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Electron Spin Echo Studies of Paramagnetic Systems*

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The temperature dependence of the spin lattice relaxation time T_1 in Ce^{+++}, Nd^{+++} and Pr^{+++} diluted in lanthanum magnesium nitrate has been measured by electron spin echo techniques at 9300 mcps. from 1.5 to 4.2°K. T_1 in Ce and Nd varies as $\exp(34/T)$ and $\exp(46/T)$ respectively, in good agreement with the Finn, Orbach, Wolf theory. In Pr, a non-Kramers system, T_1 varies as $T^{-6.5\pm0.5}$, presumably a Raman process. In all three cases, T_1 increases less rapidly at the low end of the temperature range where the transition to the direct process relaxation is taking place.

The fast pulse apparatus has a resolving time of 5×10^{-8} sec and has been used to measure T_1 and the phase memory time T_2 in a wide variety of dilute paramagnets.

In Nd and Ce the echo formation can be visualized in analogy with the arguments which Hahn developed for nuclear spin echoes. In Pr where the r.f. magnetic field is applied parallel to H_0 and to the c axis of the crystal, the formation of the echo is not clearly understood.

The spin echo technique first proposed by Hahn[1] for nuclear spin systems has been applied to relatively few electron spin systems[2,3] because of the difficulty of producing the very short microwave pulses necessary for the measurements.

We have designed and built a fast pulse x-band spectrometer which has 5×10^{-8} sec resolving time. With it we have measured the phase memory time T_2 and the spin lattice relaxation time T_1 in a wide variety of paramagnetic systems, (Table I). Our major effort has been an attempt to correlate the measured spin lattice relaxation times in a variety of rare earth impurities in lanthanum magnesium nitrate (LMN) with some recent theoretical calculations on the rare earth relaxation[4,5,6]. This paper will be divided into two parts: (I) a description of the experimental apparatus and echo formation; (II) a discussion of our results in Ce^{+++}, Nd^{+++} and Pr^{+++} diluted in LMN and the theoretical calculations which apply to them.

Experimental apparatus and echo formation

The equipment[7,8] consists of a pair of magnetrons driven by hard tube modulators which produce 5×10^{-8} sec. pulses of a few hundred watts. The outputs are coupled together and fed to a low Q reflection cavity containing the sample. The echoes, coupled out through a ferrite circulator, are amplified by a traveling wave tube amplifier, detected and presented on a Tektronix 517 oscilloscope. The sensitivity of the system is 60 dbm while most of the echoes have signal to noise ratios of 100 to 1.

The phenomenological picture with which Hahn first described the formation of nuclear echoes applies equally well to the electron spins in the usual case of a Kramers system where we apply the r.f. magnetic field perpendicular to H_0. We do not understand the echo formation in the non-Kramers system where h_{rf} is parallel to H_0.

The net magnetization due to the Boltzmann factor is considered to be aligned parallel to H_0 and the action of the first rf pulse (a so-called $\pi/2$ pulse) is to tip it into the plane perpendicular to H_0. The individual moments precess with their respective Larmor frequencies determined by the quasisteady state local fields and induce a free precession tail decaying with a time $T_2^* = 1/\gamma_A H_{\text{inhomogeneous}}$. The second pulse at time t flips the spins through π radians after which they come back into phase at time $2t$ producing an echo whose amplitude decays (as a function of t) in a time $T_2 = 1/\gamma_A H_{\text{homogeneous}}$, the phase memory time determined by mutual spin flips and spectral diffusion. We thus consider the inhomogeneously broadened line to be made up of homogeneous packets whose width we measure in

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Table I. Spin-lattice and Spin-Spin Relaxation Times.

Paramagnetic center	Concentration (spins/cc)	Temp. (°K)	T_1 (secs)	T_2 (secs)
Mn^{++} in $CaCO_3$	2×10^{18}	77 4.2	2×10^{-5} 3×10^{-3}	7×10^{-7} 3×10^{-6}
K in liquid ammonia	10^{21}	273	3×10^{-6}	3×10^{-6}
Hydrazyl (DPPH)	10^{19}	77	10^{-3}	8×10^{-7}
α-γ bisdiphenylene β- phenylallyl	10^{19}	300 77	5×10^{-6} 10^{-3}	2×10^{-7} 6×10^{-7}
Cr^{+++} in $K_3Co(CN)_6$	3×10^{18} (0.1%)	4.2	6×10^{-3}	10^{-6}
Cr^{+++} in MgO	5×10^{17}	77 4.2	2×10^{-4} 3×10^{-1}	4×10^{-6} 4×10^{-5}

this manner.

