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Trapping of optical excitation in Nd-doped PrF_3

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The dynamics of trapping of optical excitation in a disordered system of ions in a solid is studied using time-resolved fluorescence measurements. In the system PrF_3 doped with Nd, the randomly distributed Nd ions act as sinks for the Pr excitation. The transfer to the Nd traps can occur in conjunction with transfer among the Pr ions. In this system the Pr-Pr transfer is strongly temperature dependent while the Pr-Nd transfer is temperature independent at low temperatures. By changing the temperature we can span the range from no Pr-Pr transfer to very (infinitely) fast Pr-Pr transfer in one single system. We have identified these limits. In addition we have placed boundaries on the applicability of the diffusion and hopping models in describing trapping in the intermediate temperature regime where the Pr-Pr and Pr-Nd transfer rates are comparable.

I. INTRODUCTION

Energy migration among optically active ions in solids has been the subject of numerous investigations in recent years.[1] Of particular interest has been the interaction between two distinct species of ions as revealed through their fluorescence properties. The fact that electronic energy could be transferred radiatively or nonradiatively from one species to another has opened up many possibilities such as efficient optical pumping in laser and phosphor systems. From another point of view the effect on fluorescence quantum efficiencies and lifetimes due to the presence of trapping centers which draw away the optical excitation is of extreme importance at the present time in the design and performance of efficient optical systems. An understanding of the interaction between ions in solids and the effects on the fluorescence properties is a key starting point for any future developments.

In the transfer or trapping process electronic energy is transferred from excited ions which we label donors, to acceptors which act as traps for the energy. This transfer can take place either directly or indirectly, following migration among the system of donors. As a result of random strains present to varying degrees in solids, not all of the donors are in identical environments so that inhomogeneous broadening of the energy levels and of optical transitions between these levels occurs. The energy mismatch between the donors can strongly affect the migration of excitation among the donors and hence the way in which the energy is transferred eventually to the acceptors. This is especially true at very low temperatures where homogeneous linewidths are typically narrow and spectral overlap between neighboring ions in a randomly strained system is in many cases negligible. In addition, when the acceptors are present at low concentrations and distributed spatially in a random manner among the donors, there occurs a distribution of donor-acceptor separations and hence transfer rates. When the donor concentration is also less than unity, it becomes extremely complex to analyze and interpret the behavior. Such a situation has recently been considered by Chow and Powell[2] who adopted a Monte Carlo approach. Numerous experiments have been performed in the past to examine energy transfer by trapping, and many widely different systems have been used. Some experiments consisted of doping a suitable host with varying amounts of two different trivalent rare earths,[3] one of which acts as the donor and the other as the acceptor. The well-defined fluorescence properties of rare earths make them an ideal candidate for such a study. In other experiments the donors themselves acted as their own traps[4,5] due to cross relaxation or to pairing of nearest-neighbor ions whose energy levels are consequently shifted away from those of the isolated ions. The effects of an amorphous host have also been studied with great success.[6] In all of these experiments the donors were excited with a short pulse of light; the time evolution of the fluorescence from the donors, and where possible from the acceptors, was then measured and analyzed. Unfortunately, at the time when most of these studies were being performed only broadband excitation sources were available, and there was no way of distinguishing between the donors at different parts of the inhomogeneous line. Consequently all of the donors were treated as a "resonant" system, and the effect of energy mismatch and phonon assistance were unknown. The analysis of the data was based on phenomenological models[7,8] for energy transport in which the only known parameter was the concentration.

In recent times the dynamics of energy transfer within an inhomogeneous system of ions in the absence of traps have been studied experimentally[9,10] and theoretically[11,12] and are generally well understood. The technique of time-resolved fluorescent line narrowing[13] has been a powerful tool in this type of work. Hence it is possible to measure the dynamics within a system of donors in the presence of traps independently by such a technique, and such a knowledge greatly simplifies the interpretation of the trapping dynamics. In the following we address ourselves to this problem and analyze in detail the system PrF_3 doped with Nd^{3+} which can act as a trap for the Pr excitation. We measure directly the dynamics within the Pr^{3+} system and use this to study the Pr-Nd transfer. New physical insights into the microscopic nature of donor-acceptor energy transfer result from this approach, and we show that most of the salient features of the process can be obtained from just a single system by using the temperature as a variable parameter. The results are compared to recent theoretical developments appropriate to this type of study.[14]

The paper is presented along the following lines. In Sec. II we review the current status of the understanding of transfer to traps and the models that have been used in the past. Section III presents the experimental techniques. The experimental results are presented in Sec. IV and analyzed and compared to recent theoretical models in Sec. V. We conclude with some remarks on the role of this type of approach in further work.

