

Phonon-limited resonant two-phonon relaxation process: Concentration dependence for Ce^{3+} in $\text{La}_2\text{Mg}_3(\text{NO}_3)_{12} \cdot 24\text{H}_2\text{O}$ at 4.2 K†

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The concentration dependence of the spin-lattice relaxation time has been measured by saturation-recovery techniques at 8.7 GHz for Ce^{3+} in $(\text{La}_{1-x}\text{Ce}_x)_2\text{Mg}_3(\text{NO}_3)_{12} \cdot 24\text{H}_2\text{O}$ —hereafter LMN:Ce—for concentrations x ranging from 2.0×10^{-5} to 1.0, for the magnetic field perpendicular to the crystal c axis, and at 4.2 K, where the resonant two-phonon process dominates and is phonon limited. The concentration dependence of these data agrees reasonably well with a model recently advanced by Gill. At the lowest concentrations, an unbottlenecked relaxation time of $0.144 \mu\text{sec}$ is observed which agrees with the T_2 determined from linewidth data by Cristea and Stapleton and gives added confirmation of the theoretical result, $T_1 = T_2$, for the two-phonon resonant process in LMN:Ce for fields perpendicular to the symmetry axis. The ratio of the bottleneck factor Q to the concentration is 3.2×10^3 , which implies a phonon-bath relaxation time of the order of 10^{-9} sec, and indicates that the mechanism for the relaxation of phonons of 25 cm^{-1} at 4.2 K is not a surface effect, but a property of the bulk crystal. An analysis of data reported in other experiments on LMN:Ce at temperatures near 2.5 K leads to shorter phonon relaxation times than those assumed by Gill in a similar analysis. The successes and the limitations of the current theory of phonon-limited two-phonon relaxation processes are summarized.

I. INTRODUCTION

In this paper we present experimental data on the concentration dependence of the resonant two-phonon (Orbach) relaxation times for cerium ions doped into lanthanum magnesium double nitrate, $(\text{La}_{1-x}\text{Ce}_x)_2\text{Mg}_3(\text{NO}_3)_{12} \cdot 24\text{H}_2\text{O}$, hereafter denoted by LMN:Ce, for concentrations x ranging from 2×10^{-5} to 1.0. The results agree well with a mathematical formulation for the Orbach process limited by phonon relaxation (phonon bottlenecking) recently advanced by Gill.¹ Our results are also in excellent agreement with measurements of the temperature-dependent linewidths for these materials reported by Stapleton.² Gill reviewed some of the background of the bottlenecking problem in his paper. At the expense of repeating a few of his comments, we review the background from a somewhat different viewpoint in order to fully develop the relationship of our results to the many other measurements relevant to the Orbach relaxation in LMN:Ce. In the process, we relate the notation of Gill to that of others who have worked on the two-phonon relaxation process.

More than thirty years ago, Van Vleck³ showed that the limiting of spin-lattice relaxation rates by the relaxation of the phonons “on speaking terms with the spin system” was to be expected for the direct (one-phonon resonant) process. This was demonstrated experimentally more than ten years ago by the T^2 temperature dependence of the bottleneck direct process.^{4,5} Concentration and crystal-size dependence of the relaxation rates have been less convincing than the temperature depen-

dence, but the phenomena of spin-induced phonon avalanches⁶ and the demonstration of phonon heating by Brillouin light scattering⁷ have added to the evidence for and understanding of this type of bottlenecking. The experimental situation for Orbach relaxation is much less satisfactory. Although the evidence for the reality (in fact, the ubiquity) of the bottleneck is extensive most of it is somewhat indirect. Scott and Jeffries,⁵ Stoneham,⁸ and Brya and Wagner⁹ showed by calculation that unless the phonon relaxation processes were exceptionally rapid, there was likely to be a severe phonon bottleneck of the Orbach process. In an approximate analysis, Scott and Jeffries showed that the temperature dependence was unaffected by the bottleneck and this was later demonstrated to be exact for a simple model by Adde, Geschwind, and Walker.¹⁰ This fact eliminated one of the more powerful tools for investigating the bottleneck process and left concentration dependence as the only obvious approach. Adde *et al.*¹⁰ used the concentration dependence for the first demonstration of the bottleneck. They utilized the Orbach relaxation process involving two excited Kramers doublets of Cr^{3+} in ruby, in which the concentration was varied by the intensity of the optical pumping from the ground state to the lower of the two excited doublets. The concentrations attained were very low and only small amounts of bottlenecking were produced.

