PHOTON ECHO RELAXATION IN $LaF_3:Pr^{3+}$ *

Y.C. CHEN, K. CHIANG and S.R. HARTMANN
Columbia Radiation Laboratory, Department of Physics, Columbia University, New York, NY 10027, USA

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We have observed deeply modulated photon echoes from Pr^{3+} ions in LaF_3 reflecting nuclear hyperfine interactions in both the ground $^3H_4$ and excited $^3P_0$ states. We infer splittings of 0.75 MHz and 1.13 MHz for the $^3P_0$ state. Inhomogeneous broadening of the terminal levels is found to lead to echo modulation damping. A surprising concentration dependence of the photon echo relaxation rate is observed as well as a dramatically long-lived (3 min) stimulated photon echo.

Considerable attention has been given recently to the problem of energy transfer and relaxation in the optically excited states of the Pr^{3+} ion in single crystals of LaF_3 [1–10]. Both the strong $^3H_4-^3P_0$ (4777 Å) and the weak $^3H_4-^1D_2$ (5925 Å) transitions are accessible to dye laser excitation and have been studied by a wide variety of techniques: fluorescence line narrowing in normal [1] and time resolved modes [2]; coherent transients such as photon echoes [3–7] and optical free decay [8]; and optical-RF double resonance [9,10].

Phonon induced relaxation of the $^3P_0$ and $^1D_2$ states seems to be reasonably well understood [1,4]. Concentration dependent effects have been observed in measurements of absorption and non-resonant fluorescence linewidths [1,2,7] but not in measurements of the optical free decay rate [8] or photon echo decay rate [7]. These latter experiments have been interpreted as being sensitive to homogeneous relaxation processes. In this connection, Erickson's hole burning double resonance experiment [10] is relevant as it has demonstrated that the linewidths of the nuclear transitions associated with the $^3H_4$ ground state are both narrow (200 kHz) and independent of concentration. In this paper we report the observation of a concentration dependent and deeply modulated non-exponential decay for the photon echo associated with the $^3H_4-^3P_0$ transition. The strongly modulated photon echo behavior supports our view [6] that the unusually fast "decay" observed in the 40–280 ns region [7] is in part a feature of the modulation process. The concentration dependent relaxation is unexpected.

Our apparatus consists of two separate thyratron-triggered nitrogen-laser-pumped dye lasers [11] each producing 7 ns, 10 GHz wide pulses of several hundred watt peak power. Pulse separation τ is controlled electronically, allowing continuous variation and arbitrarily long delay. The laser pulses are combined and focused to a 100 μm diameter spot in the $LaF_3:Pr^{3+}$ crystal. We have made measurements on 1.0 and 0.01 atm% Pr^{3+} doped LaF_3 crystals. All runs were performed at temperatures below 3 K, so that spin lattice relaxation is negligible [1].

The data shown in fig. 1(a) are for a 1.0 atm% $LaF_3:Pr^{3+}$ crystal. They are plotted every 5 ns and represent an average of all results obtained from several experimental runs in the corresponding 5 ns interval. Our new double-laser apparatus yields the same results as the old single laser-delay line apparatus in the pulse separation region which they share in common. The sharp peak at 236 ns confirms our previous result [6]. The extended range and increased resolution of our new apparatus shows the echo behavior to be quite complex. An understandable feature is the regular rephasing which occurs every 118 ns and which corre-

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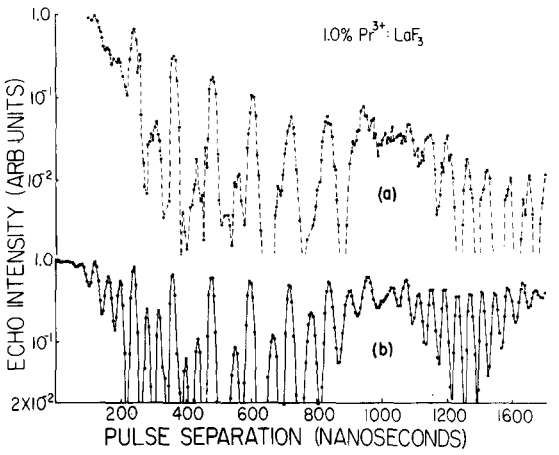

Fig. 1. Comparison of (a) experimental and (b) theoretical photon echo intensity versus pulse separation in a 1.0 atomic% sample of LaF_3:Pr^{3+}.

