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Observation of the Influence of Electron-Pair Spin Flips on Nuclear Thermal Relaxation*

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We report measurements on the thermal relaxation rate of water-of-hydration protons in magnetically dilute $La_2Mg_3(NO_3)_{12}\cdot 24H_2O:Nd^{3+}$. The observed dependence of the proton relaxation rate on the angle between the applied magnetic field and the crystal symmetry axis exhibits a complicated structure which is shown to be consistent with that arising from processes in which a proton gives up its Zeeman energy to a pair of electrons, such that the Zeeman energy for the 3-spin system is conserved. These observations constitute direct evidence for the influence of electron-pair flips on proton thermal relaxation. Estimates made of the relative strength of such multiple-spin processes are shown to correspond to observed data.

I. INTRODUCTION

Since the pioneering work of Bloembergen,[1] it has been well established that the mechanism by which nuclear magnetic moments in insulating crystals achieve their thermal-equilibrium magnetization is via a thermally modulated magnetic dipole interaction with any electron paramagnetic moments present, such that nuclear Zeeman energy is transferred to the crystal lattice. Processes in which the energy transfer occurs from a nuclear spin via several electron spins collectively have only relatively recently been investigated experimentally with success,[2–4] and the importance of such multiple-spin processes in understanding nuclear thermal relaxation phenomena in weakly paramagnetic insulators is becoming more evident.

A specific example of the observation of multiple-spin processes in a crystal similar to that of the present work is that of Swanenburg and collaborators,[3] in which the Nd^{3+}-doped $La_2Mg_3(NO_3)_{12}\cdot 24H_2O$ electron-spin-resonance line-shape distortion under conditions of large dynamic proton polarization was observed to return to an undistorted line shape with the same time constant with which the dynamic proton polarization itself decayed to equilibrium.

We wish to present direct and unambiguous evidence for a 3-spin nuclear relaxation process in which a pair of electron spins mutually flip in such a way that their Zeeman-energy difference is just equal to the nuclear Zeeman-energy change. The net effect of such a process is to transfer nuclear Zeeman energy to electron Zeeman energy, which is transferred relatively rapidly to the lattice. Figure 1 illustrates such a process.

In particular, we shall consider Nd^{3+} with naturally occurring isotopic abundances in single crystals of $La_2Mg_3(NO_3)_{12}\cdot 24H_2O$, which we write as LMN:Nd. The "electrons" are those of the Nd^{3+} ion substitutionally replacing lanthanum and the "nuclei" are the protons in the waters of hydration. The crystal structure, which is axial, is well known[5]: The Nd^{3+} electronic paramagnetism in the ground state comes[6] from a Kramers doublet which lies 33 cm^{-1} below higher levels.[7] Neodymium nuclear paramagnetism arises from the odd isotopes ^{143}Nd (12.2% natural abundance) and ^{145}Nd (8.3% natural abundance), each with nuclear spin $I=\frac{7}{2}$. The even isotopes have $I=0$, and do not contribute to the hyperfine structure. We deal primarily, then, at liquid-helium temperatures, with an effective electron-spin-$\frac{1}{2}$–proton-spin-$\frac{1}{2}$ system. The electron magnetic moment as well as the odd-neodymium-isotope hyperfine coupling constants are very anisotropic. This leads to a dependence of electron energy-level spacing on the angle between the crystal symmetry axis and the external field, which is such that there are many predicted angles at which a 3-spin process with two electrons exchanging energy with a single proton will conserve Zeeman energy for the 3-spin system. It is the resonant nature of these processes at specific angles which enables us to identify them unambiguously in their effect on the angular variation of the proton thermal relaxation time T_{1p}. The anisotropy of the electron moment also enables us to identify the over-all $T_{1p}(\theta)$ with that predicted by a free spin-diffusion model.

In Sec. II we calculate angles for the resonant 3-spin process, estimate its relative strength, and calculate the angular dependence of T_{1p} for normal spin-diffusion models. After briefly describing the apparatus and experimental method in Sec. III, we describe our results for $T_{1p}(\theta)$ in Sec. IV and compare them with our predictions.