The evidence for bottlenecking in ground-state doublets has been less direct. One source of evidence is the anomalously large field dependence of the Orbach relaxation rate first reported by Brya

and Wagner⁹ for LMN: Ce, which they speculated might come from a field dependence of the bottleneck. Hoffman and Sapp¹¹ reported an even stronger field dependence for pure cerium magnesium double nitrate (CMN), and demonstrated that it was unlikely that their field dependence and those they summarized from earlier work arose solely from the internal-field effect discussed by Orbach.¹² Another source of evidence was the comparison of T_2 for LMN: Ce and LMN: Nd, as determined from temperature-dependent linewidths at temperatures above 4.2 K, with the values inferred from T_1 measurements made below 4.2 K.^{2,13}

The Orbach relaxation in LMN: Ce is typical of a number of important examples which are simplified by the fact that the excited Kramers doublet, an energy Δ above the ground doublet, is not appreciably split by a magnetic field perpendicular to the symmetry axis. The result is that the cooling of the heated spin system by the Orbach process is frequently viewed as proceeding by transfer of phonons from an energy band centered at $\Delta - \delta/2$ to a band centered at $\Delta + \delta/2$, where $\delta = g_L \mu_B \beta H$ is the Zeeman splitting of the ground doublet. The width of these bands is of the order of the width of the excited doublets.

Brya and Wagner speculated that there might be an interband relaxation process for the phonons which would become less effective as δ increased and thus lead to a decrease in observed relaxation rates with increasing field. Sapp¹⁴ introduced the fact that the width of the excited state, and possibly even the lifetime-related width of a phonon packet, was not negligible in comparison with δ for the range of magnetic fields being discussed. This implied that the separation into two distinct phonon bands, characteristic of earlier treatments, was not meaningful. Sapp developed a simple model incorporating these ideas and could obtain agreement with the field dependence by assuming a large width for the phonon bands. Gill¹ has recently set up the phonon balance equations as a function of frequency assuming negligible spectral diffusion of the phonons and obtained a difference equation for the phonon distribution function which he solved both numerically and by an elegant approximation valid in an interesting range of the parameters. Owing to the inhomogeneous saturation properties of the phonon spectrum, the field required to reach a field-independent result does not depend on the excited-state linewidth alone, but also depends on the degree of bottlenecking.

Gill's results for the bottlenecked relaxation rates are expressed in terms of a bottleneck factor Q , which is the same as used by Stoneham, who designated it by σ . We use the expression

$$Q = \frac{N\tau_0^{-1}}{\hbar\tau_c^{-1}\rho_E(\Delta)n_0(\Delta)\tau_p^{-1}}, \quad (1)$$

which is identical to Gill's Eq. (8a) except that we have adopted the more common notation of $n_0(\Delta)$ for the equilibrium phonon occupation number at the energy Δ , and N for the number of spins per unit volume. As in Gill's equation, τ_c^{-1} is the angular frequency half-width at half-maximum of one member of the excited doublet, τ_p is the phonon relaxation time, τ_0 is the unbottlenecked Orbach relaxation time, and $\rho_E(\Delta)$ is the density of phonon states per energy interval. We find that we differ from Gill by a factor of 2 in the relationship of τ_c^{-1} to the spontaneous-emission rates from one of the excited states. To clarify the origin of this difference we state our relationship in terms of B_1 and B_2 , the two independent spontaneous-emission rates from one of the excited doublets to the ground doublet. These can be identified with $P_{c \rightarrow b}$ and $P_{c \rightarrow a}$ used by Gill, although he assumed only a singlet excited state. It has been shown that for LMN: Ce with the field perpendicular to the symmetry axis, $B_1 = B_2 = B_0$ ¹³ (in terms of Gill's notation $\kappa = 1$). The following useful relationships are taken from Ref. 13: The unbottlenecked Orbach rate is

$$\tau_1^{-1} = \tau_0^{-1} = \frac{4B_1 B_2 n_0(\Delta)}{B_1 + B_2} = 2B_0 n_0(\Delta), \quad (2)$$

and the linewidth of either of the excited states is given by

$$\tau_c^{-1} = \frac{1}{2}(B_1 + B_2) = B_0, \quad (3)$$

and for comparison with linewidth data, the width of the EPR absorption in the ground doublet due to phonon interaction is

$$T_2^{-1} = (B_1 + B_2)n(\Delta) = 2B_0 n(\Delta). \quad (4)$$

As a result of the fact that we are dealing with an excited state which is a Kramers doublet our expression (2) is twice as large as Gill's, a fact which he noted would occur. Gill's expression for τ_c^{-1} is twice as large as ours, whereas it should be identical.¹⁵ Substituting (2) and (3) into (1) we obtain the result

$$Q = \frac{2N\tau_p}{\hbar\rho_E(\Delta)} = \frac{2N\tau_p}{\rho_\nu(\Delta/\hbar)}, \quad (5)$$

which is four times as large as Gill's result, his Eq. (8b), for the reasons noted above and in Ref. 15.

