Phys. Lett. 30, 415 (1975), and to be published.
[11]K. D. Jordan, J. A. Michejda, and P. D. Burrow, J. Am. Chem. Soc. 98, 1295 (1976).
[12]S. F. Wong and G. J. Schulz, Phys. Rev. Lett. 35, 1429 (1975).
[13]J. H. Richardson, L. M. Stephenson, and J. I. Brauman, J. Chem. Phys. 63, 74 (1975).
[14]J. R. Hoyland and L. Goodman, J. Chem. Phys. 36, 12, 21 (1962).
[15]F. Gutman and L. E. Lyons, *Organic Semiconductors* (Wiley, New York, 1967), Chap. 6.
[16]W. R. Salaneck, J. W.-p. Lin, A. Paton, C. B. Duke, and G. P. Ceasar, Phys. Rev. B 13, 4517 (1976).
[17]F. J. Himpsel, N. Schwentner, and E. E. Koch, Phys. Status Solidi (b) 71, 615 (1975).
[18]C. B. Duke, W. R. Salaneck, A. Paton, S. K. Liang, N. O. Lipari, and R. Zallen, Bull. Am. Phys. Soc. 21, 458 (1976), and in *Structure and Excitations of Amorphous Solids*, AIP Conference Proceedings No. 31, edited by F. Galeener and G. Lucovsky (American Institute of Physics, in press).
[19]P. Gosar and S. Choi, Phys. Rev. 150, 529 (1966).
[20]C. B. Cuke and G. D. Mahan, Phys. Rev. 139, A1965 (1965).
[21]F. I. Vilesov, A. A. Zagrubskii, and D. A. Sukhov, Fiz. Tverd. Tela 11, 3409 (1969) [Sov. Phys. Solid State 11, 2775 (1970)].
[22]D. W. Turner, C. Baker, A. D. Baker, and C. R. Bundle, *Molecular Photoelectron Spectroscopy* (Wiley-Interscience, London, 1970), Chap. 11.
[23]D. A. Sweigurt and D. W. Turner, J. Am. Chem. Soc. 94, 5592 (1972).

Optical Free-Induction Decay in $LaF_3:Pr^{3+}$†

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The dephasing time of coherently prepared Pr^{3+} impurity ions in a LaF_3 crystal is measured by optical free-induction decay. Above 4°K, phonon processes severely shorten the decay time. Below 4°K, we observe a temperature-independent decay time of 0.38 μsec. This is surprisingly short considering that there are no contributions from first-order hyperfine, phonon, or Pr^{3+}-Pr^{3+} interactions.

Dynamic interactions in solids have been studied in the past by a variety of coherent pulse and steady-state techniques which extract a narrow homogeneous line shape from a broad inhomogeneous profile. Within the last few years, rf pulse methods have been extended to the optical region where photon echo studies have uncovered new aspects of relaxation behavior, particularly in ruby.[1] This Letter describes a related technique, that of optical free-induction decay (FID),[2] which has some unique advantages over the echo and steady-state methods and is well suited to examining interactions in optically excited solids. In optical free induction, the entire decay behavior is obtained in a single burst, as in NMR. Furthermore, because of the sensitivity afforded by optical heterodyne detection, weak transitions can be studied and the laser power may be low, avoiding the complications of power and inhomogeneous broadening present in the previous observation of FID in a solid.[3] Here we report the dephasing characteristics of coherently prepared trivalent praseodymium impurity ions in a lanthanum trifluoride crystal at low temperature. This system, unlike ruby,[1] exhibits no first-order hyperfine interaction and allows the study of other optical dephasing mechanisms.

The Pr^{3+} transition examined is between the lowest crystal-field components of $^1D_2 \leftarrow {}^3H_4$ (5925.2 Å), and the linewidth has been studied previously at lower spectral resolution[4] by the steady-state technique of fluorescence line narrowing.[5] FID signals of the type shown in Fig. 1 for $LaF_3:Pr^{3+}$ display dephasing times that correspond to an extremely narrow optical linewidth of 830 kHz (full width at half-maximum) and a

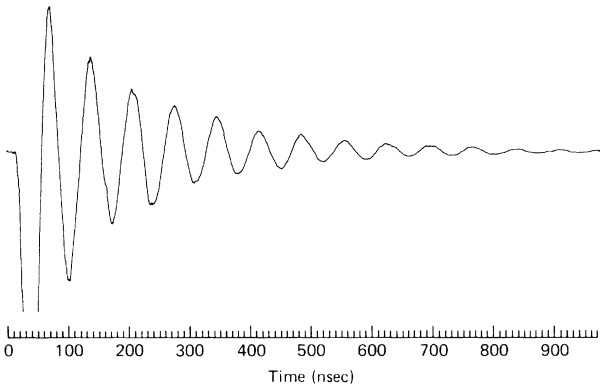

Fig. 1. Optical free-induction decay in $LaF_3:Pr^{3+}$ (0.1%) at 1.5°K. The tracing was obtained with a Tektronix 7904 sampling oscilloscope and an X-Y recorder in an 8-min interval.

spectral resolution of 6×10^8. This linewidth is unaffected by power broadening or the large inhomogeneous width of 4 GHz arising from crystal strains. On the other hand, it far exceeds the 640 Hz limit due to spontaneous radiative decay[6] of the upper transition level $^1D_2$ and raises the question of the line broadening mechanism. This work tests the role of phonon and hyperfine dephasing processes as well as that of spectral diffusion due to Pr^{3+}-Pr^{3+} interactions.

