[6]J. C. Bruyère, A. Deneuville, A. Mini, J. Fontenille, and R. Danielou, J. Appl. Phys. 51, 2199 (1980).
[7]F. K. Zellama, P. Germain, S. Squelard, B. Bourdon, J. Fontenille, and R. Danielou, to be published.
[8]J. C. Knights and R. A. Lujan, Appl. Phys. Lett. 35, 244 (1979).
[9]T. Shimada, Y. Katayama, and K. F. Komatsubara, J. Appl. Phys. 50, 5530 (1979).
[10]A. Madan, S. R. Ovshinsky, and E. Benn, Philos. Mag. 40, 259 (1979).

Measurement of Exciton Diffusion Lengths in $Nd_xLa_{1-x}P_5O_{14}$ by Four-Wave Mixing Techniques

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Transient four-wave mixing techniques have been used to measure the decay rate of the excited-state population grating in $Nd_xLa_{1-x}P_5O_{14}$ samples as a function of grating spacing. The results show that at room temperature there is diffusive energy migration over distances of the order of 0.36 μm in the highly concentrated samples.

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Degenerate four-wave mixing (FWM) spectroscopy has been shown recently to be a powerful method for studying spatial migration without spectral transfer of electronic excitation energy in solids.[1-4] This technique has been used to determine the diffusion coefficient of molecular excitons in organic solids,[1] but attempts to make similar measurements on Frenkel excitons in inorganic materials have resulted only in placing an upper bound on the diffusion coefficient because the migration is too short to observe in the samples which have been studied.[2-4] We report here the results of FWM measurements on single crystals of $Nd_xLa_{1-x}P_5O_{14}$ at room temperature. The presence of energy migration is easily observed and it is found to be diffusive with a migration distance of the order of 0.36 μm. These results are of significant importance since they represent an unambiguous determination of the range of energy migration in this class of stoichiometric materials used as "minilasers" for low-threshold, high-gain applications.[5,6] The mechanism causing concentration quenching of the fluorescence in these materials is not understood but it is known to have quite different properties from other neodymium laser materials.[5] This is not only an interesting fundamental physics question, but it is also important in material development for laser applications. The contribution of energy migration to concentration quenching in neodymium pentaphosphate has been the subject of significant interest and some controversy, with estimates of migration lengths ranging from a few angstroms to a few microns.[7-15] These FWM results provide an answer to one of the fundamental questions surrounding this controversy.

The samples used for this investigation were cleaved from high-quality single crystals grown by the technique described recently.[16] Several different experimental arrangements have been used to establish and probe population gratings of excited states. A schematic diagram of the setup used for this work is shown in Fig. 1. The 5145-Å line of an argon laser was used since it falls on one edge of a Nd^{3+} absorption line. The absorption of this light by the Nd^{3+} ions in the sample creates a spatial distribution of excited states with a sinusoidal pattern of wavelength $\Lambda \approx \lambda/\theta$, where θ is the crossing angle of the write beams and λ is the wavelength of the light in the sample. This "population grating" can cause the probe beam to be scattered with the maximum scattering efficiency occurring when the Bragg condition is satisfied.

Figure 2 shows the results from measuring the decay rate K of the scattered probe beam as a function of the square of the crossing angle of the write beams for single crystals of NdP_5O_{14} and

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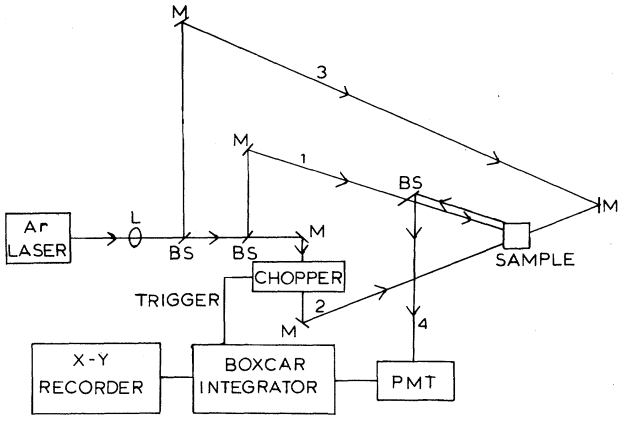

FIG. 1. Experimental setup for transient four-wave mixing measurements. 1 and 2, the write beams; 3, the incident probe beam; and 4, the scattered probe beam.

