ψ_2 for a change of Z_2 from 79 to 49. The expected change of 5% is less than the experimental error.

The change in critical angle as a function of Z_1, is investigated by comparing the results for H^+, D^+, and He^+ ions. When H^+ ions are used instead of D^+ ions, the mass is decreased by a factor of 2, while Z_1 is constant. A comparison between D^+ ions and H^+ ions is made by using the same foil and the same incident energy E. A similar comparison is made between D^+ ions and He^+ ions. The use of these ions gives a change in both Z_1 and the mass M, of a factor of 2. The results of these measurements are best presented in Table II. An approximate correction is made for the different energy losses experienced by the three different particles, so that the critical angles are compared at about the same energy $\bar{E}$. Table II shows that there is no difference between $\sigma_\theta(H^+)$ and $\sigma_\theta(D^+)$. It is also seen that $\sigma_\theta(He^+)$ is larger than $\sigma_\theta(D^+)$ by a factor of 1.13 ± 0.04, which is significantly larger than 1. The theoretical factor expected from (8) is 1.17, so the experimental result agrees with the theoretical prediction.

CONCLUSION

The critical angles for channeling of light ions at low energies are in good agreement with the approximate expression for ψ_2 calculated by Lindhard if the arbitrary constant C in Lindhard's expression is assigned the value of 2.15.

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Proton Spin-Lattice Relaxation in $(Nd, La)_2Mg_3(NO_3)_{12}\cdot 24H_2O$ in High Fields and Low Temperatures*

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The dependence of the proton relaxation time $T_{1\rho}$ on field H and temperature T in a crystal of $(Nd, La)_2Mg_3(NO_3)_{12}\cdot 24H_2O$ grown from a solution containing 1% Nd is measured over the ranges $10 \leqq H \leqq 50$ kOe and $0.5 \leqq T \leqq 3$°K using a He^3 cryostat in a superconducting solenoid. Over these wide ranges the relaxation data for $c \perp \mathbf{H}$ are well fitted by the expression

$$T_{1\rho}^{-1} = 2.1\times10^{-16}H^3 \coth(2.7\beta H/2kT)\ \mathrm{sech}^2(2.7\beta H/2kT) + 9.9\times10^{-8}H \coth(4.4\beta H/2kT)\ \mathrm{sech}^2(4.4\beta H/2kT)\ \mathrm{sec}^{-1},$$

where β = Bohr magneton, k = Boltzmann's constant, and H is in Oe. The first term is due to Nd^{3+}, the second to a small impurity of a non-Kramers ion, possibly Fe^{2+}. Both are in agreement with predictions from a shell-of-influence model, including diffusion effects. At 19.5 kOe and 0.5°K, we find $T_{1\rho}=40$ h, showing that dynamically induced proton polarization in this crystal can be maintained for very long times. In particular, the data display well the sech^2 factor, leading to exponentially increasing proton relaxation times at high fields and low temperatures, $T_{1\rho}(T) \propto \exp(g\beta H/kT)$, due to the depopulation of the upper Nd^{3+} Zeeman level.

I. INTRODUCTION

In an earlier work,[1] referred to as S-J, dynamic proton polarization and relaxation were studied in crystals of diamagnetic lanthanum magnesium nitrate containing a small fraction of paramagnetic Nd^{3+} ions, denoted by Nd:LaMN. Large proton polarizations (70%) are obtained with this crystal, and it is now being used in many polarized proton targets.[2] The object of this paper is to extend the relaxation studies to higher fields ($H\approx50$ kOe) and lower temperatures ($T\approx0.5$°K) in order to test further the theory of nuclear relaxation as well as to provide data for possible operation of targets at these fields and temperatures. A brief discussion of dynamic polarization is included.

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[1] T. J. Schmugge and C. D. Jeffries, Phys. Rev. **138**, A1785 (1965); see also Phys. Rev. Letters **9**, 268 (1962).

[2] O. Chamberlain, C. D. Jeffries, C. H. Schultz, G. Shapiro, and L. Van Rossum, Phys. Letters **7**, 293 (1963); M. Borghini, M. Odehnal, P. Roubeau, C. Ryter, G. Coignet, L. Dick, and L. di Lella, in *Proceedings of the International Conference on High-Energy Physics, Dubna, 1964* (Atomizdat, Moscow, 1965). For a recent survey of targets, see *Proceedings of the International Conference on Polarized Targets and Ion Sources, Saclay, 1966* (La Documentation Francois, Paris, 1967).

