Ultraslow Optical Dephasing in $Eu^{3+}:Y_2SiO_5$

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We report the measurement of what we believe to be the narrowest known optical resonance in a solid. This was made on the $^7F_0 \rightarrow {}^5D_0$ transition of $Eu^{3+}:Y_2SiO_5$ at 1.4 K using photon echoes with sufficiently low laser power to almost eliminate contributions from instantaneous diffusion. The optical resonance widths measured for Eu^{3+} ions in the two crystallographic sites of Y_2SiO_5 and in a magnetic field of 100 G are 122 Hz (site 1) and 167 Hz (site 2). These widths are dominated by population decay, but up to 20 Hz is attributed to ^{89}Y spin fluctuations which have been reduced by the applied magnetic field.

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The optical dephasing time of isolated ions in solids can become very long at low temperatures [1]. We have used photon echoes to measure what we believe to be the longest dephasing time (i.e., the sharpest optical resonance) yet reported in a solid: $T_2 = 2.6$ ms for Eu^{3+} ions in Y_2SiO_5 at 1.4 K. This corresponds to an optical resonance of width 122 Hz (or a resonant $Q \geq 4 \times 10^{12}$). Most of the more than 8 orders of magnitude between this value and that of the room temperature width (~ 60 GHz) comes from phonon scattering and phonon absorption processes which for rare-earth or transition-metal ion impurity systems usually become negligible below ~ 4 K. The remaining sources of dephasing are population decay by radiative or nonradiative processes or dynamic local fields due either to nuclear spin fluctuations of the host lattice nuclei, in the present case ^{89}Y, or to the presence of other excited ions (so-called "instantaneous diffusion"). Sharp optical resonances provide very sensitive probes of small interactions or external perturbations such as superhyperfine coupling [2,3], tunneling splittings [4], nuclear Zeeman effects [5], or Stark coefficients involving fields as small as mV/cm [6]. From the time domain point of view, long coherence times allow the storage of information in the form of long optical pulse trains within the coherence time of the material system [7]. In the search for long coherence times, host materials have been chosen whose constituent ions have zero nuclear spin such as oxygen, low isotopic abundance of nuclear spins such as Si, or small magnetic moments such as yttrium. In this way and using long-lived metastable optical levels, subkilohertz wide optical resonances have been observed in $Eu^{3+}:Y_2O_3$ [8,9], $Eu^{3+}:Y_2SiO_5$ [10], and $Eu^{3+}:YAlO_3$ [11,12] and resonances only several kHz wide in others such as $Pr^{3+}:YAlO_3$ [13], Pr^{3+}:YAG [14], and $Cr^{3+}:Al_2O_3$ [15].

The $^7F_0 \rightarrow {}^5D_0$ transition of the Eu^{3+} ion is a good choice for these studies because the electronic magnetic moment is quenched in the $^7F_0$ ground state and is very small in the $^5D_0$ excited state [16], making the transition frequency insensitive to magnetic fluctuations. Further, the excited state lifetime of ~ 1 ms in many materials contributes only ~ 100 Hz to the total linewidth and allows one to study other sources of dephasing with great sensitivity. For example, most of the compounds studied contain yttrium, because yttrium can be substituted by trivalent rare-earth ions without charge compensation and the fluctuating local fields due to the ^{89}Y nucleus are expected to be small since its magnetic moment is only $-0.14\mu_N$. By reducing other sources of line broadening, we have for the first time determined the contribution of the yttrium nucleus to optical line broadening and for the $^7F_0 \leftrightarrow {}^5D_0$ transition of Eu^{3+} found it to be only about 100 Hz. In all the examples cited above, the lifetime (T_1) limited value was not reached, although efforts to remove the effects of nuclear spin fluctuations by coherent spin decoupling [17] or choice of host matrix [8,10,13] led to substantial linewidth reductions. One of the effects which makes it difficult to achieve the T_1 limit is excitation-density-dependent instantaneous diffusion in which time varying fields produced by optical excitation of neighboring ions contribute to dephasing [9,18–20]. As coherence times become longer, the possibility that phonon contributions may contribute ~ 100 Hz needs to be kept in mind and the sample temperature carefully monitored.