The Pr^{3+} transition $^1D_2 \leftarrow {}^3H_4$ involves singlet states because of the even electron configuration of $Pr^{3+}(4f^2)$ and the C_2 site symmetry.[7] Each singlet couples to the $I=\frac{5}{2}$ nuclear spin of Pr^{141} via quadrupolar and second-order hyperfine interactions[8] resulting in three Kramers's doublets. Furthermore, second-order hyperfine interactions allow each hyperfine level in the lower electronic state to connect optically with each hyperfine level of the upper electronic state.[9]

Free induction decay signals are obtained using the recently introduced method of *laser frequency switching*.[10] A LaF_3:Pr^{3+} crystal (with 0.1% Pr^{3+}), which is immersed in liquid helium, is initially prepared by resonant excitation with a free running unfocused cw dye laser. When the laser frequency is abruptly switched beyond the Pr^{3+} homogeneous linewidth, the coherently prepared Pr^{3+} ions exhibit FID by freely radiating an intense coherent beam of light in the forward direction. The FID and laser beams strike a *p-i-n* diode photodetector, which monitors the transmitted light, and together produce the heterodyne beat signal displayed in Fig. 1. The laser frequency is switched electro-optically by means of a 25-V pulse applied to an intracavity deuterated ammonium dihydrogen phosphate crystal phase modulator, the frequency jump being 14.3 MHz. The 3-dB roll-off points of the detector are at 10 and 30 MHz. The laser polarization is perpendicular to the crystal *c* axis. In contrast to the echo method,[1] the decay behavior is obtained in a single burst and the laser power density may be low, e.g., 10 mW in a 0.5-mm beam diameter was used. In contrast to the fluorescence line narrowing method,[5] the FID signals are not limited by unresolved hyperfine splittings and spectral diffusion.

For steady-state preparation, the FID heterodyne beat signal is expected to be of the form[2,11]

$$(E^2)_{\text{beat}} = QE_0 \exp\{-t/T_2[1+(1+\chi^2T_1T_2)^{1/2}]\} \times \cos\Delta\omega t, \quad (1)$$

where $\Delta\omega$ is the laser frequency shift, $\chi=\mu_{ij}E_0/\hbar$ is the Rabi flopping frequency, μ_{ij} is the transition moment, E_0 is the laser field amplitude, and Q is a function of μ_{ij}, population, etc. In the low intensity regime where $\chi^2 \ll 1/T_1T_2$, the FID decay time is simply $T_2/2$. The factor $\frac{1}{2}$ arises because T_2 determines the bandwidth in the preparative step and adds an additional $1/T_2$ decay rate. Measurements of the type shown in Fig. 1 obey a simple exponential decay law that is independent of light intensity and yield T_2 directly.

It is noteworthy that during the preparative stage the laser beam bleaches a hole within the inhomogeneous line shape which is characterized by a 0.5-sec recovery time[12] and reduces the magnitude of the FID signal. This is partly due to saturation[3,11] and the fact that the population of the lower transition level is redistributed among neighboring hyperfine levels through an optical pumping cycle. A Pr^{3+} ion excited from a lower to an upper hyperfine level will decay radiatively to the three lower hyperfine levels in about 0.5 msec, and we infer that 0.5 sec is needed before the lower hyperfine levels thermalize. These ideas are supported by experiments where the laser frequency is repetitively swept at a sufficiently high rate $d\omega/dt$ so that the absorption rate is not reduced significantly but slowly enough so that the FID decay rate is not artificially increased. This is equivalent to the condition $\chi^2 \ll d\omega/dt \ll 1/T_2{}^2$. To insure large FID signals, we require that $d\omega/dt \sim 1$ MHz/msec and also that the sweep period repeat every 0.5 sec or more. This procedure also removes the accompanying and prominent *flicker* of fluorescent light which appears during steady-state excitation because of laser frequency jitter. Our experiments are thus influenced by processes that span six orders of magnitude in time: an optical dephasing time $T_2 \sim 1\,\mu$sec, a spontaneous radiative decay time of 0.5 msec, and a Pr^{3+} nuclear decay time $T_1 \sim 0.5$ sec.