Gill finds that the observed relaxation rate depends on δ and describes the field dependence of his results in terms of the parameter

$$z = \delta\tau_c/2\hbar. \quad (6)$$

The results for the observed relaxation time are simply stated for two ranges of $zQ^{1/2}$,¹⁵

$$\tau = \tau_0(1 + Q)^{1/2} \operatorname{sech}(\delta/2kT), \quad zQ^{1/2} \gg Q \quad (7)$$

and

$$\tau = 0.804\tau_0 Q^{1/4} z^{1/2}, \quad Q \gg zQ^{1/2} \gg 1. \quad (8)$$

The observed relaxation time approaches the unbottlenecked value as $zQ^{1/2}$ approaches zero.

From reasonable orders of magnitude for the parameters in Eq. (5), Gill identified in the literature measurements of the field dependence of the Orbach rate under conditions for which Eq. (8) should apply, so that

$$\tau \sim x^{1/4} H^{1/2}, \quad (9)$$

where x is the concentration of paramagnetic ions. Those measurements which he selected agreed reasonably with the field dependence exhibited in (9). In Sec. II we describe experimental measurements of the concentration dependence of τ in LMN:Ce which are shown in Sec. III to agree well with (9) at high concentrations and with exact numerical solution of Gill's difference equations at lower concentrations.

In Sec. IV, we describe the relation of our results to the phonon lifetime. In Sec. V, we discuss some of the limitations of Gill's calculations and experimental results now in the literature which have not been reconciled with a comprehensive bottlenecking theory. We suggest that such a reconciliation may be possible by a more rigorous formulation of Gill's model.

II. EXPERIMENTAL PROCEDURES AND RESULTS

A. Procedure

The relaxation times of Ce^{3+} ions in 22 LMN:Ce crystals, ranging in concentration from $x = 1.0$ (pure CMN) to 2×10^{-5} were determined by observing the recovery of the ground doublet from saturation by pulses of resonant 8.7-GHz microwaves. The crystals were placed in the cavity of a reflection-type spectrometer with variable cavity coupling and utilizing a microwave bridge. The power emerging from the detector outlet of the bridge was amplified by a Varian VTX-4415P1 traveling-wave tube (TWT), detected by a crystal diode, and displayed on a Tektronix 544 scope. The scope display was scanned by a Pacific Measurements 1001 scope-trace sampling unit and the output of the sampling unit was averaged with a Fabritek model 1062 signal averager. The response time of the system was limited by the 40-nsec decay time of the energy in the microwave cavity. Power was supplied to the cavity in 20- μsec bursts at a 300-Hz repetition rate by a Litton pulsed TWT, which amplified the power from a reflex klystron in series with a microwave-diode switch. The high-gain states of the TWT were triggered by the leading edge of the "on-pulse" of the diode switch. The length of the on-pulse defined the saturation time and was variable between 1 and 10 μsec . The recovery of the

EPR signal after saturation was observed with the 20-dB-lower power output from the TWT after the diode switch was turned off. Peak powers of up to 200 W were used.

Low concentrations yielded the shortest relaxation times as well as the weakest signals. The low-concentration measurements required the longest signal averaging and the interference from the finite cavity-response time was the most severe. This interference arises from two distinct sources.

The first source of interference is the power radiated by the cavity as the energy in the cavity decays from the level reached during the saturating pulse. This results in a very large transient pulse at the detector which decays with the cavity time constant. This pulse is much larger than the signal from the recovery of the EPR and is serious even for relaxation times much longer than the cavity decay time. This interference was removed very effectively by the following procedure. After a number of recovery signals had been averaged with the magnetic field at the resonant value, the field was set off resonance and the same number of transient recoveries were averaged with the signal averager operating in the subtract mode.