The measurement of sub-kHz wide optical resonances in the frequency domain puts very stringent requirements on laser frequency stability and has not yet been observed directly in a solid state system, although it has been demonstrated in gases, or rather in trapped single ions [21]. The use of phonon echoes in the time domain overcomes this need for stability, since the Fourier width of the excitation pulses can be chosen to be greater than the frequency jitter and this prepares a relatively broad packet in the inhomogeneous line; the second pulse of the echo sequence removes this inhomogeneous contribution to the linewidth [13]. On the other hand, for spectral hole burning or optical free induction decay it is necessary to

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TABLE I. Spectral and relaxation parameters for Eu^{3+}:Y_2SiO_5.

	Site 1	Site 2
$\lambda(^7F_0 \rightarrow 5D_0)$	579.879 nm	580.049 nm
Γ_{inh}	4.1 GHz	3.8 GHz
T_1	1.9 ms	1.6 ms
$\Gamma_{hom}(T_1)$	85 Hz	100 Hz
$T_2^{meas\,a}$	2.6 ms	1.9 ms
	(≡122 Hz)	(≡167 Hz)
$\Gamma_{hom}^{0\,b}$	105 Hz	105 Hz

[a]For $H_0 = 100$ G.
[b]Extrapolated to zero excitation intensity.

prepare a very sharp packet, less than the homogeneous linewidth. One drawback with the photon echo technique is the possibility of exciting echo modulation due to coherent preparation of three or move levels [22]. In cases where small splittings fall within the bandwidth of the excitation pulses, even a weak modulation can seriously distort the echo decays.

The Y_2SiO_5 crystal is monoclinic, belonging to the C_{2h}^6 space group with eight molecules per unit cell and two types of inequivalent Y^{3+} sites with no rotational symmetry [23]. The Eu^{3+} ions substitute for Y^{3+} ions and absorb at 579.879 nm (site 1) and 580.049 nm (site 2). Our crystal contained nominally 0.1% Eu and had peak absorption coefficients of 0.5 cm^{-1} (site 1) and 1.4 cm^{-1} (site 2) in the direction studied, corresponding to oscillator strengths of 1.2×10^{-8} and 3.1×10^{-8}, respectively. A path length of 1 cm resulted in an absorption of 40% (site 1) and 76% (site 2). Photon echoes were excited by gating a cw dye laser with two 80 MHz acousto-optic modulators in series before the sample and focusing with a lens of $f=33$ cm to a beam waist of 30 μm radius (or $f=1$ m for the lowest point in power density). The excitation power density was varied between 5 and 50 W/cm^2, and the length of the two echo preparation pulses was 1 μs. This gave a laser bandwidth of ~2 MHz. The pulse areas were significantly less than the $\pi/2$ and π values that are optimal for echo intensity, but this prevented or minimized instantaneous diffusion. Delays between the two excitation pulses (t_{12}) were varied between 10 μs and 3.5 ms. After the sample, a third acousto-optic modulator rejected scattered excitation light, and the echoes were detected in a collinear geometry with a photomultiplier. The pulse sequences were computer controlled and averages were taken of 64 echoes at each time delay. Samples were placed in liquid helium pumped to 1.4 K. Measurements were made with the sample shielded from stray electromagnetic fields by a copper box which was necessary to record the longest decays. In this configuration the measured linewidths were limited by a combination of the population decay time and dephasing due to yttrium nuclear spin fluctuations. To avoid spectral hole burning the laser was scanned over

