allowing two-dimensional flow of quasiparticles.

In conclusion, we have demonstrated that the phonons emitted from the inhomogeneous gap state are highly nonthermal and the measurements of these phonons by the two-dimensional sweep of a microsensor provide a study of nonequilibrium gap structure in detail. It will be a next interesting subject to investigate the nature of these phonons and their transmission mechanism.

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Resonant Fluorescence Line Narrowing in $La_{1-x}P_5O_{14}:Nd_x^{3+}$

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Donor-donor and donor-acceptor dynamics in $La_{1-x}P_5O_{14}:Nd_x^{3+}$ are measured directly with a high-resolution, near-ir laser system. Time-resolved fluorescence line-narrowing measurements show an absence of rapid donor-donor transfer below 20 K and an onset of spectral diffusion at ≈ 20 K for an $x = 0.75$ sample. The linear concentration quenching and exponential decay in the absence of fast diffusion are explained with existing energy-transfer theories and are consistent with room-temperature studies.

PACS numbers: 78.55.Hx, 78.20.-e, 78.45.+h

$La_{1-x}P_5O_{14}:Nd_x^{3+}$ (LNPP) is one compound of a class of high-gain Nd laser materials,[1] which show a small decrease in their fluorescence quantum efficiency (QE) as the Nd^{3+} concentration is increased up to the stoichiometric limit. Directly related to this technologically important aspect are several interesting anomalous luminescence properties. The weak concentration quenching of the QE in LNPP is linearly dependent[1-4] on the fractional Nd^{3+} concentration x, in contrast to many other similar systems,[5] e.g., YAlG:Nd^{3+} (neodymium-doped yttrium aluminum garnet), where the quenching goes as x^2. The fluorescence from the level of interest, the $^4F_{3/2}(1)$ state, shows a temperature-independent exponential decay after pulsed excitation for all concentrations[4,6] and no spectral diffusion (energy transfer) among the Nd^{3+} ions has been observed.[7] Various attempts have been made to explain the unusual behavior of this type of compounds[2-7]; however, the excitation migration and trapping mechanisms in these systems remain unclear and have resulted in some controversy.

We report here for the first time results of a study using *resonant* and *high-resolution* excitation of the $^4F_{3/2}(1)$ state of LNPP to investigate the microscopic interactions between the Nd^{3+} ions. In prior studies, spectral diffusion and the fluorescence decay in this system were measured with nonresonant pumping of the near-ir $^4F_{3/2}(1)$ level. Energy-transfer studies in similar materials[8] have clearly demonstrated the importance of probing directly into the state of interest for the proper extraction of the donor-donor and donor-acceptor interactions.

We employed the technique of time-resolved fluorescence line narrowing (TRFLN),[8] within the inhomogeneous envelope of the $^4F_{3/2}(1)$ state. The position of this state in LNPP is in the near-ir ($\approx 11\,500$ cm^{-1}), which is not conveniently accessible to narrowband, pulsed dye lasers using ir dyes. The output of an yttrium aluminum garnet–pumped high-power and narrowband oscillator-preamplifier-amplifier DCM dye laser was downshifted by stimulated Raman scattering in a high-pressure H_2 gas cell and the first Stokes component was used for resonant excitation of the $^4F_{3/2}(1)$ state. The samples were high-quality single crystals grown from a phosphoric acid flux.[10] We applied TRFLN to $x = 0.2$, 0.75, and 1.0 samples. The $^4I_{9/2}(1) \to {}^4F_{3/2}(1)$ excitation spectrum was measured at 8 K by monitoring nonresonant 1.05-μm fluorescence. All three concentrations revealed relatively narrow (~1–2 cm^{-1}), inhomogeneously broadened lines (see Fig. 1, e.g., for the $x = 0.2$ sample). The inhomogeneously broadened lines were successfully line narrowed and the decay of the narrow fluorescence line-narrowed (FLN) component and its spectral time development were measured between 5 and 20 K for the $x = 0.2$ and 0.75 samples and at 6 K for the $x = 1.0$ sample. The FLN component in the $x = 0.2$ and 0.75 samples decayed exponentially with a temperature-independent decay rate over this temperature range. The decay in the $x = 1.0$ sample at 6 K was also exponential and consistent with room temperture (RT) values.[3] There was no spectral diffusion up to 20 K for $x = 0.2$ (Fig. 1) and $x = 0.75$; the $x = 1.0$ sample showed a similar behavior at 6 K. This demonstrates that, at these temperatures and in the time scale of our measurements (on the order of the decay time), there is no spectral donor-donor transfer.