The second source of interference arises from the finite cavity response time for a change in the magnetic susceptibility in the cavity. This effect can be shown to lead to a recovery signal of the form

$$S(t) \sim 1 - (\lambda_c e^{-\lambda_c t} - \lambda_s e^{-\lambda_s t}) (\lambda_c - \lambda_s)^{-1}, \quad (10)$$

in which $\lambda_c/2$ and λ_s are the relaxation rates for the energy in the cavity and for the magnetic susceptibility. From this it is clear that for $\lambda_c \geq 2\lambda_s$, there is only a small effect on the signal during the final third of the recovery.

In addition to the effects from cavity response, it is well known that in cases in which the EPR line saturates inhomogeneously there is an initial non-exponential recovery due to spectral diffusion which decays away rapidly compared with the spin-lattice relaxation time.

Our recovery curves showed a small amount of nonexponential behavior in the early part of the recoveries. In all cases we utilized only the last third of the recovery curve to determine the spin-lattice relaxation time. The base line corresponding to full recovery was adjusted so that the last third of the recovery fitted a straight line on semi-logarithmic display. The straight-line region always included at least one decade of variation before the signal-to-noise ratio became of the order of 2 or 3.

The entire measurement process was repeated several times under identical conditions and also for different pulse lengths, power levels, and cav-

TABLE I. Experimental data for spin-lattice relaxation times of Ce^{3+} in $(\text{La}_{1-x}\text{Ce}_x)_2\text{Mg}_3(\text{NO}_3) \cdot 24\text{H}_2\text{O}$. Measurements were made near 4.2 K and 8.7 GHz with the magnetic field perpendicular to the c axis of the crystal.

Ce conc. x	Weight (mg)	Thickness (mm)	Temperature (K)	measured τ (μsec)	τ (4.200 K) (μsec)
1.00	2.6	< 0.4	4.201	0.97	0.97 ± 0.02
1.00	2.8	< 0.4	4.197	1.04	1.03 ± 0.03
0.396	2.6	0.46	4.180	0.89	0.855 ± 0.02
0.204	2.3	0.51	4.192	0.77	0.763 ± 0.04
0.107	3.6	0.74	4.189	0.67	0.658 ± 0.01
(0.1)	6.9	0.53	4.199	0.67	0.67 ± 0.02
0.041	9.8	1.32	4.187	0.503	0.490 ± 0.015
0.0174	5.8	0.64	4.190	0.410	0.402 ± 0.02
0.0174	4.6	0.38	4.194	0.045	0.397 ± 0.02
(0.01)	7.8	0.58	4.198	0.328	0.326 ± 0.01
0.00966	8.6	0.5	4.198	0.32	0.32 ± 0.02
0.00966	7.2	0.53	4.194	0.317	0.313 ± 0.005
0.00497	44.3	1.0	4.189	0.291	0.284 ± 0.03
0.00337	35.2	1.85	4.188	0.265	0.259 ± 0.01
0.00140	22.0	0.85	4.185	0.226	0.219 ± 0.01
$7.8 (\times 10^{-4})$	19.1	1.2	4.187	0.222	0.216 ± 0.015
$4.54 (\times 10^{-4})$	54.6	1.2	4.195	0.225	0.223 ± 0.015
$2.56 (\times 10^{-4})$	128.0	2.06	4.192	0.210	0.207 ± 0.015
$0.387 (\times 10^{-4})$	90.5	2.55	4.201	0.14	0.14 ± 0.01
$0.209 (\times 10^{-4})$	260.5	2.92	4.189	0.173	0.169 ± 0.025
$0.209 (\times 10^{-4})$	85.0	0.62	4.192	0.165	0.162 ± 0.01
$0.209 (\times 10^{-4})$	102.0	0.76	4.193	0.159	0.156 ± 0.015

ity couplings. We detected no statistically significant effects from the variation of these parameters and the quoted errors represent the statistical scatter of all of the results obtained for a single crystal before it was returned to room temperature.

