Concentration-Dependent Orbach Relaxation Rates in Nd-Doped Lanthanum Magnesium Nitrate*

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Electron-spin-resonance linewidth data, taken between 6 and 23 K, are compared with pulse-saturation-recovery times, measured between 2.5 and 3.5 K, for three samples of Nd-doped lanthanum magnesium nitrate. Both types of measurements indicate a dominant Orbach relaxation process. The relationship between the two types of data in the presence of a phonon-limited Orbach relaxation process is discussed. The fact that the linewidth data were uniform among the different samples, whereas the pulse-saturation-recovery data were concentration dependent, is interpreted as evidence that the Orbach relaxation process in this salt is phonon limited.

I. INTRODUCTION

We shall present data concerning the resonant two-phonon (Orbach) spin-lattice relaxation process of Nd^{3+} incorporated into single crystals of lanthanum magnesium double nitrate, $La_2Mg_3(NO_3)_{12} \cdot 24H_2O$, abbreviated LMN:Nd. We interpret the data to be presented as additional evidence that this relaxation process for rare-earth ions in LMN is phonon limited or bottlenecked.[1,2] The experimental determination of whether this type of relaxation mechanism is phonon limited is much less direct than it is for the one-phonon (direct) process. In the latter case, strongly nonexponential signal recoveries occur after a saturating pulse, and the asymptotic exponential recovery rate $1/T_b$ is changed from a $\coth(h\nu/2kT)$ dependence to a $\coth^2(h\nu/2kT)$ dependence, or approximately from T to T^2.[3,4] This change in the temperature dependence is in addition to the concentration dependence which generally appears in T_b.

On the other hand, the Orbach process displays the same temperature dependence regardless of whether it is phonon limited. The set of nonlinear differential equations which describes the resonant two-phonon process can be solved approximately for typical experimental conditions.[4-6] The approximate solution indicates that the population within the ground-state doublet returns to its thermal-equilibrium distribution with a nearly pure-exponential

time dependence characterized by

$$T_b = T_{10}(1 + NB T_{ph}/4\rho \Gamma), \tag{1}$$

where N is the total number of spins, T_{ph} is the phonon relaxation time, ρ is the density of states for those phonons involved in the relaxation mechanism, and Γ is the bandwidth for each of the phonon frequencies involved. Equation (1) assumes that a total of four energy levels are involved and that

$$\frac{1}{T_{10}} = \frac{B}{e^{\Delta/kT} - 1} \tag{2}$$

is the true Orbach relaxation rate in the absence of a phonon bottleneck. Here Δ is the energy of the excited doublet involved in the relaxation mechanism. It has been noted by Adde, Geschwind, and Walker[5] that Eq. (1) does not depend upon the system being near thermal equilibrium so that T_b is independent of the degree of spin saturation. Thus, it is sometimes stated that the phonon bottleneck is a linear phenomenon for an Orbach process. However, this statement does not apply to the determination of T_1 by means of T_2 or linewidth measurements. In their treatment of this problem, Culvahouse and Richards[2] noted that if the two matrix elements B_1 and B_2 involved in the transitions between the ground and excited Kramers doublets are equal, then

$$1/T_2 = \tfrac{1}{4}B[n(\hbar\omega_{41}) + n(\hbar\omega_{42}) + n(\hbar\omega_{31}) + n(\hbar\omega_{32})], \tag{3}$$

where $B = 2B_1 = 2B_2$ and $n(\hbar\omega)$ is the phonon occupation number for phonons at frequency ω. Furthermore, they point out that in an Orbach process, phonons are transferred from one frequency band to another in such a way that

$$n(\hbar\omega_{31}) + n(\hbar\omega_{32}) = n(\hbar\omega_{41}) + n(\hbar\omega_{42}) = \text{const} . \quad (4)$$

This means that even if a nonequilibrium distribution of phonon energies occurs, as a result of spin-lattice relaxation, there should be no effect on T_2 as measured. Thus if the ratio T_1/T_2 is known, a measurement of the "true" Orbach spin-lattice relaxation time T_{10} can be made using linewidth techniques, regardless of whether or not a potential phonon bottleneck exists.

