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Optical measurement of spin-lattice relaxation of dilute nuclei: LaF_3:Pr^{3+}

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We describe a method of measuring spin-lattice relaxation rates of dilute nuclei using optical hole burning. This was applied to ^{141}Pr nuclei doped into LaF_3 at low concentrations (0.01 to 2.0 at.%). The observed relaxation rates varied by about two orders of magnitude between 2 and 4.5 K. At the lowest concentrations the data are interpreted in terms of two mechanisms: resonant two-phonon (Orbach) relaxation with a 57-cm^{-1} activation, and praseodymium-lanthanum cross relaxation. At higher concentrations an additional hole-filling process was observed and attributed to homonuclear Pr–Pr dipolar coupling. Theoretical estimates of the phonon-induced relaxation rates are given and agree approximately with experimental values.

I. INTRODUCTION

A number of optical methods have been used to measure the spin-lattice relaxation of electron spins, principally the detection of population changes by magnetic circular dichroism[1] or Faraday rotation.[2] It is not expected that these methods would be useful in the case of nuclear spin systems since the small nuclear moments would not lead to easily observable magneto-optic effects. This is particularly true for dilute nuclear spins. Conventional magnetic resonance relaxation measurements[3] of dilute nuclei are also difficult. However, the recent discovery in LaF_3:Pr^{3+} of an optical pumping cycle which leads to laser-induced optical hole burning[4] has provided the means to monitor $Pr(I=\frac{5}{2})$ nuclear spin populations optically. Excitation by monochromatic laser light leads to (optical) frequency-selective redistribution of nuclear population which results in a reduction in absorption. The laser absorption thus provides a sensitive probe of these populations, and this has previously been used to detect nuclear spin transitions induced by rf irradiation.[5,6] The recovery time of these holes provides a direct measurement of the nuclear spin-lattice relaxation times.[7] As previously noted,[8] this recovery time varies by almost three orders of magnitude between 1.8 and 4.2 K. An understanding of this effect in terms of mechanisms for nuclear spin-lattice relaxation motivated the present study.

The optical pumping cycle used to produce the ground-state nuclear polarization[4] involves the transition from the lowest crystal-field component of $^3H_4$ (the ground state of the Pr^{3+} ion) to the lowest crystal-field component of $^1D_2$ at 5925.2 Å. The crystal field of C_2 symmetry removes the $2J+1$-fold degeneracy, leaving singly degenerate electronic levels. The ground-state nuclear spin levels consist of three doubly degenerate levels split by the second-order hyperfine interaction as well as the relatively small nuclear electric quadrupole interaction (see Fig. 1). The second-order interaction requires the presence of nearby electronic levels,[9] located in this case 57 cm^{-1} above the ground state and 23 cm^{-1} above the excited state.[10]

The presence of a three-level nuclear spin system complicates the relaxation dynamics somewhat, since the three relaxation times corresponding to the three possible transitions among these levels need not be equal. This leads to nonexponential relaxation behavior.[11] By applying saturating rf radiation at the frequency of one of the three transitions, it can be shown that the recovery reduces to a single exponential. Repetition of this experiment for the other two transitions gives enough information to derive the three individual nuclear relaxation times. This idea was first applied to relaxation studies in pure nuclear quadrupole resonance[12] and has been used with limited success for electron spin-lattice relaxation in excited triplet states of organic molecules.[13,14] In the present study, it provides the simplification needed to properly identify the nature of the relaxation mechanisms which are operative.

We have measured the relaxation times in the ground state of LaF_3:Pr^{3+} between 1.5 and 4.6 K and find contributions to T_1 from two different mechanisms: (i) Resonant two-phonon (Orbach) relaxation[15] involving the first excited crystal-field level at an energy of 57 cm^{-1}. This mechanism is dominant above ~3.5 K. (ii) A concentration and temperature-independent process which is important below 3 K and which we attribute to Pr-La cross relaxation. In addition, we find a temperature-independent but concentration-dependent hole recovery process which appears below 3 K and which is due to Pr–Pr nuclear flip flops. This T_2-like process provides a mechanism for hole recovery when ions having different optical frequencies are involved.

We also present a derivation of phonon-induced relaxation rates[16] for the case of nuclear levels which are split by the second-order hyperfine interaction.