The concentrations of the solutions from which the crystals grew were determined by weighing the cerium and lanthanum salts that were dissolved; but the concentrations of cerium ions in the crystals was determined by comparison of the integrated intensity of the cerium EPR resonance per unit mass of crystal with that of pure CMN. In order to make these comparisons, it was necessary to have a means for determining the relative gain of the spectrometer. For this purpose, a standard sample of diphenylpicrylhydrazyl (DPPH) was mounted in the cavity and never moved during the course of the experiments. To ensure stability of the DPPH, care was taken that the cavity did not reach temperatures above 20°C at any time during the course of the experiments. For each sample, we obtained a number

$$a_i = (A/hM)_i,$$

where A is the area under the cerium resonance line, h is the height of the DPPH resonance (spectrometer gain), and M is the mass of the sample. The absolute concentration x was obtained by comparing this number with those samples of pure CMN

for which x is known to be 1.0. Thus for sample i ,

$$x_i = a_i/a_{\text{CMN}}.$$

Minor errors could be produced by lack of accurate positioning of the sample in the cavity or variation of the microwave field over the sample volume. Concentrations determined in this way are believed to be accurate to 15%. At the lowest concentrations the crystal concentrations were 30–50% below the solution concentrations.

All of the measurements were made at the temperature of liquid helium boiling at the atmospheric pressure in the laboratory. All measured relaxation rates were corrected to a temperature of 4.200 K by means of helium-vapor-pressure tables and the relation

$$\tau = C e^{+\Delta/kT}, \quad (11)$$

with $\Delta/k = 36.25$ K. The maximum correction for deviation of the temperature from 4.2 K was 5%.

B. Data and characteristics of the samples

The results for 22 different crystals are listed in Table I. The table includes the concentration, the temperature, the measured relaxation time, the relaxation time corrected to 4.2 K, and the smallest dimension of the sample. All of the data in the table were taken after the first cool-down of the crystal from room temperature. Several crystals are of nearly identical concentrations and il-

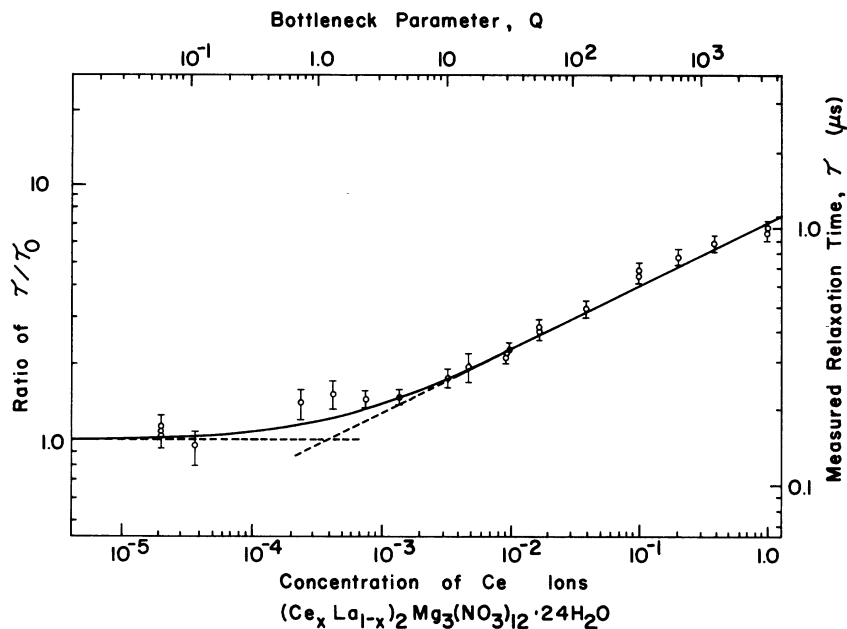


FIG. 1. Plot of data in Table I showing the concentration dependence of Ce^{3+} relaxation time at 4.2 K and 8.7 GHz. The solid line is from numerical calculations using Gill's bottlenecking model. The dotted lines are Eq. (8) and $\tau = \tau_0$. The fit is for $z = 1.3$. $\tau_0 = 0.144 \mu\text{sec}$ and $A = (Q/x) = 3.2 \times 10^3$.

illustrate the reproducibility of the results. An effort was made to choose crystals of reasonable quality. The smaller crystals used at higher concentrations were quite clear; but most of the larger crystals showed evidence of small amounts of occluded solution. Within the range of imperfections detected by visual inspection, we observed no variation of the results with initial quality of the crystals.

To further test the reproducibility of the measurements, many of the samples were measured again after they had been warmed to room temperature and removed from the cavity. The warm-up was rather violent. We pulled the cavity from the helium bath and then warmed the cavity to room temperature in a time of the order of 1 min in order to avoid condensation of water on the crystals. This procedure had been adopted in order to expedite the measurement of many crystals. The cooling of the crystals from room temperature to 77 K was a much more gentle process occurring over a period of the order of 40 min. When crystals subjected to the rapid warm-up were measured the second time we found a systematic shift to longer relaxation times. Independent of size, and concentration of Ce^{3+} , crystals subjected to the warm-up process one time showed an increase of approximately a factor of 2 in the relaxation time. Several crystals were subjected to repeated warm-ups and appeared to stabilize at a relaxation time 4 times longer than the value obtained prior to the first warm-up. Concomitant with the increase in the relaxation time, the linewidth of the resonance increased indicating an increase in internal strain.