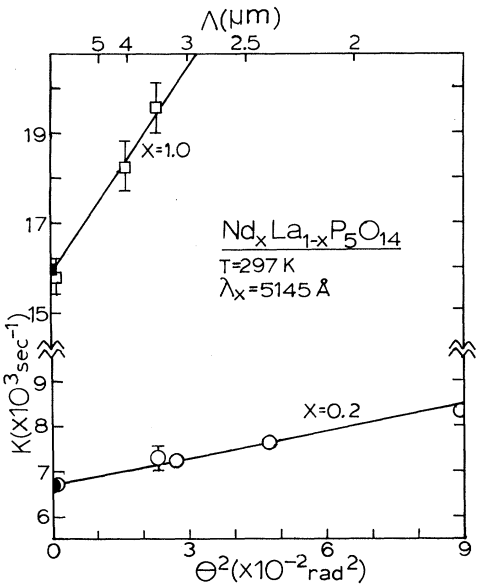

FIG. 2. Measured decay rates of the scattered probe beam for NdP_5O_{14} and $Nd_{0.2}La_{0.8}P_5O_{14}$ crystals at room temperature for various values of the crossing angle of the write beams. The filled points are twice the measured fluorescence decay rates and the straight lines represent the predictions of Eq. (4).

$Nd_{0.2}La_{0.8}P_5O_{14}$ at room temperature. The decay curves were found to be exponential and the data points shown in the figure represent the average obtained from repeating the measurements numerous times at the same crossing angle. The error bars represent the spread in the data acquired at each point. The increase in background "noise" due to extraneous light scattering and the decrease in probe beam transmission caused the data obtained on the heavily concentrated sample to be less accurate than that obtained on the 20% Nd sample.

For both of the samples investigated, the probe beam decay rate increases approximately linearly with increasing values of θ^2. This can be related directly to the mechanisms responsible for the destruction of the population grating. This grating can be destroyed both by the decrease in the excited-state population by normal fluorescence decay and by the migration of excited states (excitons) from the peak to the valley regions of the grating. If the exciton motion is diffusive the time evolution of the spatial distribution of the excited-state population $n(x, t)$ is given by the one-dimensional diffusion equation[1]

$$\partial n(x,t)/\partial t = D\partial^2 n(x,t)/\partial x^2 - \tau^{-1} n(x,t), \qquad (1)$$

where D is the diffusion coefficient and τ is the fluorescence decay time. For the initial condition of a sinusoidal spatial distribution of $n(x, 0)$ in the x direction, the solution of Eq. (1) is

$$n(x,t) = \tfrac{1}{2} e^{-t/\tau}\{1 + \exp[-(2\pi/\Lambda)^2 Dt]\cos(2\pi x/\Lambda)\}. \qquad (2)$$

The scattering efficiency is proportional to the depth of the grating.[17,18] This leads to the expression for the diffracted probe-beam intensity

$$I_s(t) = I_p(I_e \Delta n)^2 = I_p I_e^2 e^{-Kt}, \qquad (3)$$

where

$$K = 2[(2\pi/\Lambda)^2 D + \tau^{-1}] = (8\pi^2 D/\lambda^2)\theta^2 + 2\tau^{-1}. \qquad (4)$$

Here I_p is the probe beam intensity in the absence of scattering and I_e is the write beam intensity. Both λ and θ have been corrected for the index of refraction of the sample.

The theory outlined above predicts that in the presence of diffusive exciton migration the measured scattered probe-beam intensity will decay exponentially with a decay rate which increases linearly with θ^2. These predictions are consistent with the experimental results obtained on the $Nd_xLa_{1-x}P_5O_{14}$ crystals. The solid lines in Fig. 2 represent the fit of the theoretical expression in Eq. (4) to the experimental data. The intercepts of these lines should be $2/\tau$ and their slopes can be used to determine values of D. Table I lists the measured fluorescence lifetimes for these samples and they are used to plot the solid points shown in Fig. 2 at $\theta^2 = 0$. The theoretical lines extrapolate nicely to these points. Table I also

TABLE I. Exciton diffusion parameters for Nd_x-$La_{1-x}P_5O_{14}$ crystals.