II. THEORY

The spin Hamiltonian for the ground Nd^{3+} doublet is

$$\mathcal{H}=\beta\mathbf{H}\cdot\overleftrightarrow{\mathbf{g}}\cdot\mathbf{S}+\mathbf{I}\cdot\overleftrightarrow{\mathbf{A}}\cdot\mathbf{S}, \tag{1}$$

where the effective electron spin and g tensor are **S** and **g**, respectively, the nuclear spin is **I**, the hyperfine coupling tensor is **A**, and β is the Bohr magneton. For Nd^{3+}, $S=\frac{1}{2}$ and $I=\frac{7}{2}$, and in laboratory coordinates the frequency of the allowed electron transition ($\Delta S_z=1$, $\Delta I_z=\Delta m=0$) is, to second-order perturbation theory,[8]

$$\begin{aligned} h\nu=g(\theta)\beta H+K(\theta)m \\ +\frac{B^2}{4g(\theta)\beta H}\left(\frac{A^2}{K^2(\theta)}+1\right)[I(I+1)-m^2] \\ +\left(\frac{B^2-A^2}{K(\theta)}\right)^2\frac{g_{\|}{}^2g_{\perp}{}^2\sin^2\theta\cos^2\theta}{g^4(\theta)}\frac{m^2}{2g(\theta)\beta H}, \end{aligned} \tag{2}$$

where

$$g^2(\theta)=g_{\|}{}^2\cos^2\theta+g_{\perp}{}^2\sin^2\theta$$

and

$$K^2(\theta)=\frac{A^2g_{\|}{}^2\cos^2\theta+B^2g_{\perp}{}^2\sin^2\theta}{g^2(\theta)},$$

and θ is the angle between the crystal symmetry axis and the external field. The principal values of the g tensor parallel and perpendicular to the crystal axis are $g_{\|}$ and $g_{\perp}$, respectively, and A and B are the principal values of the hyperfine coupling tensor parallel and perpendicular to the crystal axis. The numerical values of these parameters are[6] $g_{\|}=0.362\pm0.01$, $g_{\perp}=2.702\pm0.006$, ^{143}Nd $A=156\pm15$ MHz, ^{143}Nd $B=936\pm3$ MHz, ^{145}Nd $A=96\pm9$ MHz, and ^{145}Nd $B=582\pm3$ MHz. We write Eq. (2) as $h\nu=g(\theta)\beta H+\Delta E$, where ΔE is the hyperfine splitting energy. Figure 2 shows ΔE as a function of angle. Crossings on this graph at $\Delta E=0$ represent angles at which an odd-isotope neodymium can flip with an even-isotope neodymium (odd-even transition), conserving energy, while crossings at ΔE not equal to zero represent odd-odd transitions.

The effect of dipole-dipole and other interactions was not included in the perturbation calculation. Other than dipole interactions are neglected, since even in the undiluted NdMN crystal the observed linewidth can be accounted for[9] in terms of a lattice sum over magnetic dipole interactions between a given Nd^{3+} with its proton and Nd^{3+} environment. In a randomly magnetically diluted crystal with fractional dilution f, the probability relative to uniform dilution of a nearest-magnetic-neighbor cluster of x ions is approximately $(Zf)^{x-1}$ for a structure with Z possible nearest-neighbor sites. Hence for $f=10^{-2}$ and $Z=6$, the relative probability for a nearest-neighbor pair is 6×10^{-2}, a nearest-neighbor triple is 3.6×10^{-3}, and so on. The dipole energy contribution of one nearest-neighbor Nd^{3+} ion is, near $\theta=10°$, for example, $\sim$10 MHz. This is negligible compared to electronic energies, but is comparable with the proton energy of 25 MHz. Although the dipole perturbation increases with the number of nearest-neighbor magnetic ions in the cluster, the probability for such a cluster drops rapidly and their contribution to observed processes is assumed to be negligible for other than pairs. We incorporate the averaged electronic dipole-dipole perturbation as an effective frequency width for each transition approximately equal to the energy of a nearest-neighbor dipole-coupled pair.

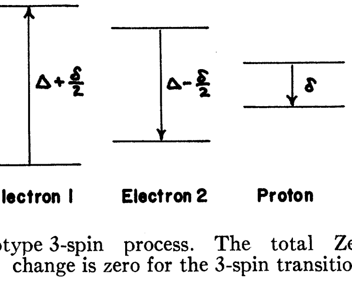

FIG. 1. Prototype 3-spin process. The total Zeeman-energy change is zero for the 3-spin transitions.