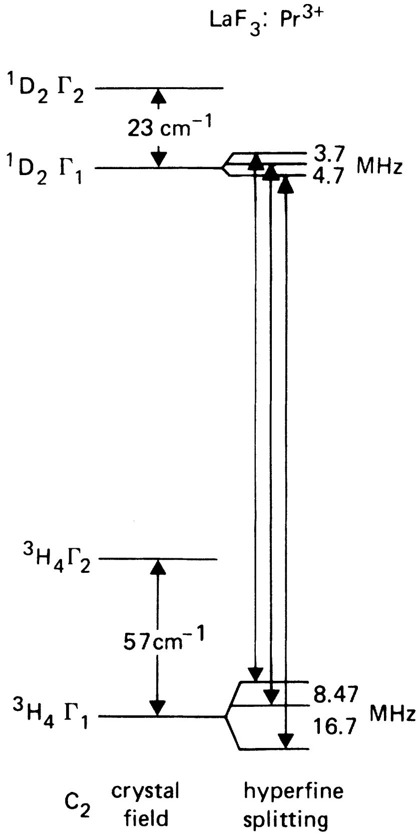

FIG. 1. Energy-level diagram for LaF_3:Pr^{3+}. The two lowest crystal-field states of the $^3H_4$ (ground state) and $^1D_2$ manifolds are shown as well as the second-order hyperfine splitting for the lowest levels. The arrows indicate the optical transitions probed by the laser light.

Expressions for direct, Raman, and resonant two-phonon (Orbach) processes are given. The basic mechanism involves coupling of the phonons and nuclei through phonon modulation of the hyperfine interaction. In the case of the Orbach process, an additional contribution appears due to the difference in magnitude and orientation of the second-order hyperfine tensor in the ground and resonant intermediate electronic levels. This mechanism is very similar to one recently considered for spin-lattice relaxation in excited triplet states of organic molecules.[17,18] Numerical estimates of these relaxation rates for LaF_3:Pr^{3+} are given and shown to be in reasonable agreement with the experiments.

The relaxation times observed at low temperatures are on the order of several minutes and longer, and provide a basis for detailed interpretation of recently observed[19,20] very long-lived stimulated photon echo decays. These decays are governed by the same relaxation processes in the ground-state hyperfine levels as are responsible for optical hole recovery.

II. EXPERIMENTAL

Holes were burned by irradiation of the sample using ~50 mW (2-mm beam diameter) of light from a single frequency rhodamine 6G dye laser operating at 5925.2 Å. Typical burning times were in the range 1–2 sec. The recovery of these holes as a function of time was recorded as an increase in the amount of fluorescence excited by a weak ($\sim 10^{-4}$ of the burning intensity) probe beam at the same laser frequency as used for burning. Up to 50 such recovery curves were averaged to improve signal to noise.

The LaF_3 crystals ($\sim 2\times 2\times 3$ mm^3) were positioned in an rf coil with the coil axis parallel to the laser propagation axis and the crystal c axis. The holes were burned and their recovery monitored in the presence of rf radiation at the frequency of each of the three ground-state splittings in turn, i.e., 8.47, 16.7, and 25.2 MHz.[5] Sufficient rf field strength was used to saturate the populations involved in a few milliseconds or less (2, 2, and 10 G, respectively, at the above three frequencies).

The rf coil and crystal were immersed in a liquid-helium cryostat and the temperature was controlled between 1.5 and 4.6 K by controlling the pressure of helium vapor by pumping or pressurizing the liquid-helium bath.

III. RESULTS AND DISCUSSION

The energy level structure[4,10] of LaF_3:Pr^{3+} is shown in Fig. 1. Since the laser linewidth and the widths of the levels are less than the hyperfine splittings, only one of the ground-state levels is optically pumped for a given ion, and the population of this level is then monitored during the hole recovery period. However, since the inhomogeneous broadening of the optical transition is much larger than the hyperfine splittings, the other levels are pumped for other ions in different environments. Thus, the measurement of the nuclear relaxation is complicated both by the superposition of hole recoveries due to these three classes of ions and by the nonexponential return to equilibrium expected for a three-level system.

For a three-level system characterized by the three spin-lattice relaxation rate constants K_{12}, K_{23}, and K_{13} and perturbed from equilibrium by some means such as optical pumping, the relaxation of the population of level i is given by:

$$n_i(t) = n_i(\infty) + n_i^{+}\exp(\lambda_+ t) + n_i^{-}\exp(\lambda_- t) \ . \qquad (1)$$

The decay constants $\lambda_\pm$ are given by

$$\lambda_\pm = -(K_{13}+K_{12}+K_{23}) \pm [(K_{13}+K_{12}+K_{23})^2 - 3(K_{13}K_{12}+K_{13}K_{23}+K_{12}K_{23})]^{1/2} \ . \qquad (2)$$

$n_i(\infty)$ is the steady-state equilibrium population and n_i^+ and n_i^- are determined by the initial populations. It should be pointed out that measurement of the decay constants λ_+ and λ_- alone is insufficient to determine the rate constants, K_{ij}.[14]