Sample (x)	τ (μsec)	D (cm^2/sec)	l_x (μm)
0.2	300	6.85×10^{-7}	0.20
1.0	125.3	5.09×10^{-6}	0.36

lists the calculated diffusion coefficients for these samples. The average displacement of an exciton along the grating directions in its lifetime is given by $l_x=(2D\tau)^{1/2}$. The values for this one-dimensional exciton diffusion length for the two pentaphosphate samples are listed in Table I.

The results reported here were all obtained with the laser beams incident on the b plane (cleavage plane) of the crystal and with the sample oriented to measure diffusion in approximately the a direction. Although some changes in the results were observed when the sample was rotated to different orientations, this experiment is so sensitive to precise alignment that it is not clear at this point whether the observed changes are due to anisotropy in the exciton diffusion or simply a slight misaligning of the experiment. The question of orientation dependence of D will be thoroughly investigated in the future. At high "probe-beam" intensities a double exponential decay was observed with a faster initial decay rate. At angles larger than those reported in Fig. 2 this fast-decay component dominated the detected signal even at smaller probe-beam intensities and thus limited the range of grating spacings available for study. The decay rate of the fast signal is independent of the crossing angle of the "write beams" and does not extrapolate to $2/\tau$ and thus is not directly associated with the "population grating." There are several other sources of refractive index gratings in crystals due to different types of nonlinear optical interactions and it is not surprising that other interference effects are present in a birefringent, ferroelastic crystal such as $Nd_xLa_{1-x}P_5O_{14}$. In this paper we focus our attention on the properties of the population grating and plan to study the characteristics of other types of gratings in future investigations. It should be pointed out that thermal gratings can also be studied by this technique and that the thermal diffusion coefficients are of the same order of magnitude as those reported here. We can be sure that the diffusion coefficients reported are not due to thermal diffusion since the observed decay rates extrapolate to twice the fluorescence decay rates and the value of D varies significantly with Nd concentration. Neither of these characteristics is true for thermal gratings.

One important aspect of characterizing energy migration is identifying the microscopic nature of the interaction causing the motion. A rough approximation for the diffusion coefficient of an exciton undergoing an incoherent random walk resulting from electric dipole-dipole interaction is[19]

$$D=\tfrac{1}{2}(\tfrac{4}{3}\pi N_s)^{4/3}R_0^{\,6}/\tau_0, \qquad (5)$$

where N_s is the sensitizer concentration, τ_0 is the intrinsic fluorescence lifetime, and R_0 is the "critical interaction distance." For NdP_5O_{14}, $N_s=4\times10^{21}$ cm^{-3} and, if concentration quenching is attributed to energy migration, $\tau_0=350$ μs. Use of these values and the measured value of D in Eq. (5) gives $R_0=45$ Å. Although this is extremely high, compared with typical values for R_0 in lightly doped solids, it is consistent with the theoretically predicted value R_0 in a stoichiometric crystal such as NdP_5O_{14} if resonant interaction between ions in identical sites with small homogeneous linewidths is assumed.[12] Also, Eq. (5) predicts that the diffusion coefficient should vary as the $\frac{4}{3}$ power of the concentration, which is consistent with the results given in Table I. In addition, it should be noted that the electric dipole-dipole interaction has a long enough range to overcome any structural anisotropy.[5]

These FWM results show that at room temperature in NdP_5O_{14}, excitons diffuse over an average distance of 0.36 μm in a specific direction. The relatively long range of the exciton diffusion measured here disagrees strongly with several of the previously published results.[6,11,15] However, it should be noted that the authors of Ref. 15 have obtained more recent results in agreement with those reported here.[5] It is not clear why the results of Weber and co-workers[6,11] are in contradiction to the present results, but one source of difference may be the greatly improved quality of the large-size crystals now available for study.[16] Although the results reported here do not give direct information concerning the mechanism of concentration quenching, they do show the presence of long-range energy migration and thus it is quite possible for exciton diffusion and trapping to play an important role in the quenching process. The complete theoretical characterization of energy transfer in $Nd_xLa_{1-x}P_5O_{14}$ must await further experimental results and this investigation is presently being extended to several other

samples with different Nd^{3+} concentrations in order to establish the concentration dependence of the diffusion parameters, which can then be compared to the variation of the quenching rate. Also, these experiments will be extended to low temperatures to see whether any coherent contribution to the exciton migration can be detected.[20]