For the operating conditions of our measurements, Culvahouse and Richards[2] have shown that T_1 must equal T_2 within 3% if there is no phonon bottleneck. Consequently, T_2 as obtained from our linewidth measurements can be equated to the unbottlenecked Orbach spin-lattice relaxation time T_{10}.

II. EXPERIMENT

Pulse-saturation and linewidth data were taken for two samples of LMN:Nd. The samples were in their natural form of hexagonal platelets with the following characteristics: 0.1-at.% nominal Nd^{3+} concentration, 19.5 mg, 0.826 mm thick; and 1.0-at.% nominal Nd^{3+} concentration, 22.7 mg, 0.630 mm thick. In addition the experimental data from these two samples were compared to similar data on another 1-at.% LMN:Nd sample published by Stapleton and Brower[1] and identified herein as 1%(S+B). Both linewidth and pulse data were taken on an X-band spectrometer operating near 9.2 GHz with the applied magnetic field perpendicular to the hexagonal crystal axis. The principal values of the g tensor are $g_\perp = 2.71$ and $g_\parallel = 0.368$.[7,8] A cylindrical TE_{111}-mode microwave cavity, constructed from oxygen-free high-conductivity (OFHC) copper, was thermally isolated from the liquid-He^4 bath by a surrounding copper can. The cavity could be weakly coupled to the bath with He^3 exchange gas or strongly coupled to it with a copper strap which passed through the bottom of the copper can into the He^4 bath. The latter coupling scheme was used for pulse-saturation-recovery measurements at temperatures below 4.2 K, obtained by pumping on the He^4 bath through a manostat. Stable cavity temperatures above 4.2 K were obtained by controlled heating with a 500-Ω coil and weak coupling to the bath. Temperature measurement and control of the heater power were accomplished with an ac bridge containing a calibrated germanium resistance thermometer attached to the cavity.

We consider first the linewidth data from the two samples. It is necessary to correct the observed

total peak-to-peak derivative linewidth ΔH for the temperature-independent contribution ΔH_0. The low-temperature line shapes in our two samples were nearly Gaussian but became Lorentzian as the relaxation-induced linewidth became dominant at higher temperatures. We therefore corrected the observed peak-to-peak derivative linewidth ΔH by treating it as a convolution of a Lorentzian shape, with peak-to-peak derivative width $\Delta H'$, and a Gaussian shape with peak-to-peak derivative width ΔH_0. An approximate expression which accomplishes this and which is valid to better than 1% was furnished by Stoneham.[9]

A "shape function" $S(T)$ based on a sampling of 18 points along the derivative of the absorption line was defined in such a way that if $S(T)$ is 1.0 the line shape is purely Gaussian, and if $S(T)$ is 0.0, the line shape is purely Lorentzian. For the 0.1-at.% LMN:Nd sample, $S(T)$ was 0.81, 0.66, 0.37, 0.20, and 0.14 when T was 4.2, 6, 7, 8, and 9 K, respectively.