II. REVIEW OF THEORY

A. Relaxation

The magnetic interaction of nuclear spins with a few paramagnetic ions usually provides the mechanism for nuclear spin-lattice relaxation in crystals. This subject has had extensive theoretical treatment,[3-6] none of which seems exactly appropriate for the present case. We prefer to use a phenomenological shell-of-influence model, introduced by S-J, but later modified to include diffusion effects.[7-9] For a fuller account of this work we refer to Refs. 8 and 9. To fix ideas we specifically consider the relaxation of protons in Nd:LaMN at low temperatures, even though our discussion is more general than this. We imagine that all the proton spins ($I=\frac{1}{2}$) in the crystal may be grouped into shells about the Nd ions ($S=\frac{1}{2}$), a typical shell being given by $r_1 \leqq r \leqq r_2$, where $r_1 \approx 4.4$ Å is the nearest La-H distance in LaMN from x-ray structure data, and $r_2=(4\pi N/3)^{-1/3}$ is half the average distance between Nd ions, of order 30 Å, where N is the number of Nd ions per cm^3. For purposes of analysis the protons in a shell are roughly divided into two groups: (1) An inner shell $r_1 \leqq r \leqq d$ containing a number n' of near protons, where d is the diffusion barrier within which mutual proton spin flips are inhibited by the local magnetic field of the Nd ion ($d \sim 10$ Å, typically). The near protons interact more strongly with the central Nd ion than with each other, and are relaxed directly by dipolar coupling with the ion at an average rate $T_{1n'}^{-1}$. (2) An outer shell $d \leqq r \leqq r_2$ containing a large number n of "distant" protons which rapidly come into internal equilibrium in a time t_d by means of mutual spin flips with neighbor protons, i.e., by diffusion of proton polarization. The diffusion time is of order $t_d \sim (r_2-d)^2/D$, where $D \approx 10^{-12}$ cm^2 sec^{-1} [1,3] is the diffusion constant for protons in LaMN, leading to $t_d \sim 0.1$ sec. The distant protons are not directly coupled to the ion but rather to the near protons at the interface $r \approx d$, with an effective cross relaxation rate T_{12}^{-1}, which may reasonably be assumed to be much less than t_d^{-1}, but much greater than $T_{1n'}^{-1}$. The coupled relaxation rate equations for the polarizations p' and p of the near and distant protons, respectively, are

$$dp'/dt = -(p'-p_0)/T_{1n'} - (p'-p)/T_{12}, \tag{1}$$

$$\frac{dp}{dt} = -\frac{p-p_0}{T_{1nl}} - \frac{n'}{n}\frac{p-p'}{T_{12}}, \tag{2}$$

where $p_0 = g_n\beta H/2kT$ is the thermal equilibrium polarization and we have assumed a leakage relaxation rate T_{1nl}^{-1} through extraneous impurities, and $n \gg n'$. Equations (1) and (2) are coupled linear first-order equations; the homogeneous solutions for $p(t)$ and for $p'(t)$ are each of the form const.$\times\exp(-t/\tau_s)+$const$\times\exp(-t/\tau_f)$. Under the approximations $n \gg n'$ and $T_{12} \ll T_{1nl}$, the two time constants are found to be

$$\tau_s^{-1} \approx T_{1nl}^{-1} + (n'/n)(T_{12}+T_{1n'})^{-1}, \tag{3}$$

$$\tau_f^{-1} \approx T_{12}^{-1} + T_{1n'}^{-1}. \tag{4}$$

It can be shown that the principal change in p occurs with the slow time constant τ_s, which we identify as the relaxation time of the distant protons. Actually since $n \gg n'$ and furthermore, because of the local field many of the near protons do not contribute to the proton nuclear magnetic resonance (NMR) signal, it is clear that the distant protons give the major contribution to the intensity of the observed NMR signal. If we further neglect T_{1nl}^{-1} and take $T_{12} \ll T_{1n'}$ we obtain

$$\tau_s^{-1} \longrightarrow (n'/n)\,T_{1n'}^{-1} = T_{1p}^{-1} \tag{5}$$

as the proton relaxation rate expected to be observed for the whole sample. This model thus predicts an essentially unique relaxation rate given by the average near-proton relaxation rate reduced by the ratio of heat capacities $(n'/n) \approx (d^3/r_2^3)$.