If one of the K_{ij} is artificially made much larger than the other two by application of rf at ω_{ij} the situation simplifies considerably. Instead of the three classes of ions mentioned above, there are two; those for which the optically pumped level is one coupled by rf and those for which it is not (Fig. 2). Therefore, the more complicated three-level system is effectively reduced to a two-level case and one expects simple exponential relaxation. By using $K_{ij} >> K_{jl}$, K_{il} in Eq. (2) and inserting appropriate initial conditions [i.e., either $n_i = n_j = \frac{1}{2}x$, $n_l = 1 - x$, or $n_i = n_j = \frac{1}{2}(1-x)$; $n_l = x$ where x is the residual population in the optically pumped level] one finds that the hole recovery is a single exponential with a rate given by

$$R_{ij} = \frac{3}{2}(K_{il} + K_{jl}) \quad . \tag{3}$$

Furthermore, by measuring this hole recovery for three experiments in which each of the three pairs of levels in turn is saturated by rf, the spin-lattice relaxation rate constants can be derived, namely

$$K_{ij} = \frac{1}{3}(-R_{ij} + R_{jl} + R_{il}) \quad . \tag{4}$$

This method was previously suggested by Grechishkin and Shishkin[12] and by Zulich *et al.*[13] for spin-lattice relaxation measurements of nuclear quadrupole systems and excited molecular triplet states, respectively.

We have used these methods to measure the temperature dependence of the relaxation rates for the 8.47 and 16.7 MHz transitions for LaF$_3$:Pr^{3+} at liquid-helium temperatures. The results are displayed for several Pr^{3+} concentrations in Fig. 3. Because the 25-MHz relaxation is considerably slower than the other two the relative error in its value is large, and the results are not shown. In order to explain the observed relaxation behavior at least three distinct mechanisms are necessary. At low temperatures there are two temperature-independent mechanisms. One of these affects only the 8.47-MHz relaxation and is concentration independent; the other affects both transitions and its contribution is approximately linear in concentration. Above 3.5 K both relaxation times are highly temperature dependent, indicating a phonon-induced relaxation mechanism. A plot of the log of the temperature-dependent part of the relaxation rate vs $1/T$ (see Fig. 4) shows that it is exponentially activated with an activation energy very close to the energy of the first excited electronic state (57 cm^{-1}). This result indicates that the temperature-dependent relaxation is due to a resonant two-phonon (Orbach[15]) process involving the first excited crystal-field level of $^3H_4$ as intermediate state [Fig. 5(a)]. No evidence of direct or Raman process relaxation (T or T^7 temperature dependence[16]) is seen, and the observed 8.47- and 16.7-MHz relaxation rates are described by the expressions (in sec^{-1}):

$$(T_1)^{-1}_{8.47} = 0.18 + 30C + 5 \times 10^7 e^{-57/kT} \quad , \tag{5}$$

$$(T_1)^{-1}_{16.7} = 10C + 3 \times 10^7 e^{-57/kT} \quad . \tag{6}$$

where C is the Pr concentration in at.%.

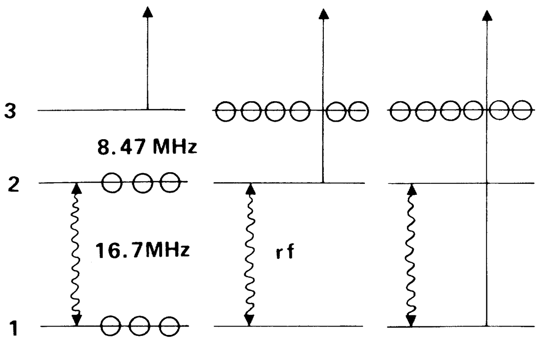

FIG. 2. Population distribution in the ground-state hyperfine levels produced by optical pumping in the presence of saturating rf at 16.7 MHz. The straight arrows designate the levels from which the population is removed by absorption of laser light. The three diagrams correspond to ions with different optical splittings due to inhomogeneous broadening. The spin-lattice relaxation rates K_{12}, K_{23}, and K_{13} correspond to the three possible transitions among these levels.