II. BACKGROUND

A. Spectroscopy of PrF_3 and PrF_3:Nd

The system PrF_3 is an ideal host for the study of donor-acceptor energy transfer since it can easily be doped with Nd over a wide range of concentrations. Whereas the Nd ions spatially form a very disordered system, at low Nd concentrations the Pr ions are reasonably well ordered, making the analysis simpler than if the Pr ions were also dilute. An energy-level diagram of Pr and Nd is shown in Fig. 1. The singlet $^3P_0$ state of Pr at 20 930 cm^{-1} is a well isolated state and gives rise at low temperature to strong fluorescence to many of the lower states with a lifetime of 750 ns. At high concentrations of Pr the resonance fluorescence to the ground state is strongly reabsorbed, but an intense sharp fluorescence line at 16 712 cm^{-1} corresponding to the nonresonant $^3P_0$-$^3H_6$ transition occurs. We use this line to monitor the fluorescence decay from the $^3P_0$ state. In this way the problem of laser scatter is also eliminated. Because of the close proximity of the Pr ions in PrF_3, strong cross relaxation[15] occurs involving intermediate levels which reduces the fluorescence lifetime of the $^3P_0$ state to 750 ns from its low concentration value of 51 μs. The inhomogeneous linewidth of the $^3H_4(1)$-$^3P_0$ transition in absorption and the $^3P_0$-$^3H_6(1)$ transition in fluorescence is 0.5 cm^{-1}. As Nd is added to the system these linewidths increased monotonically with concentration, due to the increase in the random strains in the system.[16] At a concentration of 5 at.% the linewidth is 1.9 cm^{-1}. At 2 K under narrowband excitation the $^3P_0$-$^3H_6(1)$ transition is found to be line narrowed but still possesses a linewidth which is considerably broader than the homogeneous or laser width. This residual width is inhomogeneous in nature and arises from accidental degeneracies occurring among the energy levels.[17] The width ranges from 0.13 cm^{-1} in pure PrF_3 to about 1 cm^{-1} in the case of 20 at.% Nd doping. As the temperature is raised above 2 K, Hamilton *et al.*[9] have observed the onset of Pr-Pr transfer in pure PrF_3 as revealed through the growth with time of the full $^3P_0$-$^3H_6(1)$ inhomogeneous line from that of the line-narrowed component. The nonresonant transfer has been found to proceed on the basis of an electric dipole-electric dipole ion-ion interaction and to be a two-phonon-assisted process with a temperature dependence of $T^{4.3}$. Below 7 K negligible transfer occurred on the time scale of the fluorescence decay. When Nd is added to the system in small amounts it is expected that the Pr-Pr dynamics should not differ markedly from those in pure PrF_3 and in Sec. IV we show the similarity of behavior in the two systems.

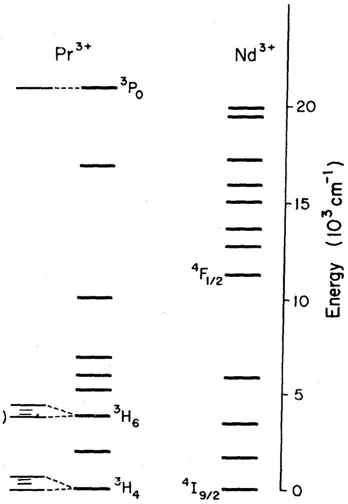

FIG. 1. Energy-level diagram of Pr and Nd in PrF_3 showing the J components of Pr relevant to this study.

B. Fluorescence in the presence of traps

As discussed in Ref. 14, the decay of the integrated fluorescence in the presence of traps falls between two limits. If we write the donor-acceptor transfer rate as α/r^s and the donor-donor rate as β/r^s, where r is the separation between ions and $s = 6$, 8, etc., then the limiting cases correspond to $\beta/\alpha \approx 0$ and $\beta/\alpha \gg 1$. In the former case there is only direct transfer from the initially excited donors to the acceptors. Apart from an overall exponential factor describing the intrinsic decay of an isolated donor ion, the fluorescence is characterized by the factor $\exp(-At^{3/s})$. In the opposite limit, which corresponds to (infinitely) rapid donor-donor transfer, the trap-related decay is exponential at all times with a rate equal to the total donor-acceptor transfer rate averaged over all donors.

In between these limits the trap-related decay is initially nonexponential but becomes exponential in the long-time limit. The asymptotic decay rates depend on the relative magnitudes of the donor-donor and donor-acceptor transfer rates. When $\beta \ll \alpha$ the diffusion model of Yokota and Tanimoto[7] is applicable, whereas when $\beta \gtrsim \alpha$ the hopping model introduced by Burshtein[8] is an appropriate first approximation. In Nd-doped PrF_3 the donor-acceptor transfer rate is temperature independent whereas $\beta \propto T^{4.3}$. By varying the temperature we are able to observe the effects of trapping over a wide range of values of β/α including the two limiting cases mentioned above.