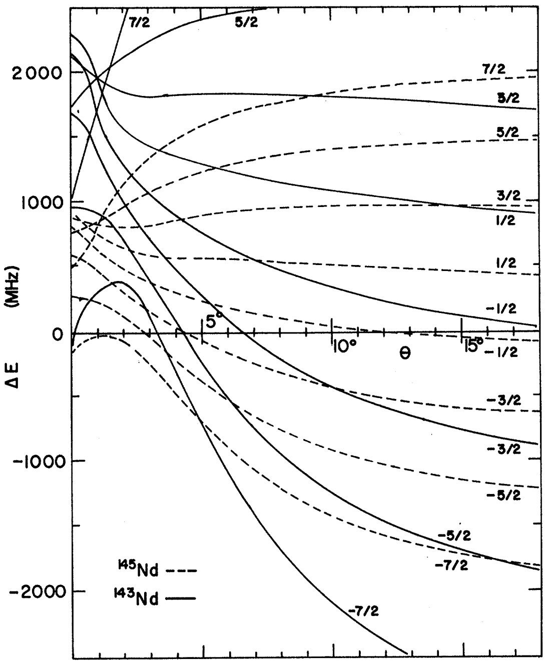

FIG. 2. Energy difference between odd-Nd-isotope-allowed electron transitions and the even-isotope transition as a function of angle between crystal symmetry axis and applied magnetic field for LMN:Nd at 6000 G. The ordinate $\Delta E=0$ represents the even-even transition.

For a given field H we calculate the angles θ for which the frequency difference for two electron-spin transitions is equal to the proton Zeeman frequency in that field. Allowing for the approximate dipolar frequency "width" discussed in the last paragraph yields many overlapping regions in angle over which the 3-spin process is energetically possible. With the exception of one at $\theta=39°$ and another at $\theta=28°$, all other 3-spin angles are for $\theta\lesssim20°$. (The results are schematically indicated on Fig. 5 below.)

In order to estimate the order of magnitude of the effectiveness of this 3-spin process in contributing to proton relaxation, we note that the dipolar Hamiltonian is bilinear in proton and electron spins. The required matrix elements will be second order in the dipolar Hamiltonian, with the lowest-order contributions from

$$\mathcal{H}'=\tfrac{3}{2}\sum_{I}\left(\frac{\sin\theta_{IS}\cos\theta_{IS}}{r_{IS}{}^3}\right)\gamma_S\gamma_I\hbar^2S_zI_{\pm}$$
$$+\tfrac{1}{4}\sum_{S'\neq S}\left(\frac{1-3\cos^2\theta_{SS'}}{r_{SS'}{}^3}\right)\gamma_S\gamma_{S'}\hbar^2S_{\pm}S_{\mp}'+\cdots,$$

where the sums are over the coordinates, relative to the electron spin S with magnetic moment $\gamma_S\hbar S$ of all the protons I with magnetic moment $\gamma_I\hbar I$ and other electrons S'. In a weak-coupling approximation using a convoluted Gaussian line-shape approach,[10] the transition rate[11] for a process in which the electron Zeeman-energy difference $E_S - E_{S'} = \hbar\omega_I$, the proton Zeeman energy, will include terms of the form

$$W_{3\text{-spin}} \sim \frac{2\pi}{\hbar^2}\left(\frac{9}{16}\sum_I \frac{\sin^2\theta_{IS}\cos^2\theta_{IS}}{r_{IS}^6}\gamma_S^2\gamma_I^2\hbar^2\frac{1}{\omega_I^2}\right) \times\left(\frac{1}{16}\sum_{S'\neq S}\frac{(1-3\cos^2\theta_{SS'})^2}{r_{SS'}^6}\gamma_S^2\gamma_{S'}^2\hbar^4\right) \times[(2\pi)^{1/2}\sqrt{2}\langle\Delta\omega^2\rangle^{1/2}]^{-1}.$$

In this expression $\langle\Delta\omega^2\rangle$ is the dipolar second moment of the electron line arising from the contributions of other electrons. We assume that the energy transfer does not alter the relative populations of the rapidly thermally relaxing electrons. Both sums are of standard form. The first appears in the theory of nuclear relaxation via the thermally modulated dipole field of single electrons.[12] After performing a spherical average for the electron-proton angular coordinates, we can write it in terms of the proton-electron separation r and the electron-spin-lattice relaxation rate T_{1e}, using the expression

$$\frac{C_1T_{1e}}{r^6} = \tfrac{9}{4}\gamma_S^2\gamma_I^2\hbar^2\frac{\sin^2\theta_{IS}\cos^2\theta_{IS}}{r_{IS}^6}\frac{1}{\omega_I^2}. \tag{3}$$