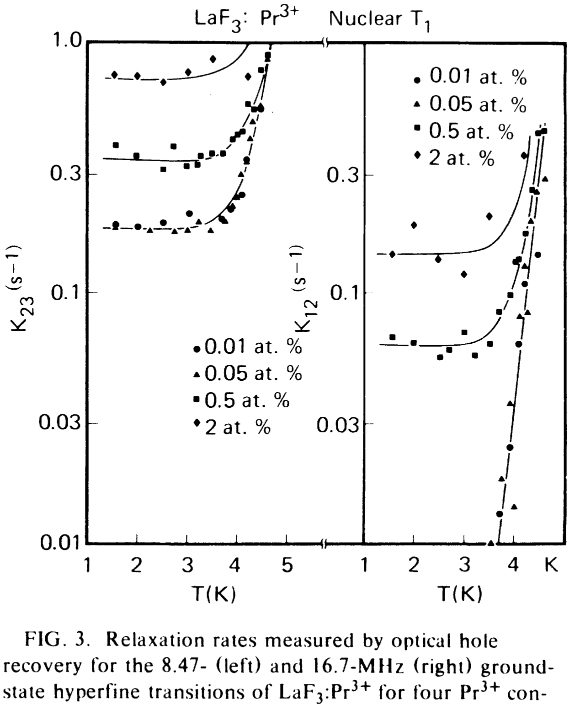

FIG. 3. Relaxation rates measured by optical hole recovery for the 8.47- (left) and 16.7-MHz (right) ground-state hyperfine transitions of LaF$_3$:Pr^{3+} for four Pr^{3+} concentrations.

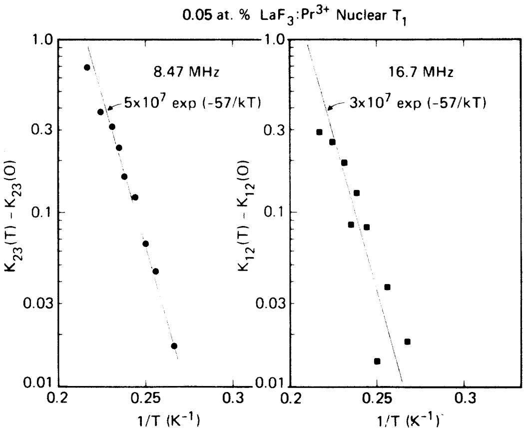

FIG. 4. The temperature-dependent part of the relaxation rates shown in Fig. 3 are plotted for the 0.05 at.% crystal. The exponential temperature dependence confirms the presence of a resonant two-phonon (Orbach) relaxation process [Fig. 5(a)] involving the first excited electronic state at 57 cm^{-1} (see Fig. 1).

There are two temperature-independent terms in Eqs. (5) and (6). At the lowest concentrations studied (0.01 and 0.05 at.%), a contribution of 0.18 sec^{-1} remains for the 8.47-MHz transition. No similar term exists for the 16.7-MHz transition. We believe that the most likely explanation involves a Pr-La cross-relaxation process involving simultaneous spin flips of the Pr nucleus and three surrounding La nuclei [see Fig. 5(b)]. The lanthanum spin flips would take place between the $\pm\frac{3}{2}$ and $\pm\frac{1}{2}$ states which are separated by 2.8 MHz,[21] and the process could thus conserve both energy (to within the 200-kHz Pr linewidth) and spin angular momentum. Assuming that the eight spin states of ^{139}La are occupied randomly, a statistical analysis shows that there is about a $\frac{1}{3}$ probability that 3 of the 12 nearest lanthanum nuclei are in appropriate spin states for this process to occur. An estimate of the resulting relaxation rate for the 8.47-MHz transition can be obtained using a perturbation treatment of the Pr—La dipolar interaction taken to third order. If the strength of the Pr—La coupling is on the order of a few kHz, this calculation yields $(T_1^{\text{Pr-La}})^{-1} \sim 0.1$ sec^{-1} which is consistent with the observed rate. This relaxation mechanism would not be possible for either of the other two transitions and should be strongly affected by an externally applied magnetic field which could detune the resonance between the Pr and La splittings. Preliminary results indicate that the 8.47-MHz relaxation time does indeed increase in the presence of a magnetic field.

The concentration-dependent terms in Eqs. (5) and (6) are most likely accounted for by Pr—Pr interactions. Although only two concentrations which show this contribution have been investigated, the data indicate that the variation with concentration is linear or nearly so. A linear dependence is consistent with a mechanism of optical hole recovery by nuclear spin flip flops induced by the Pr—Pr dipolar interaction which varies as r^{-3} where r is the Pr—Pr distance.[22]

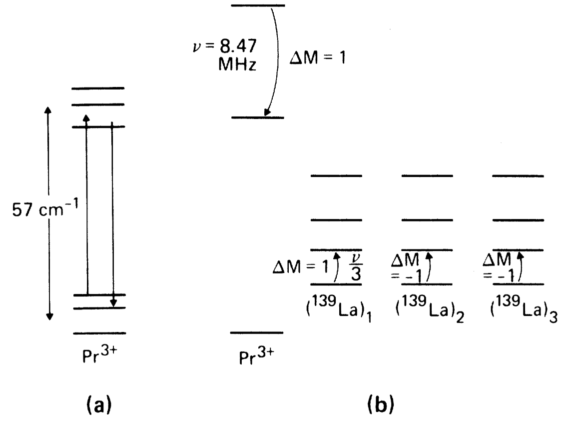

FIG. 5. Schematic representation of spin-lattice relaxation processes observed in LaF$_3$:Pr^{3+}. (a) Orbach relaxation involving phonon absorption and emission (arrows) via the first excited electronic level. (b) Cross relaxation between the Pr and surrounding La quadrupole levels conserves energy and spin angular momentum with a four spin flip process for the 8.47-MHz transition. This leads to a temperature-independent relaxation rate below 3.5 K for this transition.