The average near-proton relaxation rate may be calculated as in S-J and, in more detail in Refs. 8 and 9, to find, for the crystal c axis perpendicular to H,

$$\frac{1}{T_{1n'}} = \frac{3}{10}\left(\frac{g_\perp\beta}{H}\right)^2 \left\langle \frac{1}{r^6} \right\rangle_{n'} \frac{\mathrm{sech}^2(g_\perp\beta H/2kT)}{T_{1e}}, \tag{6}$$

where $\langle r^{-6}\rangle_{n'} = r_1^{-3}d^{-3}$ is the average over the near shell, and T_{1e}^{-1} is the spin-lattice relaxation rate of the paramagnetic ion. For a general orientation $\theta = \angle c, H$ of the crystal McColl[10] has shown that Eq. (6) may be generalized by replacing $g_\perp^2$ by a new factor g_d^2 defined by

$$[3g_d^2/10] \equiv \tfrac{3}{10}g^2 + \tfrac{7}{20}\sin^2\theta\cos^2\theta(g_\perp^2 - g_{||}^2/g)^2, \tag{7}$$

where $g^2 = g_{||}^2\cos^2\theta + g_\perp^2\sin^2\theta$, and $g_{||}$ and $g_\perp$ are the principal g factors of the ion. From Eqs. (5) and (7) we obtain finally

$$T_{1p}^{-1} = \tfrac{3}{10}(g_d\beta/H)^2(r_1^3r_2^3)^{-1}T_{1e}^{-1}\,\mathrm{sech}^2\chi \equiv \tilde{\sigma}\,\mathrm{sech}^2\chi/T_{1e}, \tag{8a}$$

$$\chi \equiv g\beta H/2kT = h\nu_e/2kT, \tag{8b}$$

for the observable proton relaxation rate. This is identical to the earlier result Eq. (14) of S-J, showing that this model is insensitive to the exact value of the diffusion barrier d provided $r_1^3 \ll d^3 \ll r_2^3$. It also shows that although diffusion is important and leads to a

[3] N. Bloembergen, Physica **15**, 386 (1949).
[4] P. G. deGennes, J. Phys. Chem. Solids **7**, 345 (1958); G. R. Khutsishvili, Zh. Eksperim. i Teor. Fiz. **42**, 1311 (1962) [English transl.: Soviet Phys.—JETP, **15**, 909 (1962)].
[5] W. E. Blumberg, Phys. Rev. **119**, 79 (1960).
[6] H. E. Rorschach, Physica **30**, 38 (1964).
[7] C. D. Jeffries, Proc. Phys. Soc. (London) **88**, 257 (1966).
[8] T. E. Gunter, thesis, University of California, Berkeley, 1966 (unpublished).
[9] C. D. Jeffries, Technical Report No. UCB-34P20-T-1, Department of Physics, University of California, 1966 (unpublished).
[10] J. R. McColl, thesis, University of California, Berkeley, 1967 (unpublished).

unique observed relaxation rate, it is too rapid to enter explicitly into the observed rate, which is limited rather by the direct relaxation of the near protons.

The factor $\mathrm{sech}^2\chi = 1-\tanh^2\chi = 1-P_0^2$ in Eq. (8a) is predicted by the rate equations of S-J and arises physically in the following way: For $\chi \gg 1$, this factor is proportional to $\exp(-g\beta H/kT)$, which is the probability that the paramagnetic ion is in its upper $M_s=+\frac{1}{2}$ Zeeman state. The nuclear relaxation is proportional to the probability of a $M_s=\frac{1}{2}\rightarrow-\frac{1}{2}$, $M_I=-\frac{1}{2}\rightarrow+\frac{1}{2}$ transition, which is just proportional to the above factor. In another view of the nuclear relaxation, we make an analogy to the Orbach[11] relaxation of a paramagnetic ion from $|b\rangle$ to $|a\rangle$ through an excited state $|c\rangle$ at energy Δ; this rate is just proportional to $\exp(-\Delta/kT)$, to be compared to $\exp(-g\beta H/kT)$ in the nuclear case. The over-all consequence of this $\mathrm{sech}^2\chi$ factor is that nuclear relaxation times become exponentially longer at high fields and low temperatures, with important consequences for polarized target technology. This factor was first observed for proton relaxation in Nd:LaMN,[12,1] and has also been observed for proton relaxation in LaMN due to Pr^{3+},[1] Dy^{3+},[13] and possibly Fe^{2+}, as discussed in Sec. IV. This $\mathrm{sech}^2\chi$ factor is also derivable from correlation time relaxation theory.[6]

We note that Eq. (8a) is not the most general expression for nuclear relaxation, but is particularly applicable to dilute paramagnetic crystals such as Nd:LaMN in the ranges of high fields and low temperatures considered in this paper. More specifically the validity conditions are $(T_{1e}\omega)^2 \gg 1$, $T_{1e} \gg T_2$, and $d \gg b$, where ω is the Larmor frequency, T_2 is the inverse nuclear-resonance linewidth, and b is the scattering length introduced by Khutsishvili,[4] typically ~ 1 Å in the cases considered here. All of these conditions are met in the present case of Nd:LaMN. We do not expect the prediction of free diffusion theory,[4] $T_{1p}^{-1} = 4\pi NbD$, to be valid, since $(d/b)\sim 10$. Blumberg[5] has given an expression sometimes called the "rapid diffusion limit", similar to Eq. (8a) but with r_1 replaced by the diffusion barrier d. This yields smaller rates by an order of magnitude and is not in agreement with our data.