The second term in parentheses for $W_{3\text{-spin}}$ has the form of the electron second-moment contribution of all the spins S',[12]

$$\hbar^2\langle\Delta\omega^2\rangle = \sum_{S'}\tfrac{9}{16}\gamma_S^2\gamma_{S'}^2\hbar^4\frac{(1-3\cos^2\theta_{SS'})^2}{r_{SS'}^6}. \tag{4}$$

Each of these expressions assumes $S=S'=I=\frac{1}{2}$. As an approximation to $W_{3\text{-spin}}$, in terms of these substitutions,

$$W_{3\text{-spin}} \sim 5\times10^{-2}\langle\Delta\omega^2\rangle^{1/2}C_1T_{1e}/r^6.$$

The corresponding relaxation time for the protons (since the *electron* thermal equilibrium is not appreciably affected by this process) is

$$(T_{3\text{-spin}})^{-1} \sim 10^{-1}\langle\Delta\omega^2\rangle^{1/2}T_{1e}C_1r^{-6} = C_2r^{-6}. \tag{5}$$

For small fractional paramagnetic-ion concentration f, $C_2 \propto f$. This result is to be compared with the relaxation time for protons "seeing" only single electrons, which involves the same factor[12] C_1:

$$(T_{2\text{-spin}})^{-1} = C_1r^{-6}. \tag{6}$$

Using values appropriate to our sample for an angle $\theta\sim10°$ between crystal axis and applied field, we have $\langle\Delta\nu^2\rangle^{1/2} \sim 9\times10^4$ sec^{-1},[13] $T_{1e}\sim0.2$ sec,[14] and $C_2\sim10^4C_1$.

To evaluate the macroscopic proton relaxation time, we note that outside a small region near the electrons where Eqs. (5) and (6) may contribute, the proton magnetization diffuses freely. Solution of the diffusion equation[12,15] for the proton magnetization yields the proton-spin-lattice relaxation time T_{1p}:

$$(T_{1p})^{-1} \simeq 4\pi N_e(C/D)^{1/4}D, \tag{7}$$

where N_e is the volume density of paramagnetic ions (which is proportional to f), C is either C_1 or C_2 as appropriate, and D is the diffusion constant defined as Wa^2, with a the distance between nearest-neighbor protons and W their probability for a flip-flop transition. The length parameter $\beta=(C/D)^{1/4}$ is the crossover distance from the electron for the transition from direct to diffusion relaxation for the proton. At all angles where the 3-spin process is not expected to contribute,

$$\beta_{2\text{-spin}} \simeq [\tfrac{3}{10}(H_e/H_0)^2(1/T_{1e}W)]^{1/4}a, \tag{8}$$

where H_e is the local field of the electron at a distance a from the electron and H_0 is the applied magnetic field. At those angles where the resonant 3-spin process occurs, we get the added contribution

$$\beta_{3\text{-spin}} \simeq \beta_{2\text{-spin}}(10^{-1}\langle\Delta\omega^2\rangle^{1/2}T_{1e})^{1/4}. \tag{9}$$

The 3-spin process should shorten T_{1p} by approximately an order of magnitude at $\theta\sim10°$.

The contribution of multiple-spin processes other than the resonant 3-spin process can be treated in an analogous manner in which the energy mismatch is transferred to the collective energy of the dipolar-coupled electrons (electron spin-spin reservoir) and thence to the lattice. The *resonant* 3-spin process itself requires the presence of electron dipolar coupling but does not store energy in the spin-spin reservoir. Even the nonresonant 3-spin process for the case $T_{1e} \ll T_{1p}$ as here would not involve energy storage in the electron spin-spin reservoir in any meaningful sense.