To test the hypothesis that the rapid warm-up rather than the gentle cool-down was the critical factor, one crystal was cooled down in the normal way, but warmed up slowly (over a 12-h period) and then cooled down in the normal manner. This sample yielded results in excellent agreement with crystals cooled down only once. Many crystals were measured again after warming slowly to 77 K and then cooling rapidly to 4.2 K. This cycle had no effect on the relaxation time.

From these tests, we conclude that the measured relaxation times in Table I are an intrinsic characteristic of the crystals and would be reproduced by the selection of crystals reasonably free of occlusions and exposed to a minimum of thermal shock.

Signal-strength considerations required that we use somewhat larger crystals at the lower concentrations than at the higher concentrations. The maximum variation in the smallest dimension of the crystals is only a factor of 7. Samples of $x = 0.0174$ in Table I are of the same concentration, are in a concentration range in which there is considerable bottlenecking, differ in smallest dimension by a factor of 2, and yield essentially the same relaxation time, indicating no dependence on crystal size.

III. COMPARISON WITH THEORY

In Fig. 1, the relaxation times in Table I are compared with calculations made from Gill's model. We estimate from data in Ref. 9 that even in pure CMN less than 5% of the relaxation is due to Raman processes. We have assumed that only the

Orbach process contributes to the relaxation time at 4.2 K. The experimental data form a plot of τ vs x . In order to compare with the calculations, we have assumed that Δ , B_0 , and τ_p are independent of concentration, and that the value of z for our experiment can be determined satisfactorily from other data. Evaluation of z requires that we know the linewidth of the excited states, which according to Eq. (3) is B_0 . We have obtained the value of B_0 from the measurements of the temperature dependence of EPR linewidths in LMN: Ce ($x = 0.01$) by Cristea and Stapleton,¹⁶ who fit their data between 5 and 15 K to an equation of the form

$$T_2^{-1} = B' e^{-\Delta/kT}. \quad (12)$$

In fitting over this temperature range, B' and Δ are tightly correlated, but if one assumes that $\Delta/k = 36.25$ K, one finds $B' = (4.2 \pm 0.3) \times 10^{10}$ sec⁻¹. From Eq. (4), $B_0 = B'/2 = \tau_c^{-1} = 2.1 \times 10^{10}$ sec⁻¹. From Eq. (6), $z = 1.3$ for our frequency of 8.7 GHz.

For $z = 1.3$, Eq. (8) is accurate to better than 10% for $Q > 3.5$ according to Gill. Numerical calculations for $Q < 3.5$ were combined with the predictions of Eq. (8) for higher Q in order to generate an analytical function

$$\tau = \tau_0 f(Q) = \tau_0 f(Ax), \quad (13)$$

which accurately represented the theoretical results over the entire range of Q . Equation (13) was fitted to the experimental data by nonlinear regression with respect to the parameters A and τ_0 . The solid line in Fig. 1 represents the best fit. The values for best fit are

$$\begin{aligned} \tau_0 &= 0.144 \text{ } \mu\text{sec}, \\ A &= Q/x = 3.2 \times 10^3. \end{aligned}$$

The two fitting parameters are tightly correlated. We find that A can be fixed at either 2 or $\frac{1}{2}$ times the value for best fit, and a linear regression with respect to τ_0 leads to a standard deviation only twice that of the best fit. The corresponding changes in τ_0 for best fit at these extremes of A are only $\pm 10\%$.

An additional check of the consistency of the theory is provided by Eq. (2). Using the value of B_0 from linewidth data and $\Delta/k = 36.25$ K, we find

$$\tau_0 = 0.135 \text{ } \mu\text{sec}.$$

If one accepts the value for Δ/k , the uncertainty in this predicted value of τ_0 is of the order of 10%, and is in excellent agreement with our experiments.