In Nd:LaMN, the Nd spin-lattice relaxation rate is observed to be[14] at $c \perp H$

$$T_{1e}^{-1} = 3\times 10^{-18} H^5 \coth(g_\perp \beta H/2kT) + 6\times 10^9 \times \exp(-47/T) + CT^9 \ \mathrm{sec}^{-1}, \quad (9)$$

where H is in Oe, the first term being the direct process, the second the Orbach process. The third term, the Raman process, is found to be negligible in Nd:LaMN. In S-J detailed proton relaxation rate measurements in Nd:LaMN over the ranges $1.3 \leqq T \leqq 4.2$°K and $1 \leqq H \leqq 20$ kOe gave good agreement with Eq. (8a), using Eq. (9) for T_{1e}^{-1}; evidence was found for the $\mathrm{sech}^2\chi$ factor. In this paper we extend the measurements to the range $0.5 \leqq T \leqq 3$°K and $10 \leqq H \leqq 50$ kOe, where the $\mathrm{sech}^2\chi$ factor is very well displayed. Proton relaxation[15] in (Yb, Y) $(C_2H_5SO_4)_3 \cdot 9H_2O$ is also in agreement with Eq. (8a).

It should be noted that Eq. (8a) and the above discussion also applies to proton relaxation via paramagnetic impurities other than Nd, if one uses the appropriate values of g, $T_{1e}(H, T)$ and r_2 in Eq. (8a). In this connection we remark that the direct process $AH^5 \coth\chi$ in Eq. (9) is appropriate for a Kramers ion such as Nd^{3+}; for a non-Kramers ion (one with an even number of electrons), the appropriate form[11,14] is $A'H^3 \coth\chi$. Likewise the Raman process takes the form $C'T^7$.

At low temperatures and high fields, only the direct process contributes significantly to the paramagnetic ion relaxation rate T_{1e}^{-1}. We then expect the proton relaxation rate $T_{1p}^{-1}(H, T)$ to take the form for Kramers doublets, e.g., Nd^{3+},

$$T_{1p}^{-1}|_{KD} = KH^3 \coth\chi \ \mathrm{sech}^2\chi. \quad (10a)$$

For non-Kramers ions the expected form is

$$T_{1p}^{-1}|_{NK} = K'H \coth\chi' \ \mathrm{sech}^2\chi'. \quad (10b)$$

B. Dynamic Polarization

The discussion in part A can easily be extended to include the effects of transitions induced by a microwave field $2H_1$ of the types $W_1(M_S, M_I \rightarrow M_S+1, M_I)$ at frequency ν_e, $W_2(M_S, M_I \rightarrow M_S+1, M_I-1)$ at $\nu_e+\nu_n$ and $W_3(M_S, M_I \rightarrow M_S+1, M_I+1)$ at $\nu_e-\nu_n$, assuming these transitions are well resolved. Saturation of the forbidden transitions W_2 and W_3 dynamically polarizes the nuclei. For the over-all rate equations for the average polarization p', p, and P of the near proton, distant protons, and paramagnetic ions, respectively, each of relative abundance n', n, and N, we find[8,9,16]

$$\frac{dp'}{dt} = -\frac{p'-p_0}{T_{1n'}} - \frac{p'-p}{T_{12}} - \bar{W}_2(p'-P) - \bar{W}_3(p'+P), \quad (11)$$

$$\frac{dp}{dt} = -\frac{p-p_0}{T_{1n}} - \frac{n'}{n}\frac{p-p'}{T_{12}} \quad (12)$$

$$\frac{dP}{dt} = -\frac{P-P_0}{T_{1e}} - \bar{W}_2(P-p')\frac{n'}{N} - \bar{W}_3(P+p')\frac{n'}{N} - 2W_1P, \quad (13)$$

