Nuclear-quadrupole optical hole burning in the stoichiometric material EuP_5O_{14}

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Hole burning, which is attributed to optical pumping of nuclear-quadrupole levels, has been observed in the stoichiometric rare-earth compound, EuP_5O_{14}. The long lifetime of these holes (~60 min) implies slow nuclear-spin flip-flop rates. The small magnetic moment of Eu^{3+} has prevented conventional magnetic-resonance measurements on Eu^{3+} compounds, but hole burning provides a sensitive method for the optical detection of nuclear-magnetic resonance and nuclear-quadrupole resonance. We have used hole burning and optically detected nuclear-quadrupole resonance to determine quadrupole splittings in the ground ($^7F_0$) and excited ($^5D_0$) states.

Optical hole burning arising from the transfer of population between nuclear hyperfine levels by means of an optical pumping cycle has recently been demonstrated.[1] This technique is proving to be a powerful one for high-resolution spectroscopy in solids with applications to the measurement of ground- and excited-state hyperfine splittings,[1,2] to Stark[3] effects, and to Zeeman[4] effects. In addition, it provides a sensitive optical probe of nuclear-spin states, which leads to optical detection of nuclear-spin resonance,[2] coherent transients,[5] and nuclear-spin-lattice relaxation.[6] In all cases reported so far, this effect has been restricted to transitions of optically and magnetically dilute impurity ions. In $LaF_3{:}Pr^{3+}$, for example, it was found[6] that nuclear-spin diffusion, which was caused by Pr^{3+}–Pr^{3+} interactions, causes recovery of the holes and limits the observation of optical pumping to Pr^{3+} concentrations of a few percent or less.

We report here the observation of hole burning in a stoichiometric, undoped system, EuP_5O_{14}, which has long hole lifetimes of ~60 min. This result sets a surprisingly small upper limit to the europium nuclear-spin diffusion rate. We conclude that Eu–Eu nuclear flip-flops are quenched by several factors, which include the anomalously small ground-state nuclear moment and inhomogeneously broadened quadrupole levels. Hole burning also provides a direct measurement of the quadrupole splittings of the two isotopes of Eu^{3+} in the excited electronic state and permits sensitive nuclear-quadrupole-resonance measurements of the ground-state splittings. Whereas conventional nuclear-magnetic-resonance (NMR) or nuclear-quadrupole-resonance (NQR) measurements of $^{151,153}Eu^{3+}$ have not been reported because of limited sensitivity, the present technique should be applicable even to dilute Eu^{3+} systems.

Crystals of EuP_5O_{14}, which were grown by F. Lutz, were kindly provided by G. Huber and H. Danielmeyer of the University of Hamburg. These crystals were in the form of platelets ~2 mm × 2 mm × 2 mm with the *ab* plane in the plane of the platelet.[7] The samples were immersed in liquid helium at 1.6 K and irradiated for ~0.1–1 sec with ~1 W/cm^2 of cw laser light into the $^5D_0 \leftrightarrow {}^7F_0$ transition at 5785 Å. The resulting holes were detected by scanning the frequency of an attenuated (10^{-3}) laser beam while monitoring the change in $^5D_0 \rightarrow {}^7F_J$ fluorescence.

The laser-induced redistribution of spin population in the ground-state quadrupole levels results in a decrease in population for some levels and an increase for others. Transitions from the former to all excited-state levels lead to decreased absorption (holes) and from the latter to increased absorption (antiholes). Thus, as found in previous examples,[1,2] one expects side holes to appear at frequencies corresponding to excited-state quadrupole splittings and antiholes to appear at frequencies corresponding to sum and difference combinations of ground- and excited-state splittings. For EuP_5O_{14}, the hole-burning spectrum is shown in Fig. 1. A striking characteristic of the hole pattern is that the ratio of the splittings of the two strongest side holes (2.6:1) is equal to the ratio of the nuclear-electric-quadrupole moments of the two naturally abundant $I = 5/2$ Eu isotopes, i.e., $Q = 0.95 \times 10^{-24}\ cm^2$ for ^{151}Eu and $Q = 2.42 \times 10^{-24}\ cm^2$ for ^{153}Eu.[8] This indicates that the splittings are due to the interaction of the quadrupole moments with the field gradient produced by surrounding ions, which is in accord with the absence of first-order hyperfine interaction for $J = 0$ states and with the relatively large quadrupole moments. For an $I = 5/2$ nucleus, three side holes are expected on each side of the central $\nu = 0$ hole, which gives the two excited-state splittings and their sum. The intensities of the side holes depend on the population distribution produced by the optical pumping cycle and on the relative probabilities of the transitions involved, as de-