IV. PHONON RELAXATION

Using a Debye model for the density of acoustic phonons at the frequency Δ/h and assuming η spins per unit cell at full concentration, one finds from Eq. (5)

$$Q = \frac{2}{3} \eta x \left(\frac{k\Theta_D}{\Delta} \right)^2 \frac{k\Theta_D}{\hbar} \tau_p. \quad (14)$$

Assuming $\Theta_D = 60$ K, $\eta = 2$, and our experimental result $A = 3200$, one finds from Eq. (14), $\tau_p = 1.86 \times 10^{-9}$ sec. This value implies a mean free path for the phonons of less than 10^{-3} cm, far less than the smallest dimension of any of our crystals. This fact and the absence of a size effect in our measurements lead us to conclude that the relaxation of the phonons of energy Δ and at the temperature 4.2 K occurs by a process characteristic of the bulk crystal and not at the surface.

In view of the fact that the relaxation process is not a surface effect, the theoretical treatment of the relaxation process for phonons of energy 30 cm⁻¹ at temperatures below 4.2 K by Orbach and Vrederoe¹⁷ may be relevant. They concluded that the transverse and longitudinal phonons should show relaxation times that differ by 4 or 5 orders of magnitude. The fact that our relaxation times at the lowest concentrations agree with the linewidth data demonstrates that there are no phonons effective in the Orbach relaxation process with relaxation times longer than 10^{-8} sec, and it seems implausible that there are phonons with relaxation times four orders of magnitudes shorter than 10^{-8} sec. There are, of course, many reasons that we may not observe these two groups of phonons. One possibility is that 4.2 K may be too high a temperature for an extreme differentiation in relaxation times to be exhibited. Also the phonons in LMN are probably not separable into pure transverse and longitudinal modes, and modes that may be predominantly of one type or the other could be strongly inhibited in their capability for driving the Orbach process.

Our conclusion that the phonon relaxation time at 4.2 K is about 10^{-9} sec and is not a surface effect is in sharp contrast to Gill's assumption that the phonon lifetime in even large LMN crystals is determined by the mean time of travel to the surface. It is true that Gill was considering data taken at temperatures near 2.5 K, whereas our result is for 4.2 K. However, an analysis of the experiments of Brya and Wagner⁹ and Finn *et al.*¹⁸ using the same values for τ_c^{-1} and B_0 as those used in Sec. III of this paper, and calculating τ_p from the experimental data (rather than presuming it to be determined by the crystal size) leads to a quite different conclusion concerning the phonon relaxation process. This revised analysis is summarized in Table II and the next paragraph.

In Table II, we display the parameters used by Gill and by us in the analysis of data taken near 2.5 K for LMN: Ce with concentrations $x = 5 \times 10^{-3}$ and $x = 1.0$. The major difference in the two lists of parameters is that we assumed an excited-state

TABLE II. Parameters for two different analyses of two sets of experimental data on the relaxation of LMN:Ce near 2.5 K. The Roman numerals I and II refer to data reported in Refs. 9 and 18. The A columns are analyses by Gill (Ref. 1) and the B columns are analyses described in Sec. IV.

	I		II	
	A	B	A	B
Material	LMN:Ce	LMN:Ce	LMN:Ce	LMN:Ce
Nominal concentration, x	5×10^{-3}	5×10^{-3}	1	1
Δ/k (K)	36.7	36.25	36.7	36.25
δ (cm^{-1})	0.37	0.37	0.086	0.086
τ_c^{-1} (sec^{-1})	6×10^{10}	2.1×10^{10}	6×10^{10}	2.1×10^{10}
τ_p (sec)	2×10^{-7}	2.8×10^{-8} ^a	2×10^{-6}	2.5×10^{-8} ^a
Bottleneck factor, Q	1.1×10^3	240	2.2×10^6	4.4×10^4
z	0.51	1.66	0.135	0.385
τ/τ_0 (calculated)	3.6 ^a	4.41	12.3 ^a	7.8
τ/τ_0 (observed)	5.3	4.41	9.4	7.8

^aResult calculated from Eq. (8).