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[1]J. R. Salcedo, A. E. Siegman, D. D. Dlott, and M. D. Fayer, Phys. Rev. Lett. 41, 131 (1978).
[2]H. J. Eichler, J. Eichler, J. Knof, and Ch. Noack, Phys. Status Solidi (a) 52, 481 (1979).
[3]D. S. Hamilton, D. Heiman, J. Feinberg, and R. W. Hellwarth, Opt. Lett. 4, 124 (1979).
[4]P. F. Liao, L. M. Humphrey, D. M. Bloom, and S. Geschwind, Phys. Rev. B 20, 4145 (1979); P. F. Liao and D. M. Bloom, Opt. Lett. 3, 4 (1978).
[5]H. G. Danielmeyer, in *Festkörperprobleme*, edited by H. J. Queisser (Pergamon, New York, 1975), Vol. 15, p. 253.
[6]H. P. Weber, Opt. Quantum Electron. 7, 431 (1975).
[7]S. Singh, D. C. Miller, J. R. Potopowicz, and L. K. Shick, J. Appl. Phys. 46, 1191 (1975).
[8]W. Strek, C. Szafranski, E. Lukowiak, Z. Mazurak, and B. Jezowska-Trzebiatowska, Phys. Status Solidi (a) 41, 547 (1977).
[9]B. C. Tofield, H. P. Weber, T. C. Damen, and P. F. Liao, J. Solid State Chem. 12, 207 (1975).
[10]M. Blätte, H. G. Danielmeyer, and R. Ulrich, Appl. Phys. 1, 275 (1973).
[11]P. F. Liao, H. P. Weber, and B. C. Tofield, Solid State Commun. 16, 881 (1973).
[12]J. M. Flaherty and R. C. Powell, Phys. Rev. B 19, 32 (1979).
[13]F. Auzel, D. Meichenin, and J. C. Michel, J. Lumin. 18/19, 97 (1979).
[14]S. J. Nettel and A. Lempicki, Optics Commun. 30, 387 (1979).
[15]G. Huber, J. P. Jeser, W. W. Krühler, and H. G. Danielmeyer, IEEE J. Quantum Electron. 10, 766 (1974).
[16]R. D. Plättner, W. W. Krühler, W. K. Zwicker, T. Kovats, and S. R. Chinn, J. Cryst. Growth 49, 274 (1980).
[17]H. Kogelnik, Bell System Tech. J. 48, 2909 (1969).
[18]A. E. Siegman, J. Opt. Soc. Am. 67, 545 (1977).
[19]Th. Förster, Ann. Phys. (Paris) 2, 55 (1948).
[20]Y. M. Wong and V. M. Kenkre, Phys. Rev. B 22, 3072 (1980); V. M. Kenkre, Phys. Rev. 18, 4064 (1978).

5*f*-Electron Localization in Uranium Compounds

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Observed 7-eV satellites in the x-ray–photoemission spectra of UGa_2 and other *B*-group compounds are shown to be due to two-hole final states as confirmed by existing Auger data. The presence of these satellites is an indication for a weak *fd* hybridization and, when compared to uranium–transition-metal compounds, increased 5*f* localization.

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The nature of the 5*f* electrons in the actinides has attracted much attention both from the experimental and the theoretical point of view. For α-U metal it has been shown recently that the 5*f* electrons have primarily itinerant character.[1] The degree of 5*f* localization depends on the overlap of the corresponding 5*f* wave functions on neighboring atoms and on the 5*f*-6*d* hybridization. Since in uranium compounds the interatomic U-U distance and the bonding properties are changed as compared to α-U, a change in the degree of the localization can be expected.

X-ray photoemission spectroscopic (XPS) investigations on uranium compounds with *B*-group elements have shown a characteristic satellite structure at 7 eV higher binding energy of the U 4*f* core-level spectra (see Table I). The only serious attempt to explain these structures has been made for UO_2 where this satellite has been attributed to a shakeup process from the oxide-derived *p* band to unoccupied 5*f* states.[2,3]

In this Letter we show that, in the XPS spectra of the intermetallic compound UGa_2, a similar structure exists for the U 4*f* as well as for the U 5*f* levels (we note that even the valence bands of UO_2 show such a structure, which has been interpreted as belonging to the O 2*p* band[2]). In UGa_2 this structure cannot be explained by a

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