[11] R. Orbach, Proc. Roy. Soc. (London) **A264**, 456 (1961).
[12] C. D. Jeffries, Proc. Roy. Soc. (London) **A283**, 471 (1965).
[13] M. Odehnal, Compt. Rend. **264B**, 334 (1967).
[14] P. L. Scott and C. D. Jeffries, Phys. Rev. **127**, 32 (1962); R. H. Ruby, A. Benoit, and C. D. Jeffries, *ibid.* **127**, 51 (1962); J. M. Baker and N. Ford, *ibid.* **136**, A1692 (1964).
[15] K. H. Langley and C. D. Jeffries, Phys. Rev. **152**, 358 (1966).
[16] Note that the present notation differs from Ref. 9 in that $p' \rightarrow p$, $n' \rightarrow n$.

where

$$W_1=\tfrac{1}{2}(\gamma_e H_1)^2 T_{2e}\times\delta_{\nu,\nu_e}, \quad (14)$$

$$\bar{W}_2=\bar{\sigma}'\,|\,W_1\,|\times\delta_{\nu,\nu_e+\nu_n}, \quad (15)$$

$$\bar{W}_3=\bar{\sigma}'\,|\,W_1\,|\times\delta_{\nu,\nu_e-\nu_n}, \quad (16)$$

$$\bar{\sigma}'\equiv\tfrac{3}{10}(g_d\beta/H)^2(r_1^3d^3)^{-1}=\bar{\sigma}(r_2^3/d^3)\approx\bar{\sigma}(n/n'), \quad (17)$$

$$s\equiv(\gamma_e H_1)^2 T_{1e}T_{2e}, \quad (18)$$

$$P_0=-\tanh(h\nu_e/2kT), \quad (19)$$

$$T_{1n'}^{-1}=\bar{\sigma}'(1-PP_0)/T_{1e}\approx\bar{\sigma}'(\operatorname{sech}^2\chi/T_{1e}). \quad (20)$$

Note that these equations differ from S-J, Eqs. (10) and (11) which are in error in the placement of the factor N/n. This correction, pointed out by Borghini,[17] affects the saturation condition, Eq. (24) below, but not the relaxation behavior.

If there is negligible leakage relaxation through undesirable impurities, then $T_{1nl}^{-1}\to 0$, and Eqs. (11), (12), and (13) can be solved for the steady-state distant-proton polarization p_{ss} assuming only forbidden transition W_2 is induced, to find

$$p_{ss}\approx\frac{P_0}{1+f}\left[\frac{s}{s+s_{1/2}}\right], \quad (21)$$

where

$$f\equiv nT_{1e}/NT_{1p}=n'T_{1e}/NT_{1n'} \quad (22)$$

is the leakage factor introduced in S-J, and

$$s_{1/2}\approx 2Nf/[\bar{\sigma}n(1+f)]. \quad (23)$$

For Nd:LaMN, $f\ll 1$ and

$$s_{1/2}\approx 2\operatorname{sech}^2\chi. \quad (24)$$

The time constant associated with the buildup of the distant-proton polarization is $\tau_{0n}^{-1}\approx\bar{\sigma}s/2T_{1e}$; at very high saturation the buildup rate approaches N/nT_{1e}.

If there is significant leakage relaxation, defined by the parameter $l\equiv T_{1p}/T_{1nl}$, then

$$p_{ss}=\frac{P_0}{1+f(1+l)}\left[\frac{s}{s+s_{1/2}}\right], \quad (25)$$

$$s_{1/2}=\frac{2N}{\bar{\sigma}n}\,\frac{f(1+l)}{1+f(1+l)}. \quad (26)$$

This assumes $(nT_{12}l/n'T_{1n})\ll 1$; otherwise this term should be added to the denominator in Eq. (25) and Eq. (26). Phonon bottleneck effects have also been considered,[17,9] but do not significantly lower the polarization in Nd:LaMN at $\nu=75$ Gc/sec at 1°K.

III. APPARATUS

The experiments were performed in the field of a Varian Model X 4123-52 end-corrected superconducting solenoid which provided fields up to 55 kOe uniform to 10^{-5} over the sample volume. A stainless steel He^4 Dewar tip was installed in the $1\frac{1}{4}$-in. i.d. bore of the solenoid, and provided temperatures in the range $1.15\leqq T\leqq 3$°K. Another stainless steel Dewar tip of 0.5-in. diameter could be installed inside the He^4 tip. A few cm³ of He^3 were condensed in this small tip, and by pumping with a Welch Model 1402K mechanical pump, temperatures down to 0.5°K were easily maintained. The temperature was determined by measuring the vapor pressures of He^3 or He^4, respectively, using Zimmerli and McLeod gauges.