spond to the nuclear splitting of 8.47 MHz associated with the ground level of the $^3H_4$ state [10]. If we assume a hamiltonian

$$H_g = P_g[I_z^2 + (\eta_g/3)(I_x^2 - I_y^2)] + \Delta H_g$$

$$(H_e = P_e I_{z'}^2 + (\eta_e/3)(I_{x'}^2 - I_{y'}^2) + \Delta H_e)$$

for the Pr^{3+} ion in the ground (excited) state with $P_g = -4.185$ MHz, $\eta_g = 0.105$ [10] ($P_e = 0.312$ MHz, $\eta_e = 0.50$), $\hat{z}' \| \hat{x}$, $\hat{x}' \| \hat{y}$, where $\Delta H_g(\Delta H_e)$ represents a 200 kHz (50 kHz) inhomogeneous nuclear transition linewidth, then we obtain the response shown in figs. 1(b) and 2(b). This response, when multiplied by $\exp(-\tau/430\ \text{ns})$, reproduces all the essential features of fig. 1(a). For the 0.01 atomic% LaF_3:Pr^{3+} sample, the overall decay rate is found to be considerably smaller than $(430\ \text{ns})^{-1}$, see fig. 2(a), and the corresponding comparison with theory, see fig. 2(b), is reasonable all the way to the 4 μs limit for which data was acquired[‡].

The hamiltonian H_e represents the interaction between the electric quadrupole moment of the Pr nucleus and the electric field gradient at its lattice site [12]. For our choice of P_e and η_e, it splits the nuclear levels of this state into three doubly degenerate levels

[‡] There is a 5% timing error for $\tau > 2$ μs which reduces the value of P_e by 5%. The fit between fig. 1(a) and 1(b) should improve. All stated energy splittings of the $^3P_0$ state have been corrected.

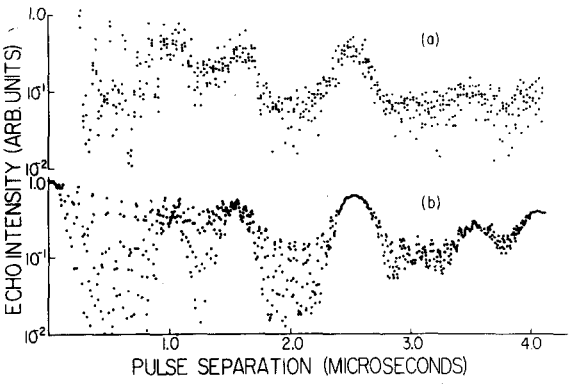

Fig. 2. Comparison of (a) experimental and (b) theoretical photon echo intensity versus pulse separation in a 0.01 atomic% sample of LaF_3:Pr^{3+}.

separated by 0.75 MHz and 1.13 MHz. A previous estimate [6] for P_e and η_e obtained by extrapolating EQR data for La in LaF_3 at temperatures above 88 K [12] differs by 30% from the values we have used. No measurement has been reported for the relative orientation of the primed and unprimed axes. The 430 ns time constant corresponds to a homogeneous linewidth of 185 kHz for the $^3H_4 - ^3P_0$ transition.

In fig. 2(a) which displays the data for our 0.01 atm% LaF_3:Pr^{3+} sample, we find wide amplitude excursions for small τ due to unresolved high frequency modulations of the echo signal which damp out with a time constant of ~ 2 μs. These are followed by low frequency modulations which correspond to the smaller splittings of the excited $^3P_0$ state. Another feature of the data is the relatively slow ($\sim (2\ \mu\text{s})^{-1}$) rate at which it decays. This corresponds to a linewidth of 40 kHz and is a factor of five narrower than the concentration independent NMR linewidth of 200 kHz reported by Erickson for the double resonance transitions in the $^3H_4$ ground state. This implies that the nuclear linewidths are inhomogeneous [9]. The effect of this inhomogeneity is to damp out the high frequency modulation with time constants of 800 ns and twice 800 ns depending on which particular terms are singled out. In the rotating frame, the dipole moment which produces the echo consists of a constant term plus a series of terms which oscillate at $\hbar^{-1}$ times the energy splittings associated with the ground and excited states [13]. The net dipole moment $P(2\tau)$ is an integral over the splitting distribution

$$P(2\tau) = A + \sum_{ijkl} B_{ijkl} \iint g(\omega_i - \omega_j)\, g(\omega_k - \omega_l)$$