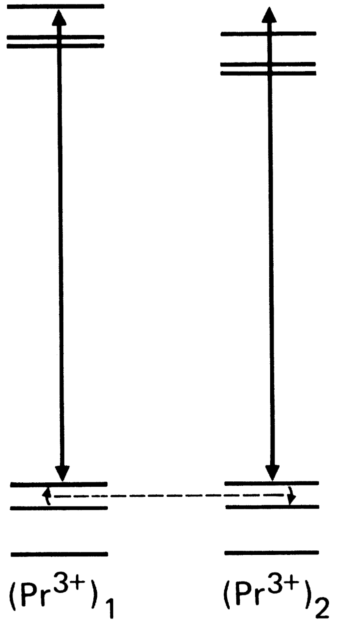

FIG. 6. Concentration-dependent optical hole recovery is caused by Pr—Pr spin flip flops (dotted line) when one Pr ion is resonant with the laser (double headed arrows) and the other is not.

Although this is not a T_1 process, since the overall spin energy is conserved, it does lead to a filling in of the hole burned by the laser and will therefore be observed by this experiment. The hole filling comes about because the two spins participating in the flip flop can have different optical transition frequencies (see Fig. 6). This provides a rather direct way of measuring the homonuclear dipolar interactions between dilute nuclei—interactions which are masked in other experiments (i.e., magnetic resonance linewidth) by stronger heteronuclear couplings. The relative size of the mutual spin flip matrix elements predicts a larger flip flop rate for the 8.47-MHz transition than for the 16.7-MHz transition and this is observed. However, when the ~10 kHz/G enhanced moment of Pr is used to estimate the dipolar interactions, one calculates a flip flop time which is 10 to 100 times shorter than the experimentally observed relaxation time. This suggests that several flip flops are needed to refill the hole, indicating the presence of some degree of correlation between the crystalline environments (and therefore between the optical transition frequencies) of nearby ions. The possibility of concentration-dependent relaxation due to the presence of paramagnetic ions introduced into the samples along with the PrF_3 dopant should also be considered. However, one should then expect a much larger concentration-independent contribution due to the same impurities which should also be present in the LaF_3 host.

IV. APPLICATION OF RELAXATION THEORY

We now turn to a discussion of the coupling between phonons and nuclear spins which leads to the observed temperature dependence of the relaxation rate. This coupling can come from phonon modulation of the local magnetic field, the electric field gradient at the Pr nucleus,[23] and/or the hyperfine field. In the case of LaF_3:Pr^{3+}, effects due to the hyperfine interaction are an order of magnitude greater than nuclear quadrupole or magnetic dipole effects.[4,5] Therefore, one can anticipate that phonon-nuclear coupling via the hyperfine interaction will be the dominant T_1 mechanism. Following the method of Orbach,[15] we use a dynamical crystal-field approach to calculate the spin-lattice relaxation rate due to direct, Raman and Orbach processes and use the results to make numerical estimates for LaF_3:Pr^{3+}.

Within the $^3H_4$ manifold, the Hamiltonian can be written as

$$H = H_{\mathrm{cf}} + A_J \vec{I} \cdot \vec{J} \ , \tag{7}$$

where H_{cf} is the crystal-field Hamiltonian, $\vec{I}$ and $\vec{J}$ the nuclear and electronic angular momenta, and A_J the hyperfine coupling constant. We write the wave functions to first order in the hyperfine coupling using as a basis the eigenfunctions $|j\rangle$ of H_{cf}, and a suitable nuclear basis, $|m\rangle$ where $m=-\frac{5}{2},-\frac{3}{2}\cdots\frac{5}{2}$. Thus, the wave functions for these hyperfine levels are

$$|j,m_j\rangle = |j^{(1)}\rangle |\tilde{m}_j\rangle; \quad j=0,1\cdots \ , \qquad m=-\tfrac{5}{2},-\tfrac{3}{2}\cdots\tfrac{5}{2} \ , \tag{8}$$