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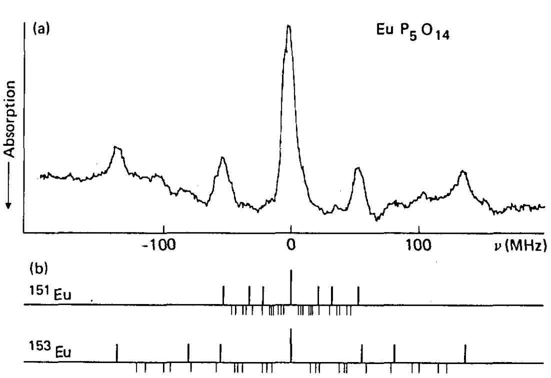

Fig. 1. (a) Nuclear-quadrupole hole-burning spectrum of the $^7F_0 \rightarrow {}^5D_0$ transition in EuP_5O_{14}. The positions of the holes (corresponding to decreased absorption) give the excited-state quadrupole splittings. (b) The predicted positions of holes (upward) and the 12 strongest of the 21 antiholes (downward) based on the energy-level scheme of Fig. 2 for ^{151}Eu and ^{153}Eu.

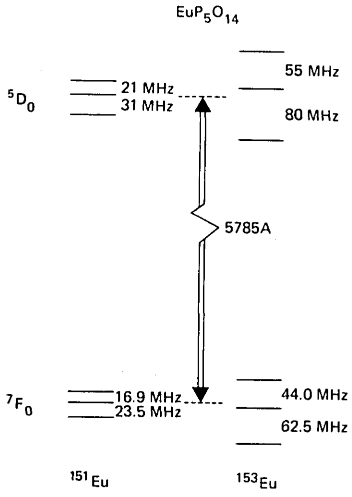

Fig. 2. Ground- ($^7F_0$) and excited- ($^5D_0$) state quadrupole splittings for $^{151}Eu^{3+}$ and $^{153}Eu^{3+}$ obtained from hole burning and optically detected magnetic-resonance measurements in EuP_5O_{14}.

termined by the overlap of ground- and excited-state nuclear-wave functions.[1] For EuP_5O_{14}, this leads to one dominant side hole and two weaker holes for each isotope. Since no features appear at frequencies greater than 135 MHz, the two prominent side holes correspond to the *sum* of the excited-state splittings for the two isotopes. Assignment of the weaker holes at ±80 and ±31 MHz to one of these splittings for ^{151}Eu and ^{153}Eu, respectively, leads to the $^5D_0$ excited-state-level diagrams shown in Fig. 2. The features at ±103 MHz are most likely due to nearby antiholes (see below). Because the assignments of individual excited-state splittings are based on fairly weak features, the numerical values of these splittings are less reliable than their sums.

The spectrum of antiholes is expected to consist of 21 enhanced absorptions for each isotope on each side of the center frequency. The assignment of these antiholes is difficult, however, because of this complexity and because the baseline for absorption changes is difficult to determine accurately. Therefore the ground-state splittings are not easily derived from the hole-burning spectrum. Furthermore, because of the hyperfine cancellation of the ground-state nuclear moment, the inhomogeneous broadening of the NQR line, and the long spin-lattice relaxation time, the sensitivity of conventional magnetic-resonance techniques is insufficient to measure these splittings, and there exist no NMR or NQR data for Eu^{3+} in solids.[9] However, these same factors quench nuclear-spin diffusion and make possible the observation of long-lived holes created by transfer of population between the ground-state quadrupole levels, which provides a sensitive means for detecting changes in these populations. As has been shown,[2] in $LaF_3:Pr^{3+}$, the application of resonant rf radiation fills in the holes by inducing transitions between the ground-state quadrupole levels. This effect was detected by monitoring the increase in fluorescence on application of the rf pulses (~8 G for 25 msec). Signals were found at all four ground-state frequencies shown in Fig. 2, and somewhat weaker signals were found at 106.5 and 40.4 MHz, corresponding with the sum of these splittings for ^{153}Eu and ^{151}Eu. The linewidth of these transitions was ~100 kHz and is attributed to the perturbation of the field gradient by random strains since the Eu–^{31}P dipolar width is estimated to be only ~100 Hz. This optically detected magnetic-resonance technique thus serves to confirm the hole-burning mechanism, as well as providing an accurate determination of the ground-state splittings (Fig. 2). It will also be useful for further magnetic-resonance studies of Eu^{3+}, even in dilute spin systems.