We now summarize the expected angular variation in the absence of the 3-spin process. Such processes have been investigated intensively.[16–18] Into the theory enter three characteristic lengths: the paramagnetic-ion proximity sphere radius R defined by $(4\pi/3)R^3N_e=1$, the crossover distance β, and the distance b from the paramagnetic ion at which energy-conserving mutual spin flips by the protons are inhibited by the electron local dipolar field. This is often called a "diffusion-barrier" radius. As in the treatment of Lowe and Tse,[18] we can note two cases. The first is the retarded-diffusion case in which $R > b \gg \beta$:

$$1/T_{1p} \cong N_e(1/b^3)(\gamma_s\hbar/H_0)^2(1/T_e). \tag{10}$$

This form can also be obtained by a suitably spatially averaged direct relaxation by all protons with the paramagnetic ion.[19,20] The second case is that of free diffusion in which $R \gg \beta \gg b$:

$$1/T_{1p} \cong 6N_eD^{3/4}(\gamma_s\hbar/H_0)^{1/2}(1/T_{1e}^{1/4}), \tag{11}$$

where D is the diffusion constant and is typically 10^{-12} cm^2 sec^{-1}.[12] At liquid-helium temperatures for the crystals used in this work an order-of-magnitude estimate for b yields $2a$ to $10a$, where a is the mean interproton spacing, while $\beta \lesssim a$, and $b > \beta$ always. It would appear that we deal here with the retarded-diffusion case.

The electron relaxation time T_{1e} appearing in this equation is relatively well understood[21,22] for LMN:Nd. It arises from a direct process, phonon bottlenecked at higher electron resonance frequencies, and an Orbach process which does not contribute for temperatures under 2°K. For protons relaxing via the electrons we do not usually observe the effects of the bottleneck and hence T_{1e} here refers to the true, direct electron relaxation time.

We can now obtain the angular dependence of T_{1p} in the absence of the 3-spin process from $\gamma_e(\theta)$ or $g(\theta)$ and $T_{1e}(\theta)$. (See Fig. 6 below.) In order to estimate qualitatively, we note that at constant magnetic field, $[T_{1e}(\theta)]^{-1}$ for LMN:Nd varies somewhat more rapidly than $g^2(\theta)$ with angle, so that for retarded diffusion at constant field $T_{1p}(\theta)\sim T_{1e}(\theta)g^{-2}(\theta)\sim g^{-4}(\theta)$, while for free diffusion $T_{1p}(\theta)\sim[T_{1e}(\theta)]^{1/4}g^{-1/2}(\theta)\sim g^{-1}(\theta)$. The diffusion constant D would be expected to be relatively isotropic.

III. APPARATUS AND TECHNIQUE

Samples are single crystals of LMN with up to a few atomic percent Nd^{3+} substitutionally replacing the La^{3+}. The crystals used are free of visible imperfections and typically weigh 50–75 mg. They are grown from saturated solution in a desiccator placed in an ice bath. The atomic percent quoted is that of the growing solution, and in each case the crystals grown represented a small fraction of the total amount of solid material in the solution. The chemicals used were Lindsay code 549 rare earths and Mallinckrodt Analytical Reagent Grade $Mg(NO_3)_2\cdot 6H_2O$.

These crystals are mounted in a Kel-F holder placed in a TE_{013} cylindrical microwave cavity as in Fig. 3. A flat, spiral rf coil of 0.6-μH inductance mounted on another Kel-F form is placed in the middle of the cavity in the plane normal to the cylinder axis. Electron and nuclear resonance can be observed simultaneously. The electron resonance of the Nd^{3+} ion is excited with a 17.5-GHz reflection spectrometer of conventional design. Nuclear resonance of the protons is observed with a Robinson self-limited oscillator which operates stably with rf levels of a few millivolts on the coil. The sample crystal symmetry axis lies in the horizontal plane so that rotation of the electromagnet about the cavity will vary the angle θ between ±90°.

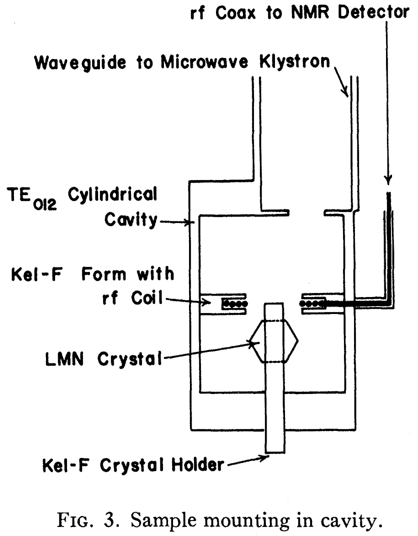

FIG. 3. Sample mounting in cavity.