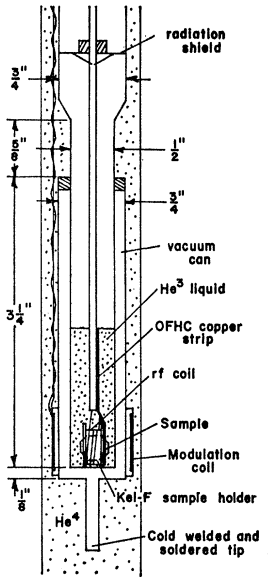

FIG. 1. Drawing of the He^3 dewar and NMR coil, for use in superconducting solenoid.

The proton relaxation time $T_{1p}(H, T)$ was measured by first dynamically enhancing the proton polarization by saturation of the forbidden transition at $\nu_e-\nu_n\approx 75$ Gc, $H\approx 19.5$ kOe, and then observing the decay of the proton NMR signal towards thermal equilibrium at the desired temperature and field. A plot of the logarithm of the signal versus time always yielded a straight line whose slope determined T_{1p}. The microwave cavity-coil arrangement used above 1.2°K was that of S-J: a simple rf coil inside a multimode cavity. In the He^3 Dewar, shown in Fig. 1, the crystal was mounted in an open rf coil, against a thermal conducting strip of oxygen-free high conductivity (OFHC) copper used to maintain uniform temperature in the He^3 bath. Microwave transitions were induced simply by coupling the 75 Gc klystron into the upper section of the stainless steel Dewar tip through a microwave horn. In this way enhancements of 50 to 150 could very easily be achieved, which was quite sufficient for relaxation time studies. Under optimum conditions at 1.2°K, enhancements of 600 were obtained corresponding to proton polarizations of 73% in the 100 mg crystal used, which is crystal No. 13 of S-J, grown from a solution containing 1% Nd of natural isotopic abundance, using 99.999% purity La, 99.999% purity Nd, both from Lindsay Chemical Co., and Mg from MgO, Catalog No. JM 130, Johnson Mathey, Ltd. The Nd concentration in the

[17] M. Borghini, Phys. Rev. Letters 16, 318 (1966).

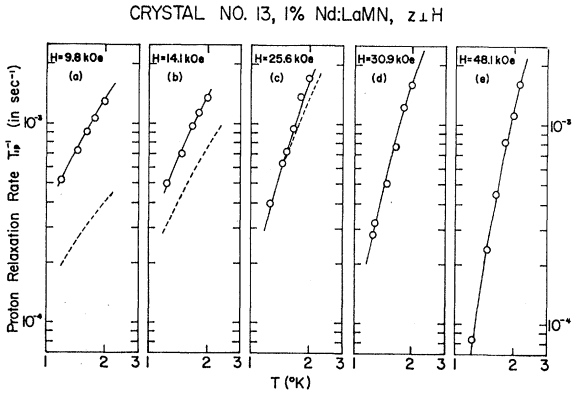

FIG. 2. Observed proton relaxation rate in 1% Nd:LaMN. The solid line is Eq. (27); the dotted line is the first term only in Eq. (27).

crystal was not measured, but may be presumed to be approximately 0.2% from the results of others.[18]

The proton NMR apparatus, as well as the over-all electrical block diagram is similar to Fig. 8 of S-J, except that as we required proton resonance frequencies in the range 40 to 250 Mc/sec, the tuned rf amplifier was replaced by a broad-band Nuvistor preamplifier followed by an APR 4 receiver. The derivative of the NMR signal was recorded on paper tape, using field modulation at 270 cps and phase-sensitive detection.

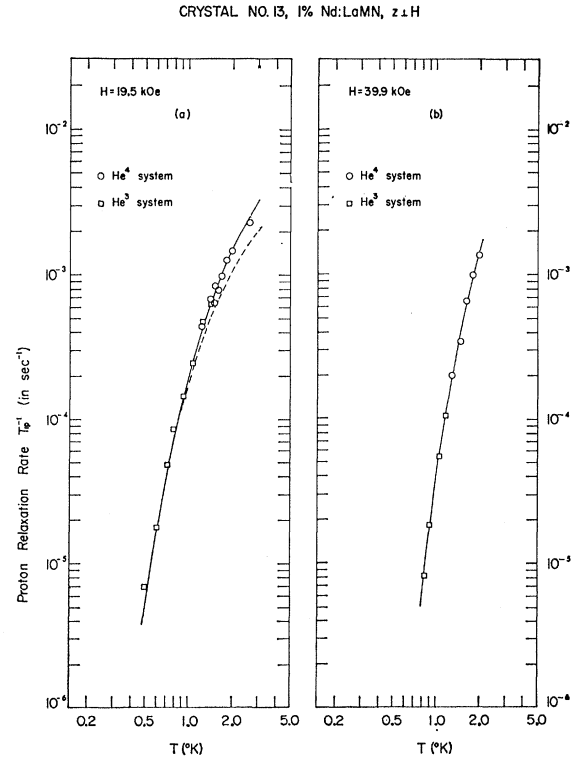

FIG. 3. Observed proton relaxation rate in 1% Nd:LaMN. The solid line is Eq. (27); the dotted line is the first term only in Eq. (27).