The quadrupole splittings shown for EuP_5O_{14} in Fig. 2 can be described by the spin Hamiltonian:

$$H = P\left[I_z{}^2 - \frac{1}{3}I(I+1) + \frac{\eta}{3}(I_x{}^2 - I_y{}^2)\right] . \qquad (1)$$

The parameters P and η are given for the two electronic states and two isotopes in Table 1. Since the field gradient is determined essentially by the arrangement of ions around the Eu^{3+} site after taking into account the different antishielding factors in the two electronic states,[10] one obtains essentially identical values for the asymmetry parameter η in ground and excited states. The ratio of P values for the two isotopes is very close to the quadrupole-moment ratio of 2.6, and the ratio of P values for $^5D_0$ and $^7F_0$ is the same for both isotopes. From the splittings one can calculate the expected frequencies of holes and antiholes. The resulting calculated spectrum is consistent with the experimental data as shown in Fig. 1.

The lifetime of the holes was measured by probing with an attenuated laser beam at 5-min intervals and

Table 1. Spin Hamiltonian Parameters Corresponding to the Energy Level Scheme in Fig. 2

		^{151}Eu	^{153}Eu
$^5D_0$	P(MHz)	8.0	21
	η	0.59	0.59
$^7F_0$	P(MHz)	6.26	16.6
	η	0.620	0.595

was found to be 60 min at 1.6 K. This lifetime is determined by both nuclear-spin-lattice relaxation (T_1) and mutual spin flips. These T_2 processes lead to hole filling because nuclear-spin flip-flops occur between ions that can have different optical splittings.[6] If the optical inhomogeneous broadening in EuP_5O_{14} is microscopically random or approximately so, one is forced to conclude that the average flip-flop is ≥60 min. Several important factors contribute to this quenching of spin diffusion. In the EuP_5O_{14} crystal structure,[7,11] each Eu^{3+} has only two near Eu^{3+} neighbors at relatively large distances of 5–6 Å. Using the intrinsic nuclear moments[12] of 3.46 μ_N (^{151}Eu) and 1.53 μ_N (^{153}Eu), one estimates the homonuclear–dipolar interaction $(\Delta\nu)_d$ to be $\mu^2/r^3 = 30$–150 Hz. However, as originally pointed out by Elliott,[13] the second-order hyperfine interaction with the $^7F_1$ level, which is ~400 cm^{-1} (Ref. 8) above the ground state, gives a contribution to the nuclear g value whose sign is opposite that of the intrinsic moment and which reduces the net magnetic moment by about a factor of 10. The corresponding reduction in the dipolar interaction gives $(\Delta\nu)_d \simeq 1$ Hz. In addition, the quadrupole levels are inhomogeneously broadened by random variations in the electric-field gradient caused by crystal strains. In the optically detected NQR measurements discussed above, we found that the inhomogeneous linewidth $(\Delta\nu)_i$ of the NQR transitions was ≃100 kHz. The rate of mutual spin flips T_f^{-1} may be estimated by using Fermi's golden rule, by taking $1/2(\Delta\nu)_i$ as the density of states in the center of the line: $T_f^{-1} \simeq (\Delta\nu)_d^2/(\Delta\nu)_i \simeq 10^{-5}\ sec^{-1}$. Because the homonuclear interaction $(\Delta\nu)_d$ is so weak, it may be important to include a higher-order process in which energy is exchanged with the ^{31}P dipolar reservoir. The presence of the two equally abundant isotopes (48% ^{151}Eu and 52% ^{153}Eu) and the multilevel $I = 5/2$ spin system further reduces the probability that neighboring ions are in the right constellation to flip flop. The observed hole-filling rate of $3 \times 10^{-4}\ sec^{-1}$ is consistent with these considerations. This rate also contains contributions from nuclear T_1 processes. Our present measurements cannot determine which of these limits the hole lifetime.

For shallow holes, the width of the central hole might be expected to give the optical homogeneous linewidth. As recently demonstrated using photon echoes, the optical homogeneous linewidth of this transition (~30 kHz) is very narrow for a stoichiometric material.[14] However, the narrowest holes we observed in our measurements were limited to ~2 MHz by the laser-frequency stability over the time scale of the experiment. (The holes in Fig. 1 were further broadened by the need to burn deep holes to obtain a good signal-to-noise ratio over the entire spectrum.)

In conclusion, we have observed optical hole burning in the undoped stoichiometric material EuP_5O_{14} that is due to optical pumping of the nuclear-quadrupole levels. This provides a means for sensitive optical detection of NQR and NMR transitions in Eu^{3+} systems, systems in which the anomalously small magnetic moment and the large inhomogeneous broadening have prevented conventional detection of magnetic resonance. Using these techniques, we have obtained the quadrupole splittings for both abundant isotopes of trivalent europium in ground- $^7F_0$ and excited- $^5D_0$ states of EuP_5O_{14}. The holes have anomalously long lifetimes of ~60 min, showing that the homonuclear T_2 of $^{151,153}Eu$ is of this order or longer.

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