACKNOWLEDGMENTS

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[22]This equation, a continuous version of Eq. (11) in Ref. 2, was obtained assuming that the concentration of acceptors is much less than the concentration of donors. A recent study of donor fluorescence at high trap concentration [D. L. Huber, Phys. Rev. B 20, 5333 (1979)] indicates that when the two concentrations are equal, as happens for cross relaxation, the equation can be used as $\alpha \lesssim 0.25\beta$, which is the case for $T \gtrsim 8$ K.
[23]The parameter r_c is chosen such that

$$\frac{4\pi}{3}\frac{n_A}{r_c^3} = c_A \sum_{n \neq 0} \frac{1}{R_{0n}^6} \ .$$

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