where

$$|\pm\tilde{m}_j\rangle = \pm C^j_{5/2,m}|\pm\tfrac{5}{2}\rangle \pm C^j_{3/2,m}|\mp\tfrac{3}{2}\rangle \pm C^j_{1/2,m}|\pm\tfrac{1}{2}\rangle \tag{9}$$

specify the nuclear states, and

$$|j^{(1)}\rangle = |j\rangle + A_J \sum_n \frac{|n\rangle\langle n|J_\alpha|j\rangle I_\alpha}{E_j - E_n} \tag{10}$$

gives the first-order mixing of the $^3H_4$ crystal-field states by the hyperfine interaction. The repeated index α implies summation over x, y, and z directions. The $C^j_{m',m}$ are chosen to diagonalize the matrix $\langle j,m_j|A_J\vec{I}\cdot\vec{J}|j,m_j'\rangle$, taken to second order in A_J. This matrix corresponds to Teplov's pseudoquadrupole spin Hamiltonian,[24] and its eigenvalues give the hyperfine splittings in state $|j\rangle$.

The interaction with the phonons is through the electronic orbit-lattice interaction, given in terms of the lattice strain ϵ, in the form of a dynamical crystal field[15]

$$V_{0l} = \epsilon \sum_{kl} V_{kl} = \epsilon \sum_{kl} A_{kl} Y_k^l(\theta,\phi) \ . \tag{11}$$

For the direct process, one needs the matrix element of V_{0l} between the two ground-state hyperfine levels involved. Since Eq. (11) contains no nuclear operators, the phonons cannot directly flip nuclear spins. However, the matrix element in question is nonzero by virtue of the mixture of states induced by the hyperfine interaction [Eq. (10)]:

$$\langle 0,m|V_{kl}|0,m'\rangle = \langle 0|V_{kl}^\alpha|0\rangle\langle\tilde{m}|I_\alpha|\tilde{m}'\rangle \ , \tag{12}$$

where

$$\langle i|V_{kl}^\alpha|j\rangle = A_J \sum_n \left(\frac{\langle i|V_{kl}|n\rangle\langle n|J_\alpha|j\rangle}{\Delta_{jn}} + \frac{\langle i|J_\alpha|n\rangle\langle n|V_{kl}|j\rangle}{\Delta_{in}} \right) , \tag{13}$$

where $\Delta_{jn} = E_j - E_n$, etc. The usual expression for the direct process relaxation rate[15] with the above matrix elements gives

$$(T_1^D)^{-1}_{m\to m'} = \left(\frac{3}{2\pi\rho v^5\hbar}\right)\omega^3_{mm'}\left|\sum_{kl}\langle 0|V_{kl}^\alpha|0\rangle\langle\tilde{m}|I_\alpha|\tilde{m}'\rangle\right|^2 . \tag{14}$$

where ρ is the crystal density, v the velocity of sound, and $\omega_{mm'}$ is the hyperfine splitting frequency between the two levels indicated by the subscripts. Note that this relaxation rate is proportional to a quantity of order $(A_J/\Delta)^2$ ($\sim 10^{-7}$ for $LaF_3{:}Pr^{3+}$) where Δ is a typical crystal-field splitting.

One can follow a similar procedure[15] to find the corresponding contribution to the two-phonon Raman and Orbach relaxation rates. As in the case of the direct process, Raman relaxation requires the presence of the hyperfine interaction to induce a net spin flip:

$$(T_1^R)^{-1}_{m\to m'}=\left(\frac{9(6)!}{4\pi^3\rho^2v^{10}}\right)\left(\frac{kT}{\hbar}\right)^7\left|\sum_n\sum_{kl,k'l'}\left(\langle 0|V^{\alpha}_{kl}|n\rangle\langle n|V_{k'l'}|0\rangle+\langle 0|V_{kl}|n\rangle\langle n|V^{\alpha}_{k'l'}|0\rangle\right)\frac{\langle\tilde m|I_\alpha|\tilde m'\rangle}{\Delta_{n0}}\right|^2 , \qquad (15)$$

where $\Delta_{n0}=E_n-E_0$.