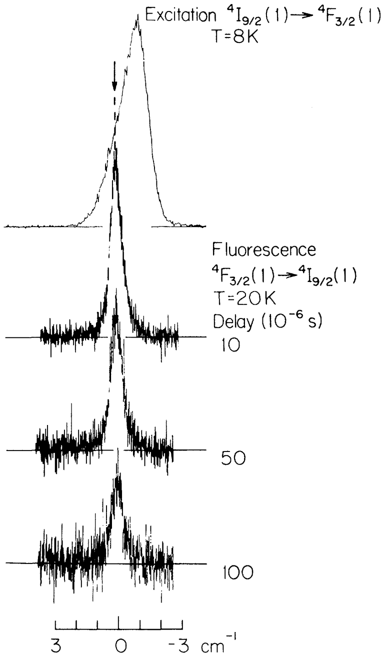

FIG. 1. Time-resolved fluorescence line narrowing in the $^4F_{3/2}(1)$ state of $La_{0.8}Nd_{0.2}P_5O_{14}$. The top trace shows the inhomogeneously broadened $^4I_{9/2}(1)\to{}^4F_{3/2}(1)$ excitation profile. The time development of the line-narrowed $^4F_{3/2}(1)\to{}^4I_{9/2}(1)$ fluorescence (bottom three traces) indicated the absence of spectral diffusion at 20 K. Arrow marks the position of excitation.

In a more recent measurement at 20 K on the $x = 0.75$ sample, we observed an onset of spectral diffusion, which is evidence for donor-donor transfer. These observations indicate that donor-donor transfer is slow and temperature dependent in this temperature regime (phonon-assisted energy transfer). This disproves assumptions made by previous investigations that donor-donor transfer is rapid[3] or absent.[7] As we shall see, this is crucial in the understanding of the linear concentration quenching and the exponential decay in these systems.

Huber has shown[10] that the decay of the donor population $N_D(t)$ in the presence of traps (acceptors) can be written as

$$N_D(t) = N_D(0)\exp(-t/\tau_0)f(t) \tag{1}$$

with τ_0^{-1} the radiative decay rate. For LNPP, various Nd^{3+} ions, neighboring the donor, act as traps resulting in quenching of the donor excitation through a cross-relaxation process.[3,4] In the limit of no donor-donor transfer, $f(t)$ in Eq. (1) can be expressed by

$$f(t) = \prod_l{}' [1 - x + x\exp(-tX_{0l})] \tag{2}$$

with x the fractional trap concentration, which for self-quenching is simply the Nd^{3+} concentration in LNPP. X_{0l} is the quenching rate between a donor at site 0 and an acceptor at site l with $\prod_l{}'$ a product over all sites excluding site 0. This expression is a configurational average of the decay of a donor at site 0; trapping by an acceptor at site l contributes a factor $\exp(-tX_{0l})$ with probability x and no trapping at site l (probability $1-x$) contributes a factor of unity. Equation (2) is a generalization of the continuum model of Inokuti and Hirayama[10] for a discrete lattice and for all trap concentrations and normally results in a nonexponential decay and a nonlinear quenching rate. The product in Eq. (2) can be written as $\exp(\sum_l \ln[1 + x\{\exp(-tX_{0l}) - 1\}])$ which, for small trapping rates (weak quenching), can be approximated by

$$f(t) \approx \exp(-tx\textstyle\sum_l X_{0l}). \tag{3}$$

This results in an exponential decay rate τ^{-1} given by

$$\tau^{-1} = \tau_0^{-1} + x\textstyle\sum_l X_{0l} \tag{4}$$

which now shows a linear dependence on the concentration. The limit of validity of Eq. (3) is established by consideration of the relative magnitudes of the radiative decay rate τ_0^{-1} and the cross-relaxation rate X_{0l}. In the case where $\tau_0 \lesssim X_{0l}^{-1}$, i.e., in the so-called early time regime, Eq. (3) guarantees then an exponential decay rate[10] which is linearly dependent on x. Our low-temperature decay measurements are entirely consistent with Eq. (3) and are also compatible with the absence of significant donor-donor transfer at these temperatures. We note again that for times much longer than X_{0l}^{-1} the donor decay no longer follows Eq. (3) and will generally be nonexponential (long-time regime). In LNPP this regime is simply never reached because of experimental limitations imposed by the radiative lifetime ($\tau_0 \simeq 341$ μs).