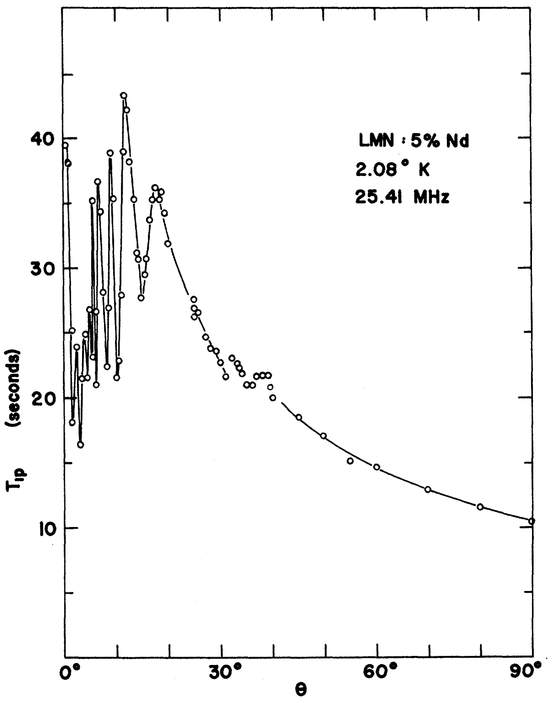

FIG. 4. Angular dependence of T_{1p} for 5% Nd in LMN at 2.08°K and a proton resonance frequency 25.41 MHz. Portions of this are also shown in Fig. 5.

The cavity is placed in a liquid-helium Dewar with liquid helium in contact with the sample in the cavity. A mechanical pump, used with a manostat, maintains the helium vapor pressure to less than a millimeter of mercury variation over a 10-h experimental run.

The experimental procedure consists of exciting strongly one of the even-even Nd^{3+}-proton-forbidden transitions so as to dynamically polarize the protons via the solid effect.[12,19] The microwave power to the sample is then turned off with a waveguide switch, the magnet rotated to the desired angle, and the resulting decay of the nonequilibrium proton magnetization absorption derivative recorded after phase-sensitive detection on a strip-chart recorder. The measured amplitude of this proton resonance signal is plotted as a function of time on a semilog graph. System sensitivity and stability are such that proton decay times can be typically measured to an uncertainty of 2–4%. After repolarizing the protons, the same procedure can be repeated to obtain

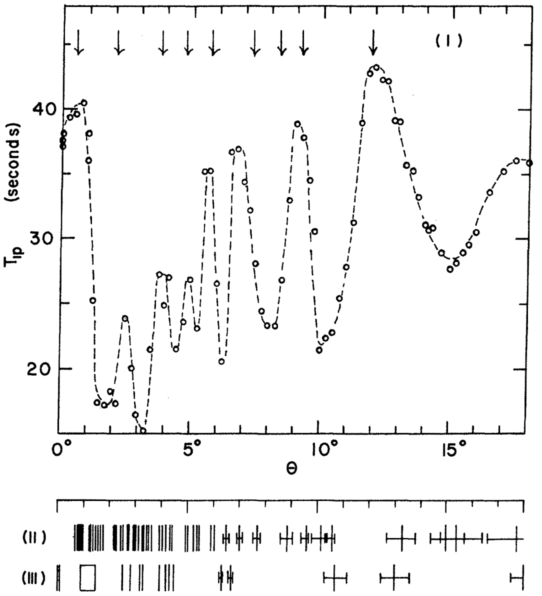

FIG. 5. Comparison of $T_{1p}(\theta)$ with predicted angles for a resonant 3-spin process. The dotted line connecting data points is intended only to guide the eye in following the angular variation. The experimental uncertainty in data points is ±1–2%. (111) Electron even-odd pair+proton transitions. (11) Electron odd-odd pair+proton transitions. (1) angles at which the resonant 3-spin process is expected not to have a large effect. This should correspond to maxima in $T_{1p}(\theta)$. The horizontal "error bars" in (11) and (111) approximate the perturbation of the Nd^{3+} dipolar interaction arising from nearest-neighbor Nd^3 pairs.

the angular dependence of the proton decay rate at fixed magnetic field.

IV. RESULTS

The proton signal amplitude is characterized at all angles by a single exponential decay time T_{1p} measured over an interval of four to five times T_{1p}. This exponential has the same value to within experimental error for the decay of proton polarization from either positively or negatively polarized conditions and does not depend on which portion of the proton absorption derivative is being monitored.