$$\times \cos(\omega_i - \omega_j + \omega_k - \omega_l)\tau \, \mathrm{d}(\omega_i - \omega_j)\, \mathrm{d}(\omega_k - \omega_l)$$

where $\omega_i - \omega_j$ ($\omega_k - \omega_l$) refers to the ground (excited) state splitting frequency, $g(\omega_i - \omega_j)$ the associated line profile of the splitting ($\omega_i - \omega_j$) and A, B_{ijkl} are constants. The echo intensity is proportional to P^2. In our calculation, we assume that the line shapes are lorentzian, i.e., $g(\omega_i - \omega_j) = (1/\pi\Delta\omega_{ij})\,[1+(\omega_i - \omega_j)^2/\Delta\omega_{ij}]^{-1}$.

On the basis of EQR measurements for La in LaF_3 [14] and the known ratio of the electric quadrupole moments of La and Pr, we estimate a 10 kHz linewidth for the transitions between the nuclear levels split by the nuclear quadrupole interaction in the $^3P_0$ state. The contribution to the linewidth from the Pr-F nuclear dipolar interaction, according to a second moment calculation, is 12 kHz. Our calculation of echo behavior indicates that the excited state linewidth is actually larger than $\sqrt{(10)^2+(12)^2}$ = 16 kHz, and we have used $\Delta\omega_{ij}/2\pi$ = 50 kHz in calculating figs. 1(b) and 2(b). The $^3H_4$ ground state levels having $\Delta\omega_{ij}/2\pi$ = 200 kHz are almost an order of magnitude more inhomogeneously broadened than the $^3P_0$ levels. This arises from two mechanisms. First, the major contribution to H_g comes from the second order effect of the nuclear hyperfine interaction $A_J \boldsymbol{I}\cdot\boldsymbol{J}$, according to [15]

$$P = -A_J\,[(\Lambda_{xx} + \Lambda_{yy})/2 - \Lambda_{zz}],$$

where

$$\Lambda_{ii} = \sum_{n\neq 0} A_J |\langle 0|J_i|n\rangle|^2/(E_n - E_0),$$

A_J is the hyperfine constant, E_0 and $|0\rangle$ (E_n and $|n\rangle$) are the energy and wavefunction of the ground state (other states) of the $^3H_4$ multiplet. Since P is inversely proportional to the energy level separations $E_n - E_0$, any associated crystal field broadening is transferred directly to a spread in the values of P. Second, the magnetic broadening from the F nuclei is increased because of the enhanced nuclear magnetism of the Pr nuclei [16]. This takes the form of an addition contribution to the nuclear gyromagnetic ratio in the amount of $\gamma_N K_i$ where γ_N is the normal gyromagnetic ratio and K_i is the ith component of the enhancement factor. In terms of Λ_{ii} it is just $K_i = 2g_J\,\Lambda_{ii}/g_{J'}$ [16], where g_J and $g_{J'}$ are the electronic and reduced nuclear g factors. Since $\Sigma_i \Lambda_{ii} \leqslant A_J J(J+1)/(E_1 - E_0)$, where the n = 1 level lies closest to the ground state, we obtain $-2P/3A_J \leqslant \Lambda_{zz} \leqslant A_J J(J+1)/3(E_1 - E_0)$ $-2P/3A$ and $P(1\pm\eta)/3A_J \leqslant \Lambda_{xx\,(yy)} \leqslant A_J J(J+1)/3(E_1 - E_0) + P(1\pm\eta)/3A_J$. For our choice of P_g and η_g with A_J = 1075 MHz [17], J = 4, $g_{J'}$ = 1/1080, g_J = 4/5, and $E_1 - E_0$ = 57 cm^{-1}, this leads to $4.5 < K_z < 11.75$ [‡].