[18] O. Chamberlain (private communication); M. Borghini, P. Roubeau, and C. Ryter, Nucl. Instr. Methods (to be published).

IV. RESULTS AND INTERPRETATION

The experimentally observed proton relaxation rates in crystal No. 13, $c \perp H$, are shown in Fig. 2 for $H=9.8$, 14.1, 25.6, 30.9, and 48.1 kOe in the range $1.2 \leqq T \leqq 2.5$°K. In Fig. 3 the temperature range is extended to 0.5°K using the He^3 system at two fields (a) 19.5 kOe, the field at which present 4mm targets are operated; and (b) 39.9 kOe, where a 2-mm target may be operated. In Fig. 4 the same data are replotted versus magnetic field H. In all figures the solid line is not just a smooth line through the data, but rather the sum

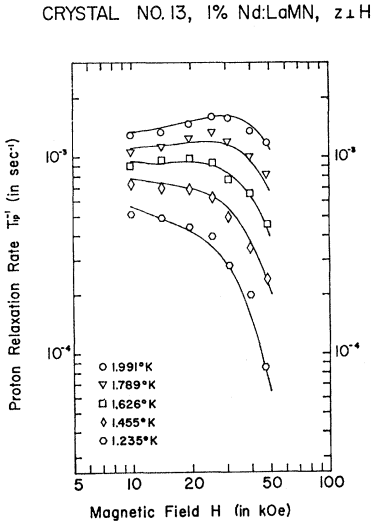

FIG. 4. Observed proton relaxation rate in Nd:LaMN.

of two terms

$$T_{1p}^{-1}=2.1\times10^{-16}H^3\coth(2.7\beta H/2kT)\times\operatorname{sech}^2(2.7\beta H/2kT)+9.9\times10^{-8}H\times\coth(4.4\beta H/2kT)\operatorname{sech}^2(4.4\beta H/2kT)\ \sec^{-1},\quad(27)$$

where H is in Oe. The first term is just the theoretical expectation from Eq. (10a) for Nd^{3+} ($g_\perp=2.70$). The second term has the expected form Eq. (10b) for an unknown non-Kramers paramagnetic impurity with $g_\perp=4.4\pm0.5$, empirically determined for best fit at low H, Figs. 2(a) and 2(b). The Nd term is usually much larger than the impurity term, which is completely negligible in Figs. 2(d), 2(e), and 3(b). For comparison, we show as dotted lines in Figs. 2(a), 2(b), 2(c), and 3(a) the contribution of the Nd term alone. Altogether the agreement between measurements and theoretical expectations is remarkably good over a wide range of temperatures and fields. In particular, the data of Figs. 3 and 4 are an unprecedented display of the $\operatorname{sech}^2\chi$ factor in Eq. (8a), and also show that

relaxation from the unknown impurity freezes out faster than that from Nd^{3+}, because of the fortuitously larger g factor. In Eq. (27) the Nd term shows that the relaxation rate increases with field due to the factor H^3, and decreases with field due to the factor

$$\mathrm{sech}^2(g\beta H/2kT) \propto \exp(-g\beta H/kT).$$

Comparison of Fig. 3(a) with 3(b) at $T=1°K$ shows that the exponential factor is much more important, and that doubling the field decreases the relaxation rate by an order of magnitude.

The longest relaxation time observed was $T_{1p}=40$ h at 0.5°K, $H=19.5$ kOe, Fig. 3(a). Extrapolation of the fitted curve to lower temperature yields $T_{1p}=310$ h at 0.4°K, and 6100 h at 0.3°K. Although the actual relaxation times may be somewhat shorter than this, because of further paramagnetic impurities with smaller g-factors, nevertheless the present experiment does indicate that relaxation times of hundreds of hours could be readily achieved, i.e., the protons can be semipermanently polarized. This suggests that the protons in Nd:LaMN could be highly dynamically polarized in say 19 kOe and 1°K using 4mm microwaves in the conventional manner. Then the microwaves could be switched off and the crystal cooled to lower temperatures using a He^3 refrigerator, and stored in a less homogeneous and perhaps higher field, e.g., that in a bubble chamber or in a balloon flight apparatus, where the polarization would decay only very slowly. Extraneous relaxation from paramagnetic centers induced by radiation damage may also be greatly reduced by the $\mathrm{sech}^2\chi$ factor. As an aid in estimating $T_{1p}(H, T)$ we have plotted Eq. (27) in Fig. 5 over wide ranges of H and T.