III. EXPERIMENTAL PROCEDURES

Samples of $Pr_{1-x}Nd_xF_3$ were obtained from Optovac, Inc. with $x = 0.0$, 0.005, 0.01, 0.05, and 0.2. The samples were polished and mounted on the cold finger of a continuous-flow helium cryostat whose temperature could be varied from 4.5 K upwards by balancing the helium gas-flow rate against a heater current on the cold finger. The temperature was measured by a carbon glass resistance sensor which was carefully attached to the cold finger and in good thermal contact with the sample so as to eliminate any temperature differences between the sample and sensor.

We perform two types of experiments on the Pr-Nd system. First is the more classical experiment in which the whole inhomogeneous system of Pr ions is excited with equal probability by a pulse of light. This is achieved with a pulsed nitrogen-pumped dye laser tuned to the Pr absorption line ${}^3H_4(1)$-${}^3P_0$ at 20 930 cm^{-1} and with a width greater by at least a factor of 2 than the inhomogeneous absorption width so as to achieve a reasonable distribution of excited ions. The dye laser was of the grazing incidence type with two gratings.[18] Since the inhomogeneous width of the ${}^3H_4(1)$-${}^3P_0$ absorption line varied from 0.5 cm^{-1} for PrF_3 to several wave numbers in the case of 20 at.% Nd doping, the laser linewidth was varied accordingly by changing the grazing angle at the first grating and choosing an appropriate order with the second grating. A linewidth ranging from 2 GHz to 15 cm^{-1} was possible in this way. Because of the high Pr concentration in these samples and the strong phonon-generating cross relaxation from the ${}^3P_0$ state, local heating of the samples was observed at low temperatures and high laser intensity. As seen in Sec. IV the fluorescence decay time of the ${}^3P_0$ state is very sensitive to temperature at low temperature in the Nd-doped samples, and we used this as a test for local heating by the laser. The laser intensity was accordingly reduced until the heating effect was eliminated while still maintaining a good signal-to-noise ratio.

The ${}^3P_0$-${}^3H_6(1)$ fluorescence was detected with a high-gain RCA 7326 photomultiplier tube, and the time evolution was measured with a PAR 162 boxcar with a minimum gatewidth of ≈ 20 ns.

In the second type of experiment we measured the energy migration within the Pr inhomogeneous system using the technique of time-resolved fluorescent line narrowing. The procedure in this experiment is similar to that used by Hamilton *et al.*[9] in the analysis of pure PrF_3. The grazing incidence dye laser was narrowed to give a minimum width of 2 GHz and tuned across the ${}^3H_4(1)$-${}^3P_0$ inhomogeneous line. The decay after pulsed excitation of the resonantly excited Pr ions and the growth of fluorescence in time from the other nonresonant ions within the inhomogeneous line were measured with a stacked two-stage Fabry-Perot etalon system in order to give a broad free-spectral range (FSR) together with a high finesse. In this way a spectrally narrow part of a broad inhomogeneous line could be selected for measurement. One etalon had an FSR of 15 cm^{-1} and the other an FSR of 5 cm^{-1}. The spacing of one etalon was mechanically tuned so that one of its orders coincided with an order of the second etalon. A finesse of about 40 was obtained giving an overall resolution of 0.4 cm^{-1}. Further processing of the data was similar to that described in the first part of the experiment.

IV. RESULTS

A. Broadband excitation

The decay of fluorescence from the ${}^3P_0$ state of Pr under broadband excitation at 5 K is shown in Fig. 2 for three concentrations of Nd ranging

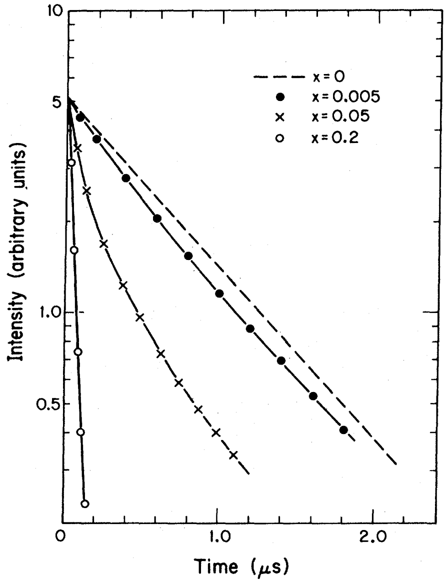

FIG. 2. Fluorescence decay from the $^3P_0$ state of Pr in $Pr_{1-x}Nd_xF_3$ at 5 K for x=0.0, 0.005, 0.05, and 0.2.

rom 0.5 at. % to 20 at. %. For comparison, the lecay in pure PrF_3 is also shown. Whereas pure PrF_3 shows a simple exponential decay, in the presence of Nd the situation is more complicated. Firstly the decay becomes more rapid as the Nd concentration is increased, indicating that trapping is occurring. Secondly the decay is no longer exponential, the deviation being most evident at early times and most pronounced in the case of 5 at. % Nd. As the temperature rises above 5 K the decay changes dramatically, becoming much faster. This is shown in Fig. 3 for the case of 5 at. % Nd. From being nonexponential at all times at 5 K the decay acquires an exponential component at late times as the temperature is raised. Above 20 K the decay is fully exponential, eventually becoming temperature independent above 40 K. A similar behavior is observed in the other Nd-doped samples. By contrast the decay in pure PrF_3 remains constant over this temperature range with a rate of 1.33×10^{-6} s^{-1}.