The spin lattice relaxation time is measured by observing the amplitude of an echo produced by a pair of pulses as a function of time following the application of a $\pi/2$ (saturating) pulse. This echo amplitude is proportional to M_z and its recovery gives T_1.

The data for T_1 which we obtain agrees well with reported data obtained by other methods in those cases where it is available. No comparable data for T_2 is available.

Paramagnetic relaxation in rare earth salts

Paramagnetic relaxation in dilute rare earth salts has recently been the subject of much interest. Orbach[6] has considered the possible relaxation processes in detail and has estimated the temperature range in which the direct process, the Raman process and the two step Finn, Orbach and Wolf[4] process will predominate in both Kramers and non-Kramers systems.

In the rare earth salts where J is a good quantum number of the free ion, the action of the crystalline field is to split the J multiplet so that there will be a series of nearby excited states and a ground state doublet. For the ions containing an odd number of electrons, this will be a Kramers doublet and resonance will normally be observed with h_{rf} perpendicular to H_0. If the ion has an even number of electrons, the non-Kramers doublet may be made up of states containing no values of J_z differing by unity and the normal type of resonance transition is not allowed. Any lack of symmetry in the crystal field which admixes the two states will allow transitions with h_{rf} parallel to the crystalline axis and to H_0. In Ce^{+++} and Nd^{+++} the echoes were observed with $h_{rf}\perp H_0$ $\perp c$ axis where $g_\perp=1.84$ and 2.72 respectively. In Pr^{+++} h_{rf} // H_0 // c axis where $g_\parallel=1.55$.

The contribution of Finn *et al.* was to suggest that in addition to a direct and Raman process relaxation, the rare earth salts relax via a two phonon process through the lowest lying excited state. If this state lies Δ above the ground state doublet, such a relaxation process should have a temperature dependence $T_1=c\exp(\Delta/kT)$.

Although at temperatures less than 4.2°K there will be very few phonons having energy Δ ($\Delta\sim40$°K), Orbach showed that if the Debye temperature is greater than Δ so that there are some phonon modes available, a resonance phenomena between the crystal field level and these phonons render them very effective in the relaxation process. Thus, in general, this process will dominate both the Raman and direct processes above ~1°K. The Debye temperature[9] is approximately 59°K and the values for Δ for the ions we have investigated are given in Table II along with the temperature dependence of T_1.

The data show that the relaxation in Ce^{+++} and Nd^{+++} is by the Finn, Orbach, Wolf mechanism from 4.2° to approximately 2°K while below this temperature a slower process takes over. On the other hand in Pr^{+++} the relaxation is of the Raman type from 4.2 to 2°K increasing less rapidly at lower temperatures. There are several possible explanations for this. An error (in the right sense) of 10% in θ_D or Δ or both would of course mean

Table II.

Ion	% Impurity	$T_1(T)$	Δ°K	
Ce^{+++}	0.2	$7\times10^{-10}\exp(34\pm2/T)$	34	(Ref. 4)
Nd^{+++}	0.2	$2\times10^{-9}\exp(46\pm2/T)$	48	(Ref. 10)
Pr^{+++}	0.6	$0.36T^{-6.5\pm0.5}$	54	(Ref. 11)

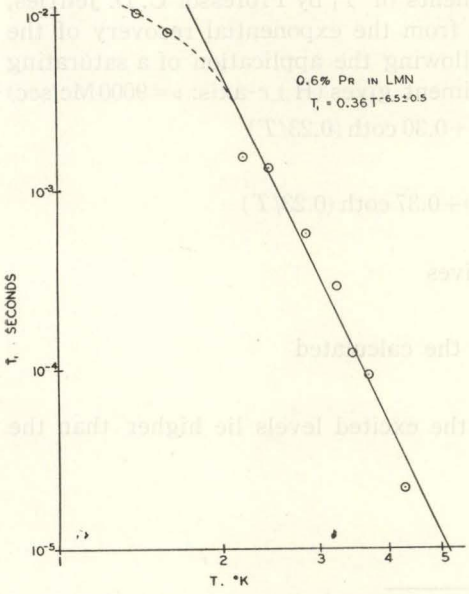

Fig. .1 Temperature dependence of T_1 for Pr^{+++} in LMN.