From the viewpoint of relaxation theory it is useful to compare the Nd term in Eq. (27) with the prediction of Eq. (8a) taking T_{1e}^{-1} from the first term of Eq. (9), and $r_2=41$ Å, appropriate for 0.2% Nd concentration in the crystal. This yields

$$T_{1p}^{-1}=0.87\times10^{-16}H^3\coth(2.7\beta H/2kT) \times \mathrm{sech}^2(2.7\beta H/2kT)\ \mathrm{sec}^{-1}, \quad (28)$$

which is in satisfactory agreement with the measurements, considering the many approximations in the theory. As for the small second term in Eq. (27) we can only say that it must be due to a non-Kramers paramagnetic impurity from the field dependence, and that $g_\perp\equiv4.4$ from the required fit of the factor $\mathrm{sech}^2(g_\perp\beta H/2kT)$ to the data. It is interesting to note that this type of relaxation measurement determines unknown g factors quite analogously to the determination of crystal field splittings by the Orbach relaxation process.[19] Since no known rare-earth non-Kramers

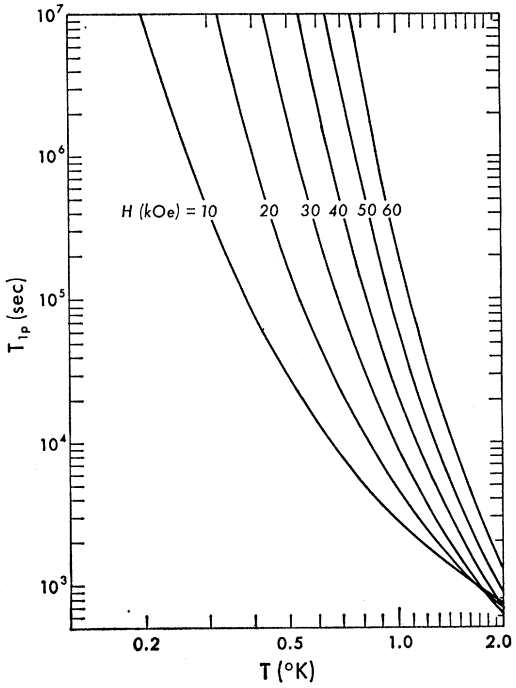

FIG. 5. Proton relaxation time $T_{1p}(T)$ from Eq. (27) for 1% Nd:LaMN, at several fields in the range $H=10$ to 60 kOe. The very long times at high fields and low temperatures are due to the $\mathrm{sech}^2(g\beta H/2kT)$ factor in Eq. (8a).

ions have the value $g_\perp=4.4$ in LaMN, we tentatively ascribe the impurity to Fe^{2+}, a common contaminant, and one known to have strong spin-phonon coupling; a representative[20] relaxation rate is $T_{1e}^{-1}\approx6\times10^4\ \mathrm{sec}^{-1}$ at 3 kOe and 1°K. Using this value to determine A' in the direct process, and $r_1\approx2.6$ Å as the nearest Mg-H distance in LaMN, we find that the second term in Eq. (27) indicates an impurity concentration of ~0.001%, which is not unreasonable for the purity of the chemicals used. This extraneous relaxation term contributes significantly to the Nd term at 19 kOe and 1.2°K, typical conditions for present targets. It is possible that it is responsible for the observed variations in relaxation times and polarizations reported for Nd:LaMN targets.[2] From Eq. (25) we see that a leakage parameter $l\approx3$, say, would seemingly not reduce significantly the fully saturated proton polarization, since $f\ll1$. But in Eq. (26) the required power is greater by a factor $1+l$ than that in Eq. (23). Since in most targets the usable power is limited by the capacity of the helium pumping system and the finite thermal conductivity of the crystals, this could reduce the attained polarization.

[19] G. H. Larson and C. D. Jeffries, Phys. Rev. **141**, 461 (1966); G. H. Larson, *ibid.* **150**, 264 (1966).

[20] N. S. Shiren, in *Proceedings of the Colloque Ampere XI, Eindhoven, 1962* (North-Holland Publishing Company, Amsterdam, 1963), p. 114.