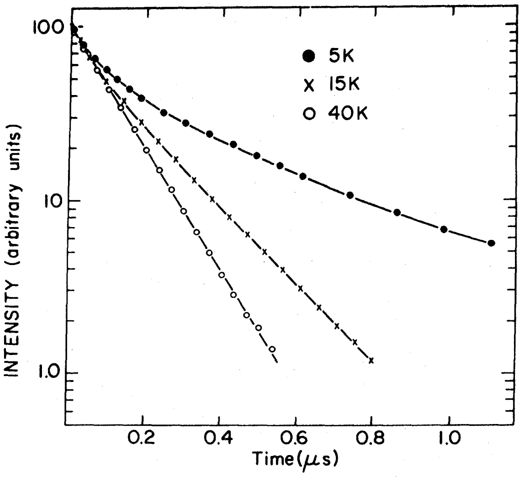

FIG. 3. Examples of the $^3P_0$ fluorescence decay in $Pr_{0.95}Nd_{0.05}F_3$ at different temperatures.

At this point some qualitative conclusions can be drawn from the observed behavior in the light of the discussion in Sec. II. Firstly the nonexponential decay observed at low temperatures is consistent with transfer of the Pr excitation to Nd traps in the absence of any Pr-Pr migration. In such a case there is a broad distribution of Pr-Nd transfer distances, and the ensemble average over many sites gives a nonexponential behavior.[11] The increase in the decay as the temperature is raised can result from either the onset of Pr-Pr migration or a dependence on temperature of the Pr-Nd transfer step. We know that transfer among the Pr ions in pure PrF_3 does indeed increase rapidly in this temperature region[9] and we expect a similar behavior in the presence of Nd. The exponential nature of the decay above 30 K suggests that the Pr-Pr transfer is much faster than the Pr-Nd transfer at this temperature, that is $\beta \gtrsim \alpha$. In this case the Pr excitation can sample all environments before being finally trapped at a Nd site. All Pr sites have the same probability of being populated, and the transfer to Nd is site independent and limited only by the Pr-Nd last step in the transfer chain. A simple rate equation describing the population of excited Pr ions can be used with a single-average Pr-Nd transfer rate. This results in an exponential decay independent of β in the limit $\beta \gg \alpha$. The fact that the decay rate becomes independent of temperature at about 40 K further indicates that the Pr-Nd transfer probability changes negligibly in this temperature range, that is, α is a constant. To see why this can be the case one must look at the energy-level diagram in Fig. 1 to examine the Pr-Nd transfer possibilities. We consider an excited Pr ion interacting with a Nd ion in the ground state. The probability of the Nd ion having two Pr neighbors simultaneously in the excited state is small because of the extremely low excitation densities used in these experiments. We estimate that 1 in 10^5 Pr ions are excited. After energy transfer the Pr ion is in a state of lower energy while the Nd ion is in some excited state. We could not observe any fluorescence from the normally fluorescing $^4F_{3/2}$ state of Nd at any stage, suggesting that the dominant transfer is by cross relaxation involving some of the intermediate states. If one or more high-frequency phonons are involved in this process to conserve energy, a very weak temperature dependence in the range of interest would result. This is consistent with the observed behavior.

B. Narrowband excitation

Before we can quantitatively analyze the dynamics involved in the Pr-Nd transfer we must first of all measure the dynamics of transfer among the Pr ions. This is done by exciting the $^3P_0$ state at some point in the inhomogeneous absorption line and monitoring either the resonant sharp-line fluorescence or the growth of fluorescence at other points in the inhomogeneous fluorescence line. We concentrate on the sharp-line decay as it is easier to handle because of the difficulty in deconvoluting the rise part from the decay part of the nonresonant fluorescence. Since the dynamics in pure PrF_3 were already measured in this way,[9] we apply the same procedures to the case of Nd doping. The analysis in this case is a little more complicated, since transfer to the Nd ions is always present. We can write the decay of the sharp-line fluorescence intensity $I(t)$ as

$$I(t)=I(0)\,e^{-t/t_0}f_{D-D}(t,\,T)f_{D-A}(t,\,T)\,, \tag{1}$$

where t_0 is the fluorescence lifetime of the $^3P_0$ state in the absence of migration and trapping, and $f_{D-D}(t,T)$ and $f_{D-A}(t,T)$ describe, respectively, transfer from the initially excited Pr ions to other Pr ions and to Nd traps. We have already shown that $f_{D-A}(t,T)$ is temperature independent up to 40 K. At 5 K no measureable Pr-Pr transfer is observed so that at this temperature $f_{D-D}(t,T)=1$. Hence at any temperature T the decay of the sharp-line fluorescence is given by