An angular structure, rich in detail, is observed as in Fig. 4 for nominal natural Nd^{3+} concentrations of 5, 2, and 1%. Although only the 5% crystals have been examined at angular intervals smaller than 1°, all crystals in the Nd^{3+} concentration range above exhibit the same over-all pattern. The structure is absent in two control crystals containing 1% ^{142}Nd in LMN. For natural Nd^{3+} concentrations less than 1% corresponding to $T_{1p} \gtrsim 10^3$ sec the proton relaxation is dominated by the effects of trace Pr^{3+} and Ce^{3+} impurities. For Nd^{3+} concentrations $>5\%$ corresponding to $T_{1p} \lesssim 10$ sec we are unable to measure the relaxation time by the method used here. The detailed comparison with the predicted angular dependence for the same crystal as in Fig. 4 is shown in Fig. 5. In view of the large number of possibilities in angle for the 3-spin process shown at the bottom of the figure in (11) and (111) we also show in (1) at the top of the figure those angles fewer in number at which the resonant 3-spin process is expected *not to occur*. These should then correspond to angles at which $T_{1p}(\theta)$ is a maximum. Except for the prediction of a maximum at $\theta = 8.3°$ which must contribute to the one observed at $\theta = 8.9°$ and the prediction at $\theta = 7.3°$ compared to the observed maximum at 6.8°, the agreement between experiment and prediction is good. The dotted curve only serves to guide the eye in the following the angular variation. However, for data taken $-10° < \theta < +10°$ in $\frac{1}{4}°$ increments, this dotted curve is symmetric about $\theta = 0°$ when drawn through *all* experimental data. Although the $\theta = 0°$ angle determined by the symmetry in $T_{1p}(\theta)$ is ±0.25°, the uncertainty in relative angle measurements is less than ±0.1°. The striking agreement in maxima for $T_{1p}(\theta)$ with those predicted at angles where the resonant 3-spin process should not occur must, in view of the complexity of the spectrum, be considered in part fortuitous; however, no departures from a monotonic angular variation for $T_{1p}(\theta)$ measured at constant magnetic field are observed at any angles other than in the vicinity of those predicted by the 3-spin resonant process. No evidence for cross-relaxation effects to Pr^{3+} or Ce^{3+} are observed in this crystal.

The angular dependence (see Fig. 6) agrees fairly well

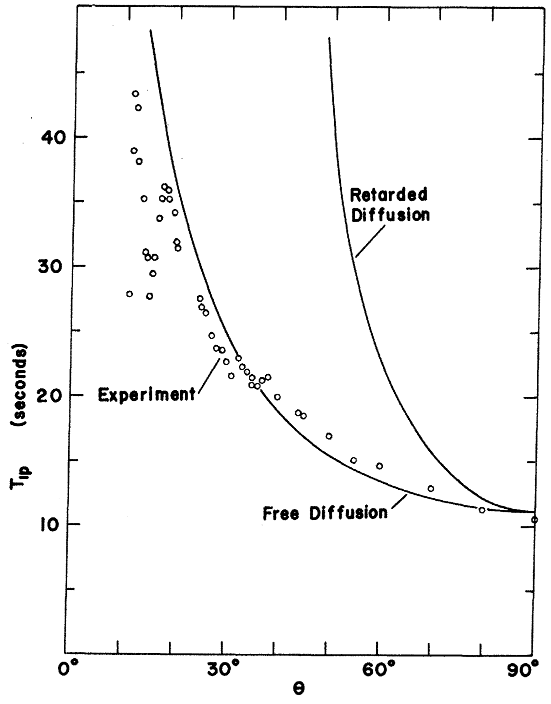

FIG. 6. Comparison of $T_{1p}(\theta)$ with the predictions of free- and retarded-diffusion models. Both curves are arbitrarily fitted to the same magnitude at $\theta = 90°$.

with that predicted in Eq. (11), where $T_{1e}(\theta)$ at constant field $[T_{1e}^{(H)}(\theta)]$ is obtained from the experimental curve[21] of $T_{1e}(\theta)$ at constant frequency $[T_{1e}^{(\nu)}(\theta)]$. This assumes a direct process $[T_{1e}(\theta)]^{-1}=g^2(\theta)H^4Tf(\theta)$ in which $f(\theta)$ is independent of the magnetic field H and the electron magnetic moment g, and T is the temperature.

The nominal paramagnetic-ion concentration dependence of T_{1p} is N_e^{-2} over the range 10–1%. The measurement uncertainty in this quadratic dependence is itself ±10%.