The corrected peak-to-peak derivative linewidths $\Delta H'$ are plotted in Fig. 1 as a function of temperature. It is clear from this figure that our two samples and the 1%(S+B) sample show essentially the same $\Delta H'$-vs-T dependence. Figure 2 shows the same data replotted assuming an Orbach process with $\Delta = 48.25$ K. An equally weighted least-squares fit produces Δ values of 48.2 ± 1.2 and 48.5 ± 1.0 for our 0.1- and 1.0-at.% LMN:Nd data, respectively. This figure also indicates that an Orbach process is the dominant relaxation mechanism.
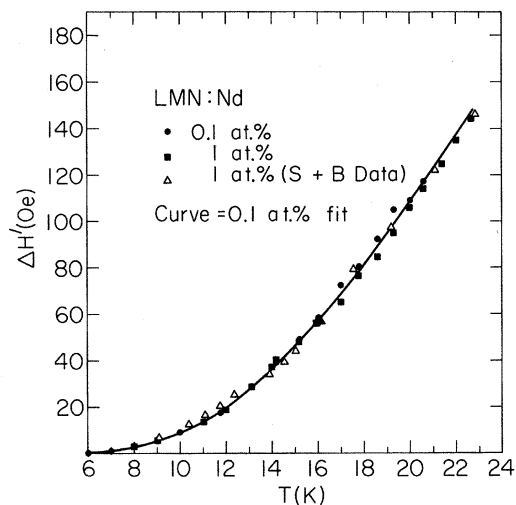
FIG. 1. Relaxation-induced peak-to-peak derivative linewidths $\Delta H'$ for three samples of LMN:Nd plotted as a function of temperature. S+B refers to data in Ref. 1. These data indicate that there is no significant concentration or size dependence among the samples. The solid curve is a weighted least-squares fit of the 0.1% data to an Orbach process.
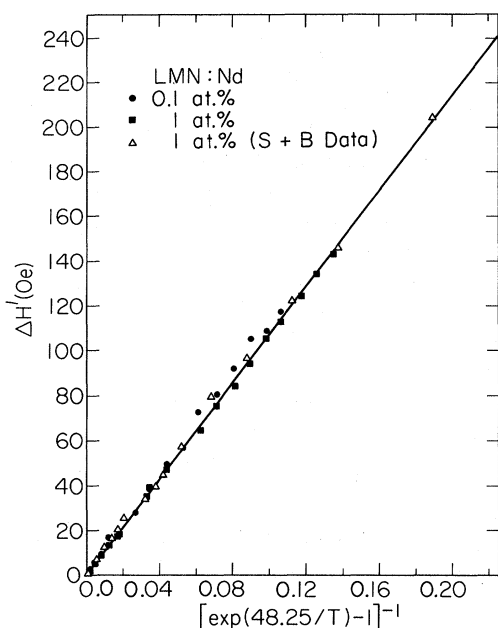
FIG. 2. Data from Fig. 1 replotted to identify the relaxation mechanism as an Orbach process. The chosen value of Δ lies between the individually fitted values of 48.2 ± 1.2 and 48.5 ± 1.0 K for our 0.1- and 1.0-at.% Nd-doped samples.

Figure 3 shows the pulse-saturation data on our two samples as well as the 1%(S+B) sample. From these data it is clear that there is a difference be-

tween the relaxation rates which could be due to concentration and/or sample-size differences. A size dependence might appear if the relaxation process is phonon limited and the phonons thermalize at the sample surface. This has been observed for a bottlenecked direct process in some LMN salts[4,10] where thicker crystals exhibited slower relaxation rates. Several facts argue against any size dependence. The faster-relaxing 0.1% crystal is 30% thicker than the 1.0% crystal. The 1%(S+B) sample was undoubtedly thicker than our 1% sample. Finally Cristea and Stapleton[10] have recently reported similar measurements in LMN:Ce but there a 1% sample was thinned from 1.0 to 0.25 mm and no change was observed in the Orbach relaxation rate. However, a concentration dependence similar to the one shown here was noted.

The T_2 of the resonance line is related to the full width $\Delta\omega_{1/2}$ (in rad/sec) at half-amplitude by

$$\frac{1}{T_2} = \frac{\Delta\omega_{1/2}}{2} = \frac{g\mu_B \Delta H_{1/2}}{2\hbar} = \frac{\sqrt{3}g\mu_B \Delta H'}{2\hbar} = 7.62 \times 10^6 \, g\Delta H' ,$$

(5)

where a relaxation-broadened Lorentzian-shaped absorption line is assumed. As noted earlier, T_2 equals T_{1O} for our experimental situation. In Fig. 4 we compare the linewidth and pulse-saturation data. We note that neither of the extrapolated pulse-saturation curves coincides with the linewidth curve. The linewidth or T_2 data, which are the same for all three samples, indicate the fastest re-
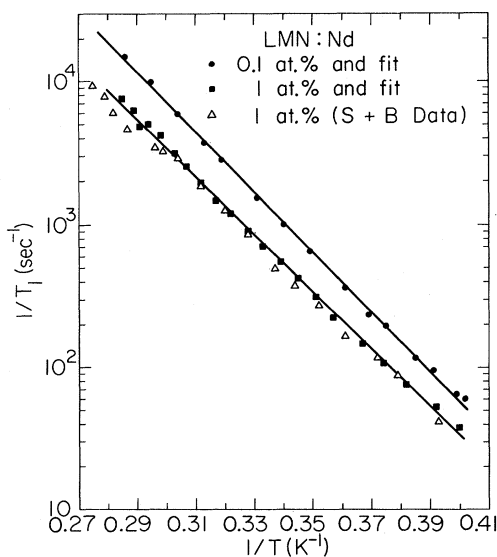