$$I(t)=I'(t)f_{D-D}(t,\,T)\,, \tag{2}$$

where $I'(t)$ is the observed decay at 5 K. In Fig. 4 we show the decay of the sharp line at 5 K and 14 K for a Nd concentration of 5 at. % when the laser is placed at 5 cm^{-1} to the high-energy side of the peak of the inhomogeneous line. The function $f_{D-D}(t,T)$ is then calculated by weighting $I'(t)$ with the appropriate function to give the decay curve at 14 K. To do this we make two simplifying assumptions regarding $f_{D-D}(t,T)$. Firstly, because the number of nearest Pr neighbors is large, we neglect back transfer to the initially excited ion on the time scale of interest. Secondly, since the donor concentration is close to unity, we overlook any disorder in the donor array and assume that the total donor-donor transfer ratio is the same for all donors. In this case the initial behavior of $f_{D-D}(t,T)$ is given by[11]

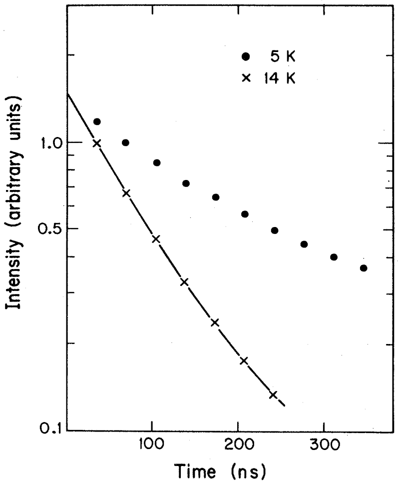

FIG. 4. Decay of the $^3P_0$-$^3H_6(1)$ sharp-line fluorescence at 5 and 14 K under narrowband excitation. The laser is such that the sharp line is displaced 5 cm^{-1} from the peak of the $^3P_0$-$^3H_6(1)$ inhomogeneous line. The solid line is $I'(t)\exp(-w_{DD}t)$ with $w_{DD}=5.46\times10^6$ s^{-1}.

$$\begin{aligned} f_{D-D}(t,T) &= \exp\Big(-c_D\sum_n w_{0n}t\Big) \\ &= \exp(-w_{DD}t)\,, \end{aligned} \tag{3}$$

where c_D is the concentration of Pr ions, w_{0n} is the transfer rate between two Pr ions at sites 0 and n separated by a distance R_{0n}, and the summation is over all lattice sites. Thus we weight $I'(t)$ by a function $e^{-w_{DD}t}$, with w_{DD} as an adjustable parameter, to give the measured decay $I(t)$. For $w_{DD}=5.46\times10^6$ s^{-1} a fit shown by the solid line in Fig. 4 is found which is in excellent agreement with with $I(t)$. We can write $w_{0n}=w_{01}(R_{01}/R_{0n})^6$, where w_{01} is the nearest-neighbor transfer rate at temperature T and where we have assumed that the Pr-Pr transfer is governed by the electric dipole-electric dipole interaction.[11] A simple lattice summation yields w_{01} to be 4.7×10^5 s^{-1} at 14 K, which agrees closely with the value found in pure PrF_3, where the rate varies as $T^{4.3}$. Hence we can write w_{DD} as

$$\begin{aligned} w_{DD} &= c_D\sum_n w_{0n} \\ &= 64.39\,T^{4.3}\,. \end{aligned} \tag{4}$$

V. ANALYSIS OF Pr-Nd TRANSFER

We now analyze the fluorescence decay of the $^3P_0$ state of Pr at 5 K for different Nd concentrations under broadband excitation. Since there is negligible Pr-Pr transfer at this temperature and since no back transfer from the Nd to the Pr ions occurs, the intensity $I(t)$ after pulsed excitation can be described by the Inokuti-Hirayama model[19]

$$\ln I(t)+\frac{t}{t_0}=-\frac{4\pi n_A}{3}R_{01}^3(X_{01}t)^{3/s}, \qquad (5)$$

where n_A is the density of Nd ions, and X_{01} is the nearest-neighbor transfer rate between a Pr-Nd pair at sites 0 and 1, respectively, with separation R_{01}. Also, s is 6, 8, or 10 depending on the multipolar nature of the Pr-Nd interaction, and t_0 is the intrinsic decay time. In PrF_3 $t_0 = 750$ ns, but as Nd is added the Pr concentration is less than 100% with a consequent decrease in intrinsic cross relaxation and an increase in t_0. In Fig. 5 we have plotted the fluorescence decay of the 5 at.% Nd-doped sample in the form of $\ln I(t)+t/t_0$ against $t^{3/s}$ for $s=6$, corresponding to an electric dipole-electric dipole interaction. The straight-line behavior indicates that our assumptions above are correct and that the choice of $s=6$ is a valid one. For 5 at.% Nd, $n_A=9.5\times10^{-4}$ ions/Å^3, $R_{01}=4.085$ Å, and from the slope in Fig. 5 we find $X_{01}=11.3\times10^6$ s^{-1}. From this α is calculated to be 5.46×10^{-38} cm^6 s^{-1}. A similar treatment for all of the other Nd concentrations yielded the same value of X_{01}, but t_0, as mentioned above, had to be increased from its value of 750 ns for pure PrF_3 to 1200 ns for 20 at.% Nd doping to achieve a good fit.