The evaluation of the Orbach process relaxation rate is similar, but is slightly complicated by the nonnegligible lifetime of the intermediate state. The general two-phonon relaxation rate is given by[15]

$$(T_1)^{-1}=\frac{9}{16\pi^3\rho^2v^{10}}\cosh\left(\frac{\hbar\omega_{mm'}}{2kT}\right)\int d\omega_p\,\omega_p^6\left|\sum_{kl,k'l'}\sum_M\frac{\langle 0m|V_{kl}|1M\rangle\langle 1M|V_{k'l'}|0m'\rangle}{h\omega_p+\Delta_{10}-\delta_M+i\Gamma}\right|^2\operatorname{cosech}\left(\frac{\hbar\omega_p}{2kT}\right) , \qquad (16)$$

where the integral is over phonon frequencies ω_p, and δ_M are the energies of the $|1M\rangle$ levels with respect to their center of gravity. $\tau=(2\Gamma)^{-1}$ is the lifetime of these intermediate levels where

$$\Gamma=\left(\frac{3}{2\pi\rho v^5}\right)\left(\frac{\Delta_{10}}{\hbar}\right)^3\left|\sum_{kl}\langle 0|V_{kl}|1\rangle\right|^2 . \qquad (17)$$

The nonresonant contribution to this integral (i.e., for phonon energies far from Δ_{10}) gives the Raman relaxation rate. The lowest order (in A_J) nonzero term which results is that given by Eq. (15). For phonon energies near Δ_{10} one obtains a large contribution to the integral corresponding to resonant two-phonon scattering via the intermediate $|1M\rangle$ levels. By using Eqs. (8) and (10), working out the squared factor, and performing the integration, one finds two important low-order contributions to the resonant relaxation process. One of these involves the same basic mechanism as the direct and Raman processes discussed above, namely phonon modulation of the hyperfine interaction. The interaction of the phonons and nuclear spins through the hyperfine field is given by the matrix element $\langle 1|V^{\alpha}_{kl}|0\rangle\langle\tilde m|I_\alpha|\tilde m'\rangle$ appearing in the following expression for the relaxation rate:

$$(T_1^{01})^{-1}_{m\to m'}=\left(\frac{3}{2\pi\rho v^5\hbar}\right)\left(\frac{\Delta_{10}}{\hbar}\right)^3\exp\left(\frac{-\Delta_{10}}{kT}\right)$$
$$\times\left|\sum_{kl,k'l'}\left(\langle 0|V^{\alpha}_{kl}|1\rangle\langle 1|V_{k'l'}|0\rangle+\langle 0|V_{kl}|1\rangle\langle 1|V_{k'l'}|0\rangle\right)\langle\tilde m|I_\alpha|\tilde m'\rangle\right|^2\Big/\left|\sum_{kl}\langle 0|V_{kl}|1\rangle\right|^2 . \qquad (18)$$

$(T_1^{01})^{-1}$ is approximately proportional to the phonon absorption rate which goes as τ^{-1} in the low-temperature limit.

The second contribution to the Orbach rate comes about due to the finite lifetime of the intermediate state together with the difference in orientation of the principal axes of the second-order hyperfine interaction as compared to the ground state. Thus, the nuclear overlap factors $\langle\tilde M|\tilde m\rangle$ are nonzero where $|\tilde M\rangle$ denotes a nuclear wave function in the excited state. In this case, phonon-induced transitions to this excited state lead to excitation of nonstationary linear combinations of spin states which evolve at the excited state hyperfine splitting frequencies. Because of this time evolution for a duration τ, the system can relax back to a different hyperfine level in the ground state. The probability for this depends on the overlap factors, the lifetime τ, and the rate of evolution in the excited state, $\omega_{MM'}$:

$$(T_1^{02})^{-1}_{m\to m'}=-\left(\frac{3}{2\pi\rho v^5\hbar}\right)\left(\frac{\Delta_{10}}{\hbar}\right)^3\exp\left(\frac{-\Delta_{10}}{kT}\right)\left|\sum_{kl}|\langle 0|V_{kl}|1\rangle\right|^2\left[\sum_{M,M'}\langle\tilde m|\tilde M\rangle\langle\tilde M|\tilde m'\rangle\langle\tilde m'|\tilde M'\rangle\langle\tilde M'|m\rangle\left(\frac{\omega^2_{MM'}\tau^2}{1+\omega^2_{MM'}\tau^2}\right)\right]$$
$$=-\tau^{-1}\exp\left(\frac{-\Delta_{10}}{kT}\right)\left[\sum_{M,M'}\langle\tilde m|\tilde M\rangle\langle\tilde M|\tilde m'\rangle\langle\tilde m'|\tilde M'\rangle\langle\tilde M'|\tilde m\rangle\left(\frac{\omega^2_{MM'}\tau^2}{1+\omega^2_{MM'}\tau^2}\right)\right] . \qquad (19)$$

In contrast with Eq. (18), this expression is proportional to τ in the limit $\omega_{MM'}\tau \ll 1$, and for very short lifetimes $(T_1^{01})^{-1} > (T_1^{02})^{-1}$. As τ increases, the two contributions become comparable, since the overlap factors in Eq. (19) are about 0.1–0.8. In fact $(T_1^{01})^{-1}$ contains a factor of order $(A_J/\Delta_{10})^2 \sim 10^{-7}$ and for example when $\omega_{MM'} = (2\pi)10$ MHz and $\tau = 10$ psec, $\omega_{MM'}^2\tau^2 \sim 10^{-7}$ also. Other factors in Eqs. (18) and (19) are of similar magnitude.