FIG. 3. Relaxation data from pulse-saturation-recovery measurements on the three samples of Fig. 1. These data indicate a dominant Orbach relaxation mechanism as well as a concentration dependence. The straight lines represent weighted least-squares fits of the data from our 0.1 and 1.0% samples and correspond to Δ values of 48.1 ± 0.2 and 46.0 ± 0.5 K, respectively.
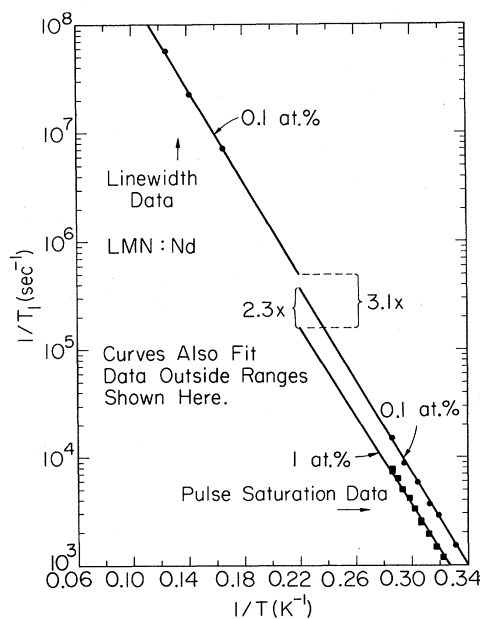

FIG. 4. Temperature dependence of the linewidth and pulse-saturation-recovery data plotted in the near-overlap region. The samples are the same as those of Figs. 1–3 and show essentially identical linewidth data.

laxation rate, while the pulse-saturation data on the 1-at.% LMN: Nd sample shows the slowest rate.

In an attempt to obtain data uniformly over the full temperature range from 2.5 to 23 K, we made continuous wave (cw) saturation measurements between 3.4 and 7 K ($1/T = 0.29-0.14$) on the 0.1-at.% LMN: Nd sample. The interpretation of these data was complicated by the fact that the line shape $S(T)$ changed significantly (0.81-0.37) over that temperature interval, so that the uncertainties in T_1 are too large to make the data useful.

III. DISCUSSION AND CONCLUSIONS

We interpret these data as indicating that the Orbach relaxation process in LMN: Nd is phonon limited, so that the pulse-saturation data do not yield the true Orbach relaxation time T_{1O}, but rather a bottlenecked relaxation time $T_b > T_{1O}$. We consider the linewidth data to represent the true Orbach relaxation time. In addition, we suspect, from the fact that all samples showed essentially the same $\Delta H'$ (or T_2)-vs-T curves, that the variations in T_1 vs T, which have been observed even among crystals grown from the same solutions,[4] are due to changes in the phonon bottleneck rather than changes in the strength of the true Orbach relaxation process.

The observed concentration dependence, illus-trated in Fig. 4, could agree with Eq. (1) only if the bottleneck factor $NBT_{ph}/4\rho\Gamma$ were close to unity. This, in turn, requires that T_{ph} be of the order of 10^{-12} sec. Therefore we do not consider the simple model leading to Eq. (1) as adequate. Mechanisms probably exist which tend to reduce the effects of a bottleneck. Brya and Wagner[11] have proposed that such a mechanism might be a direct interaction between the "hot" phonons at energy $\hbar\omega_+ = \Delta + \frac{1}{2}g_\perp\mu_B H$ and the "cold" phonons at energy $\hbar\omega_- = \Delta - \frac{1}{2}g_\perp\mu_B H$. Only the ground doublet g value enters here since the excited doublet is not split by a perpendicular magnetic field.[12] Sapp[13] has proposed a quantitative model of this interaction and it appears capable of explaining the weak concentration dependence as well as the magnetic field dependence.

It also seems quite probable that a large fraction of rare-earth salts are phonon limited in the Orbach relaxation process.

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