As the temperature is increased above 5 K, w_{01} increases as $T^{4.3}$ while X_{01} remains constant. At sufficiently high temperatures the fast-transfer limit can be reached where $w_{01}\gg X_{01}$ or $\beta\gg\alpha$. Since at this point all Pr sites are equivalent due to rapid migration among them, the donor population decays exponentially.[14] The corresponding decay rate X_{DA} can be written as a sum of transfer probabilities to all lattice sites but with each site weighted by the probability of it being occupied by a Nd ion. This occupation probability is just the concentration c_A of Nd. Hence we have

$$X_{DA}=c_A\sum_n X_{0n} = c_A X_{01}\sum_n\left(\frac{R_{01}}{R_{0n}}\right)^6 . \qquad (6)$$

In this regime $X_{DA}\propto c_A$. The measured decay rate is the sum of X_{DA} and $1/t_0$ where t_0 is the fluorescence lifetime in the absence of traps which is given by the value used to fit the Inokuti-Hirayama model at low temperature. For 5 at.% Nd, $t_0=900$ ns. In Fig. 6 we have plotted the value of X_{DA} measured at high temperatures where the decay is temperature independent, against c_A. A linear dependence on c_A is obtained in accordance with Eq. (6) showing that at 40 K we are already in the fast-transfer limit. Taking the value of X_{DA} and c_A and performing a simple lattice summation X_{01} is calculated from Eq. (6) to be 11.65×10^6 s^{-1}, in close agreement with the low-temperature value. At 40 K, β can be calculated from Eq. (4) to be 1.7×10^{-37} cm^{6}s^{-1}, whereas $\alpha=5.46\times10^{-38}$ cm^{6}s^{-1} so that the condition $\beta\gg\alpha$ is well satisfied at this temperature.

The consistency between the low- and high-temperature behavior now enables us to investigate the more complex intermediate temperature regime where the Pr-Pr and the Pr-Nd transfer processes are competing. As discussed in Sec.

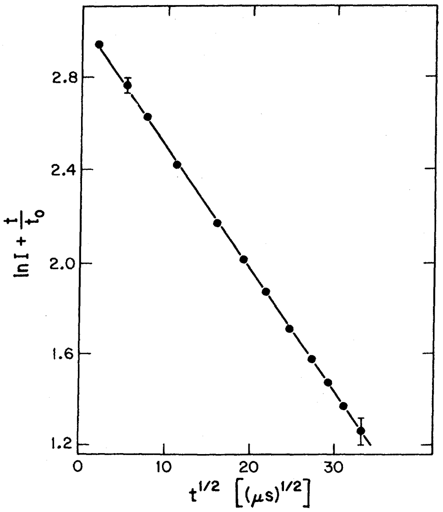

FIG. 5. The $^3P_0$ fluorescence-decay data at 5 K plotted according to the Inokuti-Hirayama model for an electric dipole-electric dipole Pr-Nd interaction. The Nd concentration is 5 at.%. The solid line is obtained from Eq. (5).

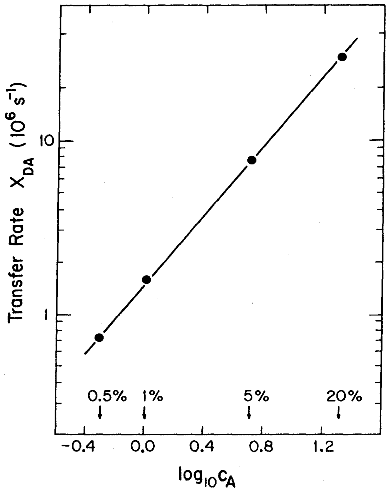

FIG. 6. Plot of the saturated values of Pr-Nd transfer rates X_{DA}, measured in the fast-transfer, high-temperature limit, against Nd concentration c_A on a log-log scale.

II this region can be divided into two regimes $\beta \ll \alpha$ and $\beta \gtrsim \alpha$ which correspond, respectively, to the diffusion[7] and hopping[8] models. Since we know β and α and since β can be set at any value with respect to α by changing the temperature, we can now test the ability of these models to describe migration of energy to traps.