To elucidate the dephasing mechanism, experiments were carried out to measure its dependence on temperature, Pr^{3+} concentration, and magnetic field. We observe that T_2 increases dramatically in the range $6.5 \rightarrow 4$°K, and has the temperature-independent value $T_2 = 0.38\,\mu$sec (830 kHz) in the range $4 \rightarrow 1.5$°K. The temperature dependence of the linewidth at elevated temperatures has been interpreted previously in terms of stimulated phonon processes.[4] This model predicts a linewidth of 830 kHz at 4.7°K, which is consistent with our results, and a 0.4

Hz width at 1.5°K which is even less than the radiative width. Stimulated phonon processes, therefore, cannot account for the residual temperature-independent width. Spontaneous phonon emission from the $^1D_2$ transition level cannot be important either as this process is already included in the 0.5-msec radiative decay time. The possibility that T_2 is shortened by laser heating is removed also because the FID rate does not vary when the light intensity is varied by a factor of 5.

Another mechanism is that of spectral diffusion arising from dipolar Pr^{3+}-Pr^{3+} interactions. We have excluded this possibility, however, because at 1.5°K the same 830-kHz width is obtained in two crystals having a different Pr^{3+} concentration, 0.03% and 0.1%. Furthermore, by tuning the laser to different parts of the 4-GHz-wide inhomogeneous line shape, we find that the free-induction signal always gives the same 830-kHz result independent of the density of Pr^{3+} ions which are in near resonance. In addition, if spectral diffusion is important, the decay law should deviate from the exponential behavior observed.

Hyperfine interactions constitute another temperature-independent relaxation mechanism.[1] Since the Pr^{3+} transition states are electronic singlets, they have no first-order electronic magnetic moment. However, Bleaney[8] has pointed out that second-order hyperfine interactions can induce a magnetic moment which is much larger than the intrinsic nuclear moment. This is not the case for the ground state, as NMR measurements[13] of PrF_3 give a Pr^{3+} moment of 3.8×10^{-3} Bohr magnetons (β). This would lead to a broadening due to dipolar interactions with La and F nuclear moments and is two orders of magnitude too small. However, the moment of the excited state, which is unknown, might be sufficiently large; a magnetic dipole matrix element between adjacent singlet states of about 4β would be required to explain our observed T_2. However, this possibility seems to be excluded since an enhanced moment in zero field implies that the relaxation should be magnetic field dependent, and we find that T_2 is unaffected by fields up to 8 kG which would induce a moment larger than that present in zero field.

Instability in the laser frequency can be an additional broadening mechanism. If the laser frequency jitters more than the Pr^{3+} homogeneous width in a time T_2 during the preparative step, the resulting bandwidth will cause the FID signal to dephase faster than $T_2/2$. It appears doubtful, however, that this is an important contribution because with the same laser, I_2 vapor exhibits free-induction decay times[10] that are significantly longer than the FID signals of LaF_3:Pr^{3+}. Nevertheless, as an additional test, we plan to repeat these measurements with a frequency-locked dye laser.

We also note that photon echo studies by Takeuchi[14] of the $^3P_0 \rightarrow {}^3H_4$ transition of LaF_3:Pr^{3+}, which involves a different upper state, exhibit a similar anomalous broadening of 3 MHz; he suggested a Pr^{3+}-Pr^{3+} dephasing mechanism which is excluded in the present work.

The nature of the limiting relaxation behavior in optically excited singlet electronic states cannot be considered resolved yet, but remains an intriguing subject for future studies, one that we plan to pursue further by optical-radio frequency double resonance.

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[1]N. A. Kurnit, I. D. Abella, and S. R. Hartmann, Phys. Rev. Lett. 13, 567 (1964), and Phys. Rev. 141, 391 (1966).

[2]R. G. Brewer and R. L. Shoemaker, Phys. Rev. A 6, 2001 (1972).

[3]P. L. Liao and S. R. Hartmann, Phys. Lett. 44A, 361 (1973). A. Szabo [in the appendix to Abstracts of the Ninth International Conference on Quantum Electronics, Amsterdam, 1976 (unpublished)] has observed FID in ruby by the Stark-switching technique (see Ref. 2).

[4]L. E. Erickson, Opt. Commun. 15, 246 (1975).

[5]A. Szabo, Phys. Rev. Lett. 27, 323 (1971).

[6]M. J. Weber, J. Chem. Phys. 48, 4774 (1968).

[7]S. Matthies and D. Welsch, Phys. Status Solidi (b) 68, 125 (1975).

[8]B. Bleaney, Physica (Utrecht) 69, 317 (1973).

[9]Y. C. Chen and S. R. Hartmann, to be published.

[10]R. G. Brewer and A. Z. Genack, Phys. Rev. Lett. 36, 959 (1976).

[11]K. L. Foster, S. Stenholm, and R. G. Brewer, Phys. Rev. A 10, 2318 (1974).

[12]L. E. Erickson, Phys. Rev. B 11, 77 (1975).

[13]F. L. Aukhadrev and I. S. Konov, Fiz. Tverd. Tela 15, 2884 (1973) [Sov. Phys. Solid State 15, 1929 (1974)].

[14]N. Takeuchi, J. Luminesc. 12/13, 743 (1976).