Ultraslow Optical Dephasing of $LaF_3:Pr^{3+}$

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Optical free-induction dephasing times as long as 16 μsec, corresponding to an optical homogenous linewidth of 10 kHz, have been observed for the $^3H_4 - ^1D_2$ transition of Pr^{3+} ions in LaF_3 at 2°K. Measurements are facilitated by a frequency-locked cw dye laser and a new form of laser frequency switching. Zeeman studies reveal a Pr-F dipole-dipole dephasing mechanism where the Pr nuclear moment is enhanced in both $^1D_2$ and $^3H_4$.

In this Letter, we report a new advance in the observation of extremely long optical dephasing times in a low-temperature solid. Coherently prepared Pr^{3+} impurity ions in a LaF_3 host crystal exhibit optical free-induction decay (FID) where the dephasing times correspond to an optical linewidth of only 10 kHz half width at half maximum (HWHM) and a spectral resolution of 5×10^{10}. At this level of resolution, which represents a fiftyfold increase over our previous measurements,[1] it is now possible to perform detailed optical studies of magnetic Pr-F dipole-dipole interactions in the ground and optically excited states. Heretofore, such weak relaxation effects could be detected only in the ground state by spin resonance techniques[2-4] or radio-frequency optical double resonance.[5,6]

The Pr^{3+} transition $^3H_4 \leftrightarrow ^1D_2$ monitored at 5925 Å involves the lowest crystal-field components of each state. These are singlet states where the $2J+1$ degeneracy is lifted by the crystalline field because of the low Pr^{3+} site symmetry, perhaps C_2 or C_{2v}. The nuclear quadrupole interaction[7] of Pr^{3+} ($I=\frac{5}{2}$) splits each Stark level into three hyperfine components which are each doubly degenerate ($\pm I_z$), and to a first approximation, three equally probable optical transitions connecting these states occur, namely, $I_z'' \leftrightarrow I_z' = \pm\frac{5}{2} \leftrightarrow \pm\frac{5}{2}$, $\pm\frac{3}{2} \leftrightarrow \pm\frac{3}{2}$, and $\pm\frac{1}{2} \leftrightarrow \pm\frac{1}{2}$. All three transitions overlap and can be excited simultaneously by a monochromatic laser field since the Pr^{3+} hyperfine splittings, of order 10 MHz, are considerably less than the inhomogeneous crystalline strain broadening of ~5 GHz. Weaker transitions of the type $\frac{5}{2} \leftrightarrow \frac{1}{2}$, $\frac{5}{2} \leftrightarrow \frac{3}{2}, \ldots$ also occur among these hyperfine states because of a nonaxial field gradient at the Pr^{3+} nucleus which mixes the $|I_z\rangle$ wave functions slightly. As noted previously,[1,8] the weaker transitions redistribute the ground-state hyperfine population distribution drastically in an optical pumping cycle, and play an important role in the optical dephasing measurements reported here.

Bleaney[9] has shown that when an electronic singlet of a rare-earth ion admixes with close-lying Stark-split levels of a given J manifold, it produces in second order a pseudoquadrupole moment and an enhanced nuclear magnetic moment

$$m_i = (g_N\beta_N - 2g_J\beta\Lambda_{ii})I_i, \tag{1}$$

where the notation is that of Teplov.[4] Here, the principal axes are labeled $i=x,y,z$, the nuclear and electronic g values are g_N and g_J, the electronic matrix element

$$\Lambda_{ii} = \sum_{n\neq0} A_J|\langle 0|J_i|n\rangle|^2/(E_n - E_0)$$

connects the lower state $|0\rangle$ with an excited state $|n\rangle$ removed in energy by $E_n - E_0$, and A_J is the Pr^{3+} hyperfine constant. Now imagine that a fluctuating local magnetic field $\tilde{H}_z$ exists at the Pr^{3+} site due to distant pairs of F nuclei participating in mutual spin flips, and ignore other dephasing mechanisms for the moment. This field modulates the optical transition frequency randomly through a Pr-F dipole-dipole interaction and produces a HWHM homogeneous optical linewidth

$$\Delta\nu = |\gamma_z'' I_z'' - \gamma_z' I_z'|\tilde{H}_z/2\pi, \tag{2}$$

where γ_z'' and γ_z' are the Pr^{3+} *enhanced* gyromagnetic ratios ($\gamma_z = m_z/\hbar I_z$) of $^3H_4$ and $^1D_2$. Because the Pr nuclear wave functions are mixed to some extent,[7] rigorously I_z is not a good quantum number. Nevertheless, to a good approximation[5,8] $I_z'' \sim I_z'$ and, as already mentioned, we expect three strong optical transitions $|\pm\frac{5}{2}\rangle \to |\pm\frac{5}{2}\rangle$, $|\pm\frac{3}{2}\rangle \to |\pm\frac{3}{2}\rangle$, and $|\pm\frac{1}{2}\rangle \to |\pm\frac{1}{2}\rangle$. Therefore, from (2) three different decay times should appear in an optical FID. We shall see that this idea is supported and that γ_z' for $^1D_2$ can be obtained since γ_z'' is known[5] and $\tilde{H}_z = 2\pi\Delta\nu_{rf}/\gamma_z''$ can be deduced from an rf-optical double resonance linewidth[6] of the $^3H_4$ state. Furthermore, these experiments offer a new way of testing *ab initio* calculations[10] of Λ_{ii} as well as the Pr^{3+} site symmetry, which remains controversial.[10,11]

The technique adopted for observing optical FID relies on laser frequency switching,[12] but in a new form. A cw dye laser radiates a beam at 5925 Å, which is linearly polarized, at a power of ~4 mW. The beam passes through a lead molybdate acousto-optic modulator which is external to the laser cavity and oriented at the Bragg angle. The Bragg-diffracted beam is focused to a 200-μm diameter in a $7\times7\times10$-mm^3 crystal of $LaF_3:Pr^{3+}$ (0.1 or 0.03 at.% Pr^{3+}) which is immersed in liquid helium at 2°K, and the emerging laser and FID light, which propagates parallel to the crystal c axis, then strikes a p-i-n diode photodetector. The Pr^{3+} ions are coherently prepared while the modulator is driven continuously and efficiently at 110 MHz. FID follows when the rf frequency is suddenly shifted (100 nsec rise time) from 110 to 105 MHz, the duration of the switching pulse being 40 μsec. Note that the laser is switched through 500 homogeneous linewidths. Figure 1 shows FID signals produced in this way where the dephasing time $T_2/[1+(1+\chi^2T_1T_2)^{1/2}] \sim T_2/2$ is independent of power broadening since $\chi^2T_1T_2 \ll 1$, χ being the Rabi frequency. The anticipated heterodyne beat of 5-MHz frequency is readily observed, because the shifted laser and

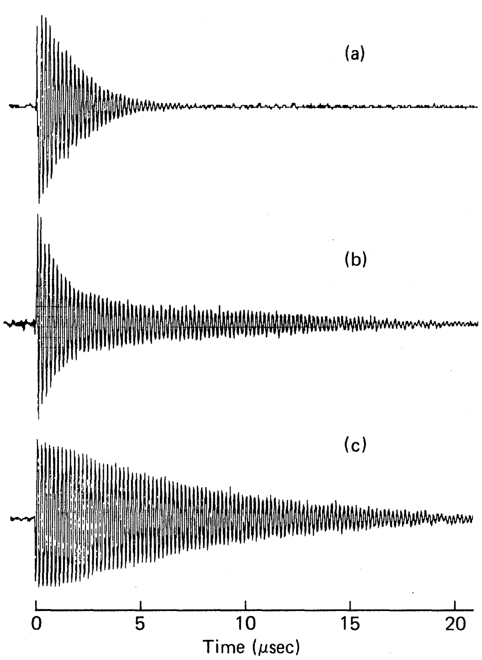

FIG. 1. Free-induction decay of 0.1 at.% Pr^{3+} in LaF_3 at 2°K in the presence of an external magnetic field H_0 $\perp c$ axis. H_0 equals (a) 0.5 G (Earth's field), (b) 19 G, and (c) 76 G. The optical heterodyne beat frequency is 5.005 MHz. Cases (a) and (c) are plotted in Fig. 2.

FID beams overlap since the change in the Bragg angle (0.4 mrad) is less than the beam divergence (7 mrad). This type of extracavity laser frequency switching is compatible with laser frequency locking which we now consider.

To detect ultraslow dephasing times by FID, the the laser frequency must remain fixed within the sample's narrow homogeneous linewidth $\Delta\nu = 1/(2\pi T_2)$ for an interval ~T_2—a stability condition which is less stringent than in a linewidth measurement. In the present work, a frequency stability of ~10 kHz in a time of ~16 μsec is required. To this end, our laser is locked to an external reference cavity which provides an error signal in a servo loop of high gain for correcting slow frequency drift and high-frequency jitter. The noise spectrum as seen from the error signal or a spectrum analyzer is not flat but is dominated by isolated jumps of 30 to 100 kHz in a 10-μsec period. At such times, the sample is prepared at two (or more) discrete frequencies which results in a deeply modulated FID pattern. This behavior agrees with a computer simulation of FID which assumes a bimodal spectrum. However, at other times frequency jumps do not occur, and the free induction decays monotonically as in Fig. 1. Under these conditions, a laser jitter of <10 kHz permits a reliable decay-time measurement of these *single events* which are considerably longer lived than the time-averaged value of many decays. These signals are captured with a Biomation 8100 Transient Recorder and then reproduced on an X-Y chart recorder.

A key feature of the measurement is an optical pumping absorption-emission cycle which transfers population from any given hyperfine level of the $^3H_4$ ground state to its two neighbors, for example from $|\frac{3}{2}\rangle$ to $|\frac{5}{2}\rangle$ and $|\frac{1}{2}\rangle$ within the same inhomogeneous packet. As a result, each of the three $^3H_4$ hyperfine states excited (three packets) will be depleted and FID cannot be detected. However, by sweeping the laser frequency at a slow rate of $\leqslant$(10 kHz)/(16 μsec) so as not to influence the decay rate, the pumping cycle can be reversed[1] and the hyperfine population partially restored. The $^3H_4$ hyperfine population distribution which results depends on the sweep rate and the relative transition probability among the hyperfine states as they decay from $^1D_2$ to $^3H_4$ via intermediate states. Therefore, the pumping cycle dictates which of the three strong transitions can be prepared to yield FID.

In Fig. 1, a dramatic variation in the FID occurs when a weak external field H_0 is applied per-

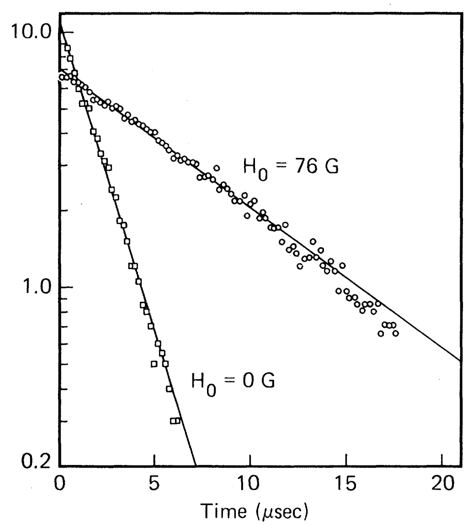

FIG. 2. Semilog FID plots of the data of Figs. 1(a) and 1(c) showing a simple exponential decay.

pendicular to the crystal c axis. The T_2 dephasing times for the three cases are (a) 3.6 μsec at $H_0 = 0.5$ G (Earth's field), (b) 3.5 and 15.6 μsec at $H_0 = 19$ G, and (c) 15.8 μsec at $H_0 = 76$ G. Note that case (c) corresponds to a 10-kHz HWHM linewidth which appears to be the *narrowest homogeneously broadened optical transition detected in a solid.* Its magnitude is comparable to NMR linewidths[2,4,6] which result from a magnetic dipole-dipole dephasing process. Cases (a) and (c) are single exponentials (Fig. 2), the ratio of the two decay times being 4.6. The intermediate case (b) is dominantly a biexponential and displays precisely the same two decay times found in (a) and (c). It is significant that the decay-time ratio approximates 5 and that the magnitude of these decay times is essentially independent of magnetic field. These results are consistent with Eq. (2) where we expect three decay times in the ratio 5 : 3 :1, and we conclude that case (a) represents dephasing due to the $|\frac{5}{2}\rangle$ state, case (c) to the $|\frac{1}{2}\rangle$ state, and case (b) to both of these states with possibly a small contribution from $|\frac{3}{2}\rangle$ as well. We conclude that application of a weak magnetic field modifies the optical pumping cycle and the $^3H_4$ population distribution in a sensitive way by mixing the nuclear wave functions $|I_z\rangle$ further since the $^1D_2$ Zeeman and quadrupole energies[8] can be comparable. This model is also consistent with the zero-field rf-optical double-resonance observation[6,8] that the $^3H_4$ quadrupole transition $|\frac{5}{2}\rangle \leftrightarrow |\frac{3}{2}\rangle$ is more intense than the $|\frac{3}{2}\rangle \leftrightarrow |\frac{1}{2}\rangle$. More detailed calculations of the nuclear wave functions are needed to test these ideas further and will require determining the orientation of the principal axes x, y, and z for both $^3H_4$ and $^1D_2$.

We now turn to Eq. (2) to determine the $^1D_2$ enhanced gyromagnetic ratio γ_z'. A fluctuating local dipolar field of $\tilde{H}_z = 0.41$ G at the Pr^{3+} site due to the fluorine nuclei can be deduced from the ground-state value[5] $\gamma_z''/2\pi = 23$ kHz/G and a ground-state linewidth[6] of 9.5 kHz for the $^3H_4$ quadrupole transition $|\frac{5}{2}\rangle \leftrightarrow |\frac{3}{2}\rangle$ at $H_0 = 0$ G. The same local field modulates the optical transition frequency producing a considerably broader linewidth of 44 kHz ($I_z = \frac{5}{2}$) at $H_0 = 0$ G. Therefore, we find from (2) that $\gamma_z'/2\pi = 20 \pm 4$ kHz/G where we have taken the enhanced moments of $^3H_4$ and $^1D_2$ to be of opposite sign. This quantity is bounded by $1.29 < \gamma_z'/2\pi < 19$ kHz/G, the lower limit being derived from the first term of (1), i.e., with no enhancement. The upper limit follows from the second term of (1) where we assume that in Λ_{zz} the maximum element $\langle 1|J_z|0\rangle = 2$, the lowest Stark level of $^1D_2$ mixes with the first excited state where $E_1 - E_0 = 23$ cm^{-1}, $g_J = 1$, and $A \sim 1.093 \times 10^9$ Hz. If γ_z'' and γ_z' are assumed to be of the same sign, $\gamma_z'/2\pi = 66$ kHz/G which exceeds the upper limit. In addition, *ab initio* calculations[10] of $\langle J_z\rangle$ are in serious disagreement with our experimental results.

Other broadening mechanisms we have considered appear to be negligible. They include a $^1D_2$ radiative decay time[13] of 0.5 msec (0.16 kHz) and phonon processes[8] (0.8 kHz). Our linewidths are also independent of Pr^{3+} concentration in the range 0.03 to 0.1 at.% so that Pr^{3+}-Pr^{3+} interactions are excluded. Since the width is independent of laser power and a nutation signal is not detected, we estimate that the optical transition matrix element $\mu_{ij} \leq 4.5 \times 10^{-5}$ debye. This implies that only 10^{-5} of the $^1D_2$ ions return directly by radiative decay to the ground $^3H_4$ state; the remainder radiate to excited Stark-split states of $^3H_4$ and other states[13] followed by rapid spontaneous phonon emission processes to the ground state. Clearly, the optical pumping cycle is not simple. The contribution of laser frequency jitter to the linewidth appears to be small since the decay time varies with external magnetic field in a predictable manner. We expect that a significantly higher spectral resolution can be achieved in the near future and will further improve precision measurements of this kind where ultraslow optical dephasing processes occur.

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Propagating Energy Modes in the Classical Heisenberg Chain: "Magnons" and "Second Magnons"

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The ferromagnetically coupled classical Heisenberg chain in an applied magnetic field has been studied by computer simulation. The results indicate the presence of a second collective mode, in addition to the damped spin-wave–like modes which have previously been observed in the absence of a magnetic field. For intermediate wavelengths, the mode manifests itself by well-defined oscillations in the energy-density correlation function, and by a second peak in the spectrum of the longitudinal spin-density correlation functions.

It is now well established that a classical one-dimensional Heisenberg magnet can support short-wavelength propagating spin-density modes, in spite of the lack of long-range order. The existence of such modes can be understood in terms of the strong short-range order present in one-dimensional magnets at low temperature ($k_B T < |J|$), the short-range order being characterized by an inverse correlation length κ which, for low temperatures, is proportional to the temperature. For wavelengths less than κ^{-1} the system appears ordered, and can therefore support collective spin-density oscillations, or "magnons"; however, the overall lack of long-range order leads to a damping of these excitations, and this damping increases as the temperature is raised. This qualitative picture is confirmed by a number of theoretical[1,2] and computer-simulation studies,[1,3,4] and is also in agreement with experimental results on $(CD_3)_4NMnCl_3$.[1,5]

In this Letter, we report computer simulation results which show that an applied field leads to striking new features in the response functions of the classical Heisenberg chain, for the case of ferromagnetic coupling.

Our computer-simulation calculations are based on the method described in detail in Steiner, Villain, and Windsor[1] and in Windsor and Wheaton.[6]