Both of the models predict that the decay should initally be nonexponential but should become exponential in the asymptotic long-time limit. From Fig. 3 we see that above 10 K in the 5 at.% Nd sample an exponential tail to the decay is indeed observed. We now test how well this exponential part agrees with the predictions of the diffusion model of Yokota and Tanimoto.[7] According to the model the asymptotic decay rate c, after subtracting out the intrinsic rate, should be given by

$$c = 8.6 n_A \alpha^{1/4} D^{3/4}, \tag{7}$$

where D is a diffusion constant and n_A is the acceptor concentration. For an ordered array of donors, in a cubic symmetry approximation D can be expressed as [14]

$$\begin{aligned} D &= \tfrac{1}{6} \sum_n w_{0n} R_{0n}^2 \\ &= \tfrac{1}{6} \beta \sum \frac{1}{R_{0n}^4}, \end{aligned} \tag{8}$$

assuming electric dipole-electric dipole interactions. Here we see that D has a weaker dependence on distance than w_{0n} so that interaction between neighbors at large separations will play a significant part in the diffusion. Since from Eq. (4) $\beta \propto w_{DD}$, the rate corresponding to the initial decay of the sharp line in fluorescence line narrowing, then $c \propto w_{DD}^{0.75}$. In Fig. 7 a plot of c against w_{DD} is shown for the temperature region 10–40 K where w_{DD} is normalized to the high-temperature transfer rate X_{DA}/c_A of Eq. (6). Such a normalization corresponds to plotting against the ratio β/α and provides a sample-independent measure of the boundaries of the diffusion and hopping regimes. Between 10 and 13 K ($0.01 \lesssim w_{DD}c_A/X_{DA} \lesssim 0.05$) a straight-line behavior is seen with a slope of 0.78 ± 0.8 in close agreement with the expected value. The diffusion approach would thus seem to be valid in this temperature range. From Eq. (7) we obtain $D = 6.81 \times 10^{-9}$ cm^2 s^{-1} at 12 K. Since $w_{DD} \propto T^{4.3}$ then D also scales at $T^{4.3}$.

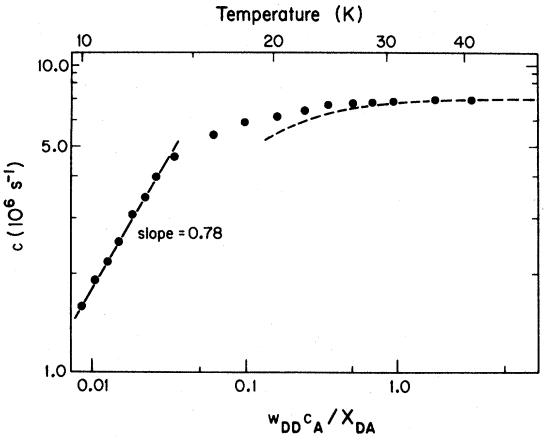

FIG. 7. Plot of the asymptotic slope of the $^3P_0$ fluorescence decay as a function of the total Pr-Pr transfer rate w_{DD} normalized to the rapid-transfer decay rate X_{DA}/c_A. Temperature is indicated on the upper scale. The broken line is the behavior predicted by the hopping model. The solid line indicates the diffusion regime.

A comparison can be made between the theoretical value of the diffusion constant D obtained by a numerical calculation of Eq. (8) (allowing for noncubic symmetry), with the measured value from Eq. (7). A discrepancy exists, however, between the two values, the theoretical value being about a factor of 5 lower than the measured value. A possible explanation for this is that the asymptotic rate c was measured in a time interval before the asymptotic limit was reached, thereby overestimating c. The decay region in which c was measured, however, was exponential over about two orders of magnitude of intensity, suggesting that this is not the reason. A more likely explanation for the discrepancy arises from the fact that since the Pr-Pr transfer is believed to be a two-phonon-assisted process, there is an interference term in the transfer rate which can be important for near-neighbor transfer. The transfer rate w_{0n} between two Pr ions at sites 0 and n is modulated by this phase term so that we must make the replacement $w_{0n} \to w_{0n} f(R_{0n})$ where w_{0n} is the rate in the absence of interference and $f(R_{0n})$ is the phase term. Equation (4) must be rewritten as

$$w_{DD} = c_D \sum_n w_{0n} f(R_{0n}). \tag{9}$$

The form of $f(R)$ is arrived at by treating the two-phonon-assisted transfer in second-order perturbation theory[20] with the result that

$$f(R) = \frac{\displaystyle\int_0^{k_c} \frac{k^2 dk\, e^{\hbar v k/k_\beta t}}{(e^{\hbar v k/k_\beta T} - 1)^2} \left(1 - \frac{\sin kR_{0n}}{kR_{0n}}\right)^2}{\displaystyle\int_0^{k_c} \frac{k^2 dk\, e^{\hbar v k/k_\beta T}}{(e^{\hbar v k/k_\beta T} - 1)^2}}, \tag{10}$$