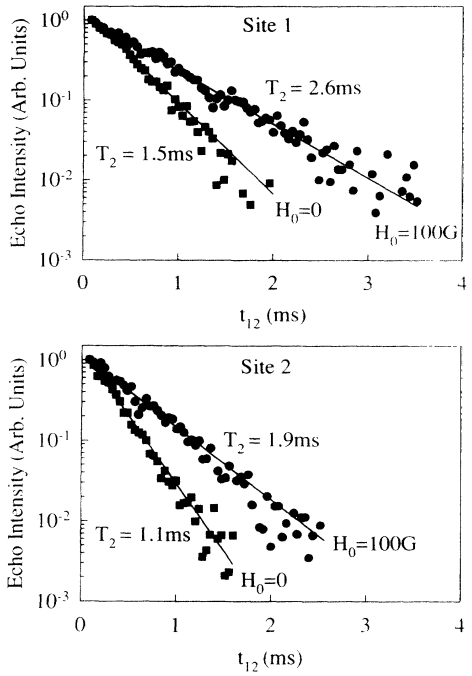

FIG. 1. Photon echo decays on the $^7F_0 \rightarrow {}^5D_0$ transition of Eu^{3+}:Y_2SiO_5 at 1.4 K. The excitation density was 6 W/cm^2 and the straight lines are exponential fits to the decays yielding the dephasing times shown.

300 MHz in 2.5 s intervals. Measurements were made at the center of the inhomogeneous line.

Table I summarizes the important spectroscopic and relaxation parameters for Eu^{3+} in the two sites of Y_2SiO_5. Fluorescence decay times (T_1) for the two sites were measured by monitoring the fluorescence from $^5D_0$ to $^7F_2$ after resonantly exciting the $^5D_0$ level by gated cw laser pulses of 1 μs duration. For site 1 $T_1 = 1.9$ ms and for site 2 $T_1 = 1.6$ ms. This contributes 85 and 100 Hz, respectively, to the homogeneous linewidths. Photon echo decays were recorded in zero field and in an applied magnetic field of 100 G, and a typical result is shown in Fig. 1. The decays as a function of excitation power density are shown in Fig. 2. The excitation power dependence is ascribed to instantaneous diffusion [9,18–20] due to the local multipole field or "crystal field" changes induced by the excitation of neighboring Eu^{3+} ions. In zero field the decays were exponential and corresponded to homogeneous linewidths of 210 Hz for site 1 and 290 Hz for site 2. We made the small correction for instantaneous diffusion using the results of Fig. 2, resulting in 195 Hz (site 1) and 230 Hz (site 2). These values are the sum of two contributions: that of population decay measured independently (above) and the contribution from ^{89}Y nuclear spin fluctuations obtained by subtraction to be 110 Hz (site 1) and 130 Hz (site 2). In $YAlO_3$ the dephasing of this transition is dominated by aluminum spins which have a magnetic moment 25 times larger than that of yt-

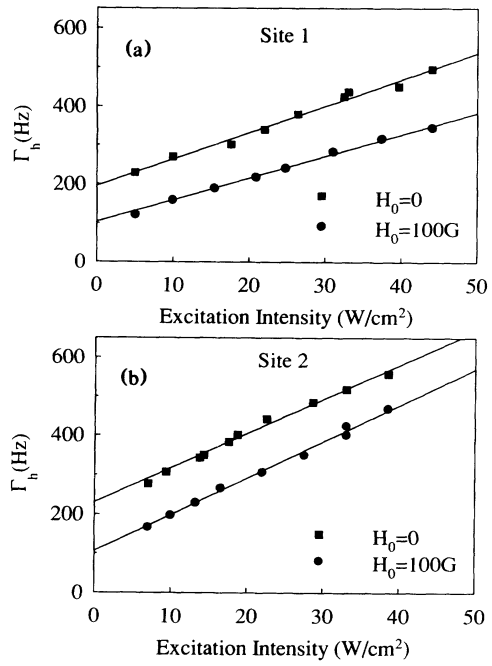

FIG. 2. Dependence of the homogeneous linewidth on excitation power density (a) for site 1 and (b) for site 2, varying both echo preparation pulses simultaneously. This shows the contribution from instantaneous diffusion. The linewidths extrapolated to zero laser power for $H_0 = 100$ G are 105 Hz for both site 1 and site 2.