These low-temperature results can be compared to room-temperature (RT) and broadband excitation results of Lenth, Huber, and Fay.[3] In their analyses rapid donor-donor transfer is assumed. Recent four-wave mixing studies[11] in LNPP at RT apparently indicated *spatial* transfer over large distances, strongly suggesting also the presence of fast donor-donor transfer at RT. These results and assumptions are, however, not inconsistent with our results for we know that the donor-donor transfer rate is rapidly increasing with the temperature with a T^3 or higher-power dependence.[8,12] In the limit of fast donor-donor transfer all donors have equal probability of being excited and $f(t)$ in Eq. (1) has the form[10]

$$f(t) = \exp(-tx\textstyle\sum_l X_{0l}) \tag{5}$$

with x and X_{0l} defined as before. According to Eqs. (1) and (5), fast donor-donor transfer results in an exponential decay rate τ^{-1} and replicates the early-time regime results of Eq. (4) for no donor-donor transfer. This fast-diffusion limit behavior has been confirmed in a number of systems.[8,13] In order to explain the generic behavior of pentaphosphates, Lenth, Huber, and Fay[3] have advanced the hypothesis that fast donor-donor transfer occurs at RT, whereas our results indicate an absence of donor-donor transfer at low temperatures. We believe that overall consistency is attained simply by assuming that different donor-donor transfer rates and hence different time regimes are involved at low and high temperatures.

This consistency may be derived as follows: Lenth, Huber, and Fay's[3] RT quenching data can be used to calculate a value for X_{01} (the nearest-neighbor trapping rate) under the assumption of fast donor-donor diffusion. In this limit, Eq. (4) is employed and the lattice sum is carried out by assuming an electric dipole-dipole interaction between donor and trap[3] and summing over a sufficient number of lattice sites. The resulting value for X_{01} is then substituted in the generalized Inokuti-Hirayama model [Eq. (2)] and the behavior of $f(t)$ as a function of concentration at low temperature can be calculated. These calculations show that the donor decay is exponential with a linear quenching rate which is consistent with our low-temperature decay measurements. Employing the RT value of X_{01} for the low-temperature decay-rate calculations is reasonable because of the large energy mismatch in the cross-relaxation process[4] (≈ 1000 cm^{-1}) and is consistent with the observed temperature independence of τ between 4 and 300 K.[4,6]

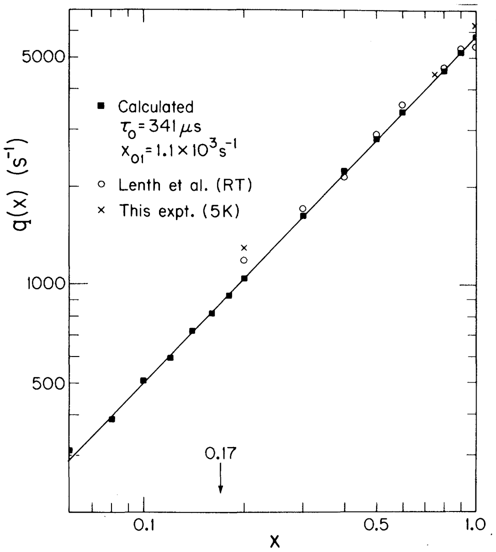

FIG. 2. The quenching rate q, $\tau^{-1}-\tau_0^{-1}$, as a function of the concentration x in $\mathrm{La}_{1-x}\mathrm{Nd}_x\mathrm{P}_5\mathrm{O}_{14}$. Open circles correspond to room-temperature and nonresonant excitation data from previous investigations; crosses are low-temperature data with narrow-band, resonant excitation (this study). Squares are theoretical values and show a linear quenching rate (solid line). The calculated values for $x < 0.17$ do not take into account a phase transition in the crystal structure, which occurs at $x = 0.17$ (arrow).