where the sin term gives rise to the interference. In this expression v is the sound velocity and the integration is cut off at a value of k which depends on the form of the phonon density of states and in particular on those phonons which take part in the transfer process. If we assume a Debye density of states with a Debye temperature T_D which determines k_c, we can numerically integrate Eq. (10) after first averaging over the known transverse and longitudinal acoustic velocities. In Fig. 8, $f(R)$ is plotted against R_{0n} for two temperatures 10 and 13 K. As seen from the figure $f(R)$ is considerably less than unity out to about 20 Å at both temperatures, which incorporates an extremely large number of ions. Consequently the transfer rates between near-neighbor Pr ions is reduced relative to the long-range transfer. The effect of this is readily seen from Eq. (9): if the total measured rate w_{DD} is to remain fixed, the long-range terms in the sum must be adjusted upwards. As mentioned previously these long-range terms contribute considerably to the diffusion constant and, if they are now larger, then D will also be larger. We have reevaluated D in Eq. (8) including the interference term, and obtained a value of $D = 5.54 \times 10^{-8}$ cm^2 s^{-1} at 12 K which is in good agreement with the experimentally measured value of 6.81×10^{-4} cm^3 s^{-1}. Since, however, D is very sensitive to the density of phonon states participating in the Pr-Pr transfer it is difficult to be any more quantitative until the density is better known. It is obvious, however, that in any discussion of highly concentrated systems, one must consider interference effects in the interion transfer whenever two-phonon processes are important.

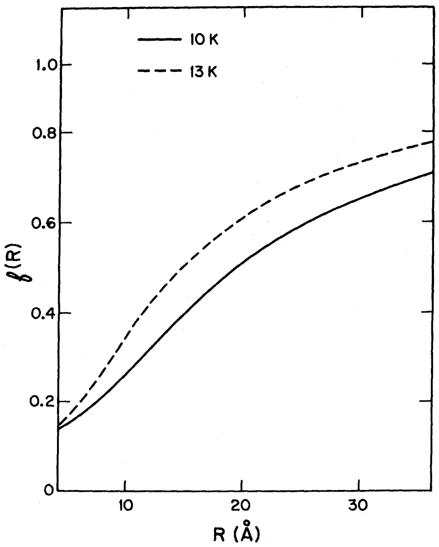

FIG. 8. Plot of the strength of the interference term $f(R)$ [Eq. (10)] against R, the separation between the two interacting Pr ions, for two different temperatures 10 and 13 K.

To complete the discussion on the diffusive approach we note that Yokota and Tanimoto[7] attempted to fit the early nonexponential and later exponential behavior by a single interpolation formula. However, as the asymptotic slope given by this formula differed from their exact slope by 30%, a comparison of our data to their model was impossible. A more detailed treatment of the total time behavior is presented elsewhere.[21]

As mentioned previously the hopping model[8] pertains to the limit $\beta \gtrsim \alpha$ or equivalently $w_{DD}\ c_A/X_{DA} \gtrsim 1$. The asymptotic decay rate is given by an expression of the form[14]

$$c = c_A \sum_n \frac{X_{0n}}{1 + X_{0n}\tau}, \tag{11}$$

where c_A and X_{0n} have the same meaning as before. The symbol τ denotes the donor-donor "hopping time" and can be identified with the time integral of $f_{D\text{-}D}(t, T)$, the donor-donor factor appearing in the expression for the decay of the narrowband fluorescence, Eq. (1).[14] In applying (11) we take $X_{0n} = \alpha/R_{0n}^6$ and, following the discussion in Sec. IV, identify τ with w_{DD}^{-1}, i.e.,

$$\tau = \int_0^\infty f_{D\text{-}D}(t', T)\,dt = \int_0^\infty e^{-w_{DD}t}\,dt = w_{DD}^{-1}. \tag{12}$$

The broken line in Fig. 7 shows the results obtained using Eqs. (5.8)-(5.10) with experimentally determined values for α and w_{DD}. It is apparent that the model works reasonably well in the region where the theory is applicable, $w_{DD}c_A/X_{DA} \gtrsim 1$. However, the data do not provide a very stringent test of the theory since the rapid-transfer limit applies for $w_{DD}c_A/X_{DA} \gtrsim 2$.

VI. CONCLUSION

In this paper we have made a reexamination of the dynamics of trapping of optical excitation in a disordered system. The basis of our approach has been an independent measure of the dynamics within the system of donors which enables us to examine the microscopic nature of the trapping process. In the system PrF$_3$ doped with Nd the Pr-Pr transfer at low temperature is phonon assisted with a strong dependence on temperature. The Pr-Nd transfer, on the other hand, is insensitive to temperature in the low-temperature region so that by merely changing the temperature we could span the range $\beta \ll \alpha$ to $\beta \gg \alpha$ in a single system. The extremes of this range correspond to no donor-donor transfer and very (infinitely) fast transfer. In the intermediate regime we have examined the limits of applicability of the diffusion and hopping models. This is the first time that it has been possible to identify all of these processes in a single system and to place quantitative boundaries on each process. Since trapping of energy in disordered systems is a universal phenomenon, such an approach can be used to great advantage in interpreting the complex behavior that results from such trapping.

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