In the limit $\omega_{MM'}\tau \gg 1$, Eq. (18) becomes

$$(T_1^{02})^{-1}_{M\to m'} = \tau^{-1}\exp\left[\frac{-\Delta_{10}}{kT}\right] \times \left[\sum_M |\langle \tilde{m}|\tilde{M}\rangle\langle\tilde{M}|\tilde{m}'\rangle|^2\right] . \quad (20)$$

In this case $(T_1^{02})^{-1} \sim 10^7 (T_1^{01})^{-1}$. The form of Eq. (20) indicates that in the long-lifetime limit the three hyperfine levels in the excited state can be considered as independent relaxation channels since no interference terms appear. The relaxation rate is then governed by the phonon absorption rate and the individual overlap factors for each level.

Results similar to those of Eqs. (18) and (19) were previously obtained by Culvahouse and Richards[25] and by Lyo[26] in the context of electron spin resonance and more recently for the case of excited electronic triplet states of organic molecules by Verbeek *et al.*,[17] and by Levinsky and Brenner.[18]

We have estimated the magnitudes of these various contributions to the spin-lattice relaxation rate for the ground-state hyperfine levels of $\mathrm{LaF_3{:}Pr^{3+}}$, using the crystal-field parameters tabulated by Matthies and Welsch[27] as the starting point. The $^3H_4$ crystal-field Hamiltonian was diagonalized numerically and the resulting eigenfunctions used as a zero-order basis in the calculation of the hyperfine splittings and nuclear spin functions [see Eqs. (7)–(10)]. In calculating matrix elements of V_{kl}, the dynamical crystal-field parameters were approximated using the static values, as discussed by Schultz and Jeffries.[28] The density and sound velocity of $\mathrm{LaF_3}$ were also taken from Ref. 28. From fluorescence line narrowing data of Erickson,[29] the lifetime of the crystal-field state 57 $\mathrm{cm^{-1}}$ above the ground state is $\tau = 3.2$ psec. For comparison, the crystal-field calculation using Eq. (17) gave $\tau = 10$ psec. From Eqs. (14), (15), (18), and (19) one obtains the following estimate of the relaxation rate for the 16.7-MHz transition:

$$(T_1)^{-1} = 2\times10^{-6}T + 7\times10^{-8}T^7 + (3\times10^6 + 2\times10^4) \times \exp(-57\ \mathrm{cm^{-1}}/kT)\ \mathrm{sec^{-1}} . \quad (21)$$

Similar estimates are obtained for the 8.47-MHz transition while those for the 25.2-MHz transition are about an order of magnitude smaller. The two factors in parentheses are the contributions to the Orbach relaxation rate from Eqs. (18) and (19), respectively. The calculation of the Orbach relaxation rate gives reasonable agreement with experiment [see Eqs. (5) and (6)], considering the relatively large error in determining the prefactor of the exponential due to the narrow range of temperature covered by the data. From these estimates, it can be seen that the direct and Raman processes will be important only for $T < 3$ K and are masked in the experiments by the presence of other temperature-independent relaxation processes, or by experimental limitations resulting from long-term laser frequency drift.

V. CONCLUSIONS

We have shown that optical hole burning in $\mathrm{LaF_3{:}Pr^{3+}}$ can be used to accurately measure nuclear spin-lattice relaxation rates of these dilute (0.01 to 2.0 at.%) nuclei. The relatively complicated relaxation dynamics of the $I = \frac{5}{2}$ system were simplified by saturating one of the three zero-field hyperfine transitions to effectively produce two-level behavior. In this way, the relaxation rates for each of the three hyperfine transitions could be determined. The temperature-dependent relaxation was shown to be due to a resonant two-phonon (Orbach) relaxation process involving the first excited crystal-field level 57 $\mathrm{cm^{-1}}$ above the ground state. The phonon absorption and emission processes couple to the Pr nuclear spins through the hyperfine interaction which admixes the spin states differently in the ground and excited crystal-field states. Theoretical estimates of the phonon-induced relaxation rates come within an order of magnitude of the experimentally observed rates. The 8.47-MHz transition showed an additional temperature-independent contribution to T_1, due to Pr–La cross relaxation.

A concentration dependent hole-filling process was observed and interpreted in terms of Pr–Pr flip flops due to homonuclear dipolar interactions. This experiment thus offers a rather direct probe of these weak interactions between dilute nuclei.

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