The quenching rate, $\tau^{-1}-\tau_0^{-1}$, calculated in this manner, is plotted as a function of concentration in Fig. 2, which shows also Lenth, Huber, and Fay's RT data[3] and our low-temperature results. The linear concentration dependence of the quenching rate is clearly visible over the range $x = 0.06$ to $x = 1.0$, both for the RT and the low-temperature data, as well as for the calculated quenching rate. The value of X_{01} is $\approx 1.1 \times 10^3$ s^{-1}, which is indeed comparable to the radiative decay rate in this compound. An estimate of the nearest-neighbor donor-donor transfer rate w_{01} can be made using the RT four-wave mixing results,[11] which yielded a value of the RT diffusion coefficient D of a fully concentrated sample. This value for D can be extrapolated back to the low-temperature regime[10,13]; with a T^3 dependence[12] of the donor-donor transfer rate, the value of w_{01} at 5 K is[10,13] $\approx 7.1\times10^3$ s^{-1} which is on the same order as the decay rate of the $x = 1$ sample and is consistent with the TRFLN value extracted from the $x = 0.75$ sample. This small value for w_{01} shows again the consistency between the high- and low-temperature regimes.

In conclusion, we have reported the first direct measurements of donor-donor and donor-acceptor interactions within the inhomogeneous envelope of the ${}^4F_{3/2}(1)$ state of LNPP. Using TRFLN, we have demonstrated that very little donor-donor transfer occurs in the temperature range 5–20 K. The absence of donor-donor transfer at low temperatures and the observed onset of spectral diffusion at 20 K for the $x = 0.75$ sample show the phonon-assisted nature of the donor-donor interaction. A correct application of the generalized Inokuti-Hirayama model explains the observed exponential decay and the linear concentration quenching rate, and provides consistency with other studies at different temperatures. No resonant energy-transfer processes[14] or excitonic effects[15] are required to explain the properties of LNPP. A comparison with RT data[3,11] yields a nearest-neighbor trapping rate and a donor-donor transfer rate at 5 K which are consistent with our low temperature FLN data.

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Persistent Holes in the Spectra of Localized Vibrational Modes in Crystalline Solids

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Persistent nonphotochemical spectral holes have been burnt at low laser intensity in the vibrational absorption line of a spherical-top molecule in alkali halide crystals. These observations complement earlier studies on electronic transitions in organic crystals and glasses and demonstrate that persistent hole burning is a general solid-state phenomenon.

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Persistent spectral nonphotochemical hole burning (NPHB) has been reported for a number of inhomogeneously broadened optical transitions in solids.[1-3] A natural question to ask is the following: What are the fundamental conditions necessary for the formation of permanent spectral nonphotochemical holes that last much longer than the excited-state lifetimes? Hayes, Stout, and Small[1] have reviewed the persistent spectral holes observed for the electronic transitions of photostable molecules imbedded in organic glasses. They postulate that the impurity molecules interact with the two-level systems (TLS's) characteristic of the glassy state, and that transitions of the TLS's induced by the electronic excitation are responsible. NPHB in the mixed molecular crystal pentacene in benzoic acid has been explained as due to TLS's associated with the hydrogen bonds in the dimer lattice.[2] For vibrational transitions, Dubs and Günthard[3] have reported the formation of persistent holes for 1,2-difluoroethane dispersed in an amorphous Ar matrix.

For all of these cases, persistent NPHB appears to depend upon some internal structure or rearrangement of the nearby matrix (such as TLS's in glasses). In this Letter we demonstrate that persistent spectral holes can be burned in the vibrational absorption line of a high-symmetry photostable molecule in a simple, ordered crystalline host. The intrinsic symmetry and simplicity of this hole-burning (HB) system have enabled us to conclude that hole formation is mediated by reorientation of the impurity molecule during vibrational deexcitation.

The samples used for these experiments were annealed, Czochralski-grown single crystals of KI or RbI that were doped by the addition of from 0.02 to 0.8 mole % of $KReO_4$ or $RbReO_4$ to the melt. Holes were burned in the inhomogeneously broadened line with a $Pb_{0.86}Sn_{0.14}Te$ diode laser (10-MHz linewidth) or a CO_2 laser (2-MHz linewidth), and were detected in transmission with either a second CO_2 laser or the diode laser as a tunable probe. Intensities at the samples were on the order of 100 $\mu W/cm^2$, orders of magnitude below the saturation intensity[4] of 10 W/cm^2. The high-resolution absorption spectrum[5] and vibra-