Our hamiltonian predicts that the residual echo intensity after the modulations have damped out should be roughly 16% of its initial value. For the 0.01 atm% LaF_3:Pr^{3+} sample, we found that echoes continued to decay for excitation pulse separation greater than 4 μs and reached the 4% level at 5.5 μs. This reflects the effect of homogeneous relaxation. A possible source of such relaxation is the fluctuating time dependent magnetic field at the Pr^{3+} sites due to the interacting F nuclei. This leads to spectral diffusion in what would be called a T_2 sample [18]. To the extent that our crystal is a T_1 sample, we can estimate the overall effect by using formula 5.14 of ref. [19] which yields a kind of limiting decay time constant $\tau^* = \pi^{1/3}/\Delta\omega_{1/2}$. Assuming an overall enhancement factor of about 6, then $\Delta\omega_{1/2}/2\pi \approx 40$ kHz and $\tau^* \approx 5$ μs. This is consistent with our data. The question remains as to why the overall echo intensity decay rate depends on concentration. Pr^{3+}–Pr^{3+} magnetic interactions appear unlikely since the Pr^{3+} ions have no magnetic moment. It is possible that the concentration dependent relaxation behavior is due to paramagnetic impurities which would be expected to be present in proportion to the Pr^{3+} concentration. In this case, the LaF_3:X:Pr^{3+} sample (where X stands for an impurity) could well be characterized as a T_1 sample. The most probable impurity present in LaF_3:Pr^{3+} is the paramagnetic ion Nd^{3+} [20]. Photon echo studies in LaF_3:Nd^{3+} [21] indicate that at 3 K, the T_2 of Nd^{3+} is as long as 3 ms. In our experiment, the Pr–Nd^{3+} interaction can be viewed as static and cannot explain the more than 84% reduction in echo intensity. At higher concentrations, the added lattice distortion from the oversized Pr^{3+} ions may modify the Pr nuclear–ion interaction by way of the second order hyperfine interaction. The measurement of Erickson [10], however, does not in-

[‡] Erickson's work implies K_z = 17. The recent work of Shelby et al. [9] implies K_z = 9.2.

dicate any concentration dependent linewidths for Pr^{3+} ion concentrations up to 1.0 atm%.

The Pr^{3+} ion in LaF_3, owing to its lack of an electronic moment, is essentially isolated and behaves in a relatively simple manner. Photon echoes in ruby [22], on the other hand, are only seen at greatly reduced amplitude in zero magnetic field, and one must apply large magnetic fields to study them. The simplicity of the LaF_3:Pr^{3+} system is only apparent, however, since this very simplicity unveils a puzzling concentration dependent effect. Another remarkable effect we have found is the observation of a very long-lived three-pulse stimulated photon echo. We find that three excitation pulses at $t = 0$, $t = 100$ ns and $t = 100$ ns + T produce an echo at $t = 200$ ns + T for values of T as long as 3 min. These latter echoes have a signal-to-noise ratio better than 2:1 and appear after 10^6 times the excited state's 47 μs lifetime. Stimulated photon echoes can be produced with phase information stored solely in the population distribution of the ground state levels [23]. Our experiment demonstrates this dramatically. Our stimulated echoes most likely relax via nuclear spin lattice relaxation induced by paramagnetic impurities [17], an effect which should be temperature and concentration dependent. Preliminary measurements show a strong temperature dependence. No measurements of concentration dependence have been made yet.

In conclusion we have shown that photon echoes associated with the $^3H_4$–$^3P_0$ transition in LaF_3:Pr^{3+} are deeply modulated. The low frequency modulation component shows the $^3P_0$ state is split by 0.75 MHz and 1.13 MHz. The persistent character of the modulation proves that the nuclear hyperfine levels are inhomogeneously broadened. The effect of this broadening is to damp the modulation; the low frequency modulations damp more slowly than the high frequency modulations and imply thereby a narrower linewidth for nuclear hyperfine transitions in the $^3P_0$ state than in the $^3H_4$ state. The large linewidth associated with this latter state is due in part to the second order effect of the hyperfine interaction. We provide a theoretical limit of $K = 11.75$ for the maximum value of the magnetic enhancement factor due to this effect. We also find that there is a homogeneous component to the relaxation behavior of the photon echo which is concentration dependent. For the 1.0 atm% sample we find a homogeneous time constant of 430 ns, for the 0.01 atm% sample we find ~2 μs. Finally we report the observation of anomalously long-lived (3 min) stimulated echoes.

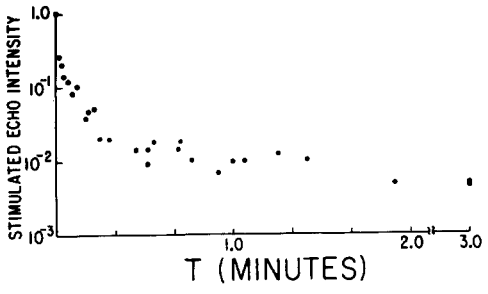

Fig. 3. Dependence of the stimulated photon echo intensity on T, the time interval between the second and third excitation pulses when the first and second pulses are separated by 100 ns. Measurements are made in a 1.0 atomic% sample of LaF_3:Pr^{3+}.

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