lifetime about three times longer than Gill assumed and we calculated τ_p from the other data in the list using Eq. (8), whereas Gill used an assumed phonon lifetime to calculate the ratio τ/τ_0 . Some very minor differences arise from the difference in the assumed value of Δ because in both Gill's analysis and ours, the value of C in Eq. (11) is adjusted to best fit the experimental data with Δ constrained to the assumed value. The striking result of our analysis is that the phonon relaxation time in the two samples, which have a much different size and concentration, is the same within the uncertainties of the experimental data. Also the value of the phonon relaxation time deduced in our analysis is much too fast to be a surface relaxation. The phonon relaxation times in Table II which we have obtained from our analysis are about 15 times longer than those obtained from our data at 4.2 K. It may not be implausible that the phonon relaxation time would increase this much between 4.2 and 2.5 K, but it is not possible to firmly conclude that this effect is real without much more information concerning the condition of the crystals used in the 2.5 K experiments. Our crystals showed spin-lattice relaxation times longer by a factor of 2 after a violent warm-up. A factor of 2 in the spin-lattice relaxation time leads to a factor of 16 in the inferred phonon relaxation time. In addition, the experiments at 2.5 K require a much larger correction for the Raman contribution than do the experiments at 4.2 K, and we point out in Sec. V that there is serious doubt that the methods used for extracting the Raman component are valid in the presence of a strong bottleneck.

We do not believe that the increase of spin-lattice

relaxation times produced by thermal shock is related to a change in the phonon lifetime. There are many arguments supporting this conclusion, but the most direct one is that the effect appears as the same multiplicative factor at both low and high concentrations. It appears that the value of τ_0 or Δ is changed by the thermal shock.

V. CONCLUSIONS AND DISCUSSION

We conclude that our measured concentration dependence of the relaxation times in LMN:Ce at 4.2 K is a strong confirmation of the general features of Gill's bottlenecking model for the Orbach process. Our results also further substantiate the Culvahouse-Richards result $T_1 = T_2$ for LMN:Ce with the magnetic field perpendicular to the symmetry axis. Earlier results obtained by Cristea and Stapleton¹⁶ for concentrations of $x = 1 \times 10^{-3}$ and 1×10^{-2} in LMN:Ce strongly indicated that T_1 approached T_2 as the concentration was lowered, but the present experiments are much more definitive because they cover a wider range of concentrations and are correlated by a theory for the concentration dependence.

Some results in the literature appear to disagree with the bottlenecking model used here. The original demonstration of the bottlenecked Orbach process presented in Ref. 10 is one example. Those results were analyzed with the relation

$$\tau = \tau_0(1 + Q)\text{sech}(\delta/2kT), \quad (15)$$

rather than Eq. (7), which should apply under the

conditions of the experiment if spectral diffusion is negligible. We have found that Eq. (7) provides a slightly better fit to the experimental data presented in Ref. 10, although the authors had another explanation for the deviation of the observations from Eq. (15).

There remain some field dependences such as those of Ref. 11 which do not fit Eq. (9) in regions in which they should. The measurements reported in Ref. 11 yield the longest relaxation times ever reported for LMN: Ce and require appreciable correction for the Raman process. We believe that the results of Ref. 11 might be explained by a more precise treatment of the bottleneck problem in which the artificial separation into an Orbach and Raman process is not assumed,¹⁹ and one does not assume equal populations for the spin levels as Gill did (i. e., $m_a = m_b = \frac{1}{2}$).

We have set up the difference equations without the approximation $m_a = m_b = \frac{1}{2}$ and solved them numerically for several temperatures and magnetic fields. We find results that are not seriously modified for the range of temperatures and fields which we encounter in the experiments reported in Sec. II. The corrections that will be required for data with Q in excess of 1000 at temperatures as low as 2.5 K, and $\delta/2kT \geq 0.1$, may be very significant.

The separation into an Orbach process and a Raman process is likely to be a poor approximation

in strongly bottlenecked samples at low temperatures. The energy bandwidth of phonons involved in what is nominally called the Orbach process is of the order of $Q^{1/4} \tau_c^{-1} \hbar$. A large value for Q enhances a number of serious difficulties in the analysis of the temperature dependence of relaxation times that have been noted before. Young and Stapleton²⁰ noted that if $\tau_c^{-1} \hbar$ is significant relative to Δ , one can underestimate the true value of Δ in the fitting of relaxation data. Stoneham¹⁹ noted that except for very large values of $\Delta/\tau_c^{-1} \hbar$, the usual procedure of separating the temperature dependence into a T^9 and $e^{a/T}$ component is unsatisfactory. The potential of the bottlenecking effect in destroying the sharp distinction between Raman and Orbach processes is dramatically illustrated by assuming the value of Q , τ_c^{-1} , and Δ given by Gill¹ for CMN. One finds $(\Delta/\tau_c^{-1} \hbar Q^{1/4}) \sim 2$.

These are strong indications that further refinements of the treatment of bottlenecking even within the limitations of a single characteristic phonon relaxation time may correlate a vast majority of the two-phonon spin-lattice relaxation results.

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