trium and contribute about 1 kHz to the linewidth [12]. A signature of nuclear spin-flip-induced dephasing is its sensitivity to external magnetic fields (H_0) since these modify the spin dynamics, slowing the nuclear mutual spin flips and narrowing the optical linewidth; in this case to 122 Hz (site 1) and 167 Hz (site 2) for $H_0 = 100$ G. With the correction for instantaneous diffusion applied, this gives an extrapolated homogeneous linewidth of 105 Hz for both site 1 and site 2. Thus in a field of 100 G, the yttrium spin contribution to the homogeneous width of the Eu^{3+} transition drops to only 20 Hz for site 1 and 5 Hz (i.e., it is effectively zero) for site 2 in which case the T_1 limit is reached. This appears to be the first time that the contribution of the yttrium nucleus to optical line broadening has been obtained. In the past there have always been other, larger contributions masking it. The final measured and extrapolated linewidths are dominated by the T_1 contribution. Since the echo decays are exponential it appears that the yttrium spin fluctuation rate is rather homogeneous and "frozen core" effects seen in the echo decays of Pr^{3+} (Ref. [24]), Er^{3+} (Ref. [25]), and Cr^{3+} (Ref. [26]) are very weak here. This is consistent with the fact that the ground state of Eu^{3+} has a very small (quenched) magnetic moment of $\sim$0.1-0.2 kHz/G [16].

The contribution from instantaneous diffusion was also investigated by varying separately the power of the first and second pulses of the echo sequence. As found by Liu and Cone [18] and Huang *et al.* [9], increasing the second pulse intensity produced a stronger effect on the echo decay time. This is expected because the second pulse creates a local field during the rephasing half of the echo sequence that is different from that present in the first half. We observed, in addition, a noticeable shortening of the echo decay when varying the intensity of pulse 1. This was also observed in Y_2O_3:Eu^{3+} by Huang *et al.* [9] using an amplified first pulse. They attributed the effect to the decay of the excited state population during the echo sequence. The same interpretation is given here and the magnitude of the effect is consistent with the lifetime of $^5D_0$ and with the excess dephasing induced by population changes as measured from the pulse 2 power dependence. This effect is particularly apparent for cases where T_2 is comparable with T_1 and is different from the usual manifestation of instantaneous diffusion, where excited ions do not decay appreciably during the echo pulse sequence such as in Tb:$YLiF_4$ where the lack of a pulse 1 dependence was very clearly shown [18]. We note that in $YAlO_3$:Pr^{3+} Bai and Kachru [19] observed a dependence of the dephasing on pulse 1 intensity and attributed it to dephasing induced by nonequilibrium phonons created during the relaxation of excited ions. This is not expected to be the mechanism in the present case because the lifetime of phonons created in the relaxation process will be very short.

In conclusion, by careful elimination of the effects of instantaneous diffusion and shielding the sample from electromagnetic fields, we have succeeded in measuring the intrinsic homogeneous linewidth of the $^7F_0 \rightarrow {}^5D_0$ transition in Eu^{3+}:Y_2SiO_5 at 1.4 K. The total linewidth could be separated into two contributions; one due to population decay and the other due to the spin fluctuations of the ^{89}Y nucleus. The homogeneous linewidths measured in these experiments, i.e., 122 Hz for ions in site 1 and 167 Hz for ions in site 2 and the values corrected for instantaneous diffusion 105 Hz for the two sites are, to the best of our knowledge, the narrowest optical resonances yet measured in the solid state. Isolated rare-earth ions at low temperatures behave in some respects like trapped single ions and by careful selection of host crystal it should be possible to achieve linewidths less than 100 Hz which would rival the narrowest resonances observed in trapped single ions in the "gas phase." Such extremely narrow resonances can provide very sensitive probes of local dynamics or external fields in solid state systems.