V. CONCLUSIONS

The angular dependence of T_{1p} for a few percent Nd in LMN is described quantitatively with respect to relative angular variation and qualitatively with respect to relative strength by a model in which proton Zeeman energy is transferred resonantly via an electron pair to the lattice at those angles allowing Zeeman-energy conservation for the 3-spin system.

An influence of electron spin-spin interactions is also indicated by the over-all angular variation of $T_{1p}(\theta)$. The difference in predicted angular variation of Eqs. (10) and (11) is sufficiently large that one can confidently identify $T_{1p}(\theta)$ with that predicted by a free-diffusion model. These results imply that the diffusion-barrier radius is effectively such that $b\lesssim\beta$ and not as one estimates, $b>\beta$. A possible physical mechanism accomplishing this would be the presence of dipolar-coupled electrons yielding a resonant 4-spin process in which proton flip-flop energy mismatch plus electron flip-flop energy mismatch equals zero. The required energy transfer would now be of the order of the energy equivalent of the proton linewidth rather than its Zeeman energy. The suggestion that a form of cross relaxation between proton and electron pairs would transport magnetization across the diffusion-barrier region has been made[23] frequently. The net result here is to force $b\lesssim\beta$. The quadratic dependence of T_{1p} on nominal electron paramagnetic concentration is suggestive of a contribution of electron-pair processes at all angles. However, since we have not measured independently the actual concentration in these crystals, we simply point out the consistency. The experiments reported in this work constitute an experimental observation of the influence of electron-pair spin flips on proton thermal relaxation both in resonant 3-spin processes and in modifying the influence of the diffusion barrier.

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[1] N. Bloembergen, Physica **15**, 386 (1949).

[2] V. A. Atsarkin, A. E. Mefed, and M. I. Rodak, Zh. Eksperim. i Teor. Fiz. **55**, 1671 (1968) [Soviet Phys. JETP **28**, 877 (1969)].

[3] W. Th. Wenckeback, G. M. van den Heuvel, H. Hoogstraate, T. J. B. Swanenburg, and N. J. Poulis, Phys. Rev. Letters **22**, 581 (1969).

[4] Brother Eric Vogel, F.S.C., and O. S. Leifson, Bull. Am. Phys. Soc. **14**, 1183 (1969).

[5] A. Zalkin, J. D. Forrester, and D. H. Templeton, J. Chem. Phys. **39**, 2881 (1963).

[6] A. H. Cooke and H. J. Duffus, Proc. Roy. Soc. (London) **A229**, 407 (1955).

[7] G. H. Dieke and L. Heroux, Phys. Rev. **103**, 1227 (1956).

[8] B. Bleaney, Phil. Mag. **42**, 441 (1951).

[9] N. Ford, Ph.D. thesis, University of California, Berkeley, 1965 (unpublished).

[10] P. S. Pershan, Phys. Rev. **117**, 109 (1960).

[11] W. B. Grant, R. L. Ballard, and L. F. Mollenauer, University of California, Berkeley Technical Report No. UCB-34P20-T-2, 1968 (unpublished).

[12] A. Abragam, *The Principles of Nuclear Magnetism* (Oxford U. P., London, 1961).

[13] This is calculated using the lattice sums of Ref. 9.

[14] This is calculated from the data of Ref. 21.

[15] Reviews of the role of diffusion in nuclear magnetic relaxation appear in G. R. Khutsishvili, Usp. Fiz. Nauk **87**, 211 (1965); **96**, 441 (1968) [Soviet Phys. Usp. **8**, 743 (1966); **11**, 802 (1969)].

[16] H. E. Rorschach, Physica **30**, 38 (1964).

[17] E. Fukushima and E. A. Uehling, Phys. Rev. **173**, 366 (1968).

[18] I. J. Lowe and D. Tse, Phys. Rev. **166**, 279 (1968).

[19] C. D. Jeffries, *Dynamic Nuclear Orientation* (Interscience, New York, 1963).

[20] C. D. Jeffries, University of California, Berkeley Technical Report No. UCB-34P20-T-1, 1966 (unpublished).

[21] G. H. Larson and C. D. Jeffries, Phys. Rev. **145**, 311 (1966).

[22] P. L. Scott and C. D. Jeffries, Phys. Rev. **127**, 32 (1962).

[23] See, for example, Ref. 20.