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[1] R. M. Macfarlane and R. M. Shelby, in *Spectroscopy of Solids Containing Rare Earth Ions*, edited by A. A. Ka-

plyanskii and R. M. Macfarlane (North-Holland, Amsterdam, 1987), p. 51.
[2] P. Hu, R. Leigh, and S. R. Hartmann, Phys. Lett. **40A**, 164 (1972).
[3] R. M. Macfarlane and J.-C. Vial, Phys. Rev. B **36**, 3511 (1987).
[4] C. von Borczyskowski, A. Oppenlander, H. P. Trommsdorff, and J.-C. Vial, Phys. Rev. Lett. **65**, 3277 (1990).
[5] R. M. Macfarlane and R. M. Shelby, Opt. Lett. **6**, 96 (1981).
[6] A. J. Meixner, C.M. Jefferson, and R. M. Macfarlane, Phys. Rev. B **46**, 5912 (1992).
[7] T. W. Mossberg, Opt. Lett. **7**, 77 (1982); W. R. Babbitt and T. W. Mossberg, Opt. Commun. **65**, 185 (1988).
[8] R. M. Macfarlane and R. M. Shelby, Opt. Commun. **39**, 169 (1981).
[9] J. Huang, J. M. Zhang, A. Lezama, and T. W. Mossberg, Phys. Rev. Lett. **63**, 78 (1989).
[10] R. Yano, M. Mitsunaga, and N. Uesugi, Opt. Lett. **16**, 1884 (1991).
[11] R. M. Shelby and R. M. Macfarlane, Phys. Rev. Lett. **45**, 1098 (1980).
[12] R. Yano, M. Mitsunaga, and N. Uesugi, Phys. Rev. B **45**, 12752 (1992).
[13] R. M. Macfarlane, R. M. Shelby, and R. L. Shoemaker, Phys. Rev. Lett. **43**, 1726 (1979).
[14] R. M. Shelby, A. C. Tropper, R. T. Harley, and R. M. Macfarlane, Opt. Lett. **8**, 304 (1983).
[15] J. Ganem, Y. P. Wang, R. S. Meltzer, and W. M. Yen, Phys. Rev. B **43**, 8599 (1991); A. Szabo and R. Kaarli, Phys. Rev. B **44**, 12307 (1991).
[16] R. M. Shelby and R. M. Macfarlane, Phys. Rev. Lett. **47**, 1172 (1981); K. K. Sharma and L. E. Erickson, Phys. Rev. B **23**, 69 (1981).
[17] S. C. Rand, A. Wokaun, R. G. DeVoe, and R. G. Brewer, Phys. Rev. Lett. **43**, 1868 (1979); R. M. Macfarlane, C. S. Yannoni, and R. M. Shelby, Opt. Commun. **32**, 101 (1980).
[18] G. K. Liu and R. L. Cone, Phys. Rev. B **41**, 6193 (1990).
[19] Y. S. Bai and R. Kachru, Phys. Rev. B **46**, 13735 (1992).
[20] S. Kroll, E. Y. Xu, M. K. Kim, M. Mitsunaga, and R. Kachru, Phys. Rev. B **41**, 11568 (1990).
[21] J. C. Bergquist, F. Diedrich, W. M. Itano, and D. J. Wineland, in *Laser Spectroscopy IX*, edited by M. S. Feld, J. E. Thomas, and A. Mooradian (Academic, San Diego, 1989), p. 274.
[22] D. Grischkowsky and S. R. Hartmann, Phys. Rev. B **2**, 60 (1970).
[23] B. A. Maximov, Yu. A. Charitonov, V. V. Ilyikhin, and N. B. Belov, Dokl. Acad. Nauk SSSR Ser. Mat. Phys., **183**, 1072 (1968).
[24] R. M. Shelby, C. S. Yannoni, and R. M. Macfarlane, Phys. Rev. Lett. **41**, 1739 (1978).
[25] R. M. Macfarlane, R. Wannemacher, D. Boye, Y. P. Wang, and R. S. Meltzer, J. Lumin. **48/49**, 313 (1991).
[26] A. Szabo, Opt. Lett. **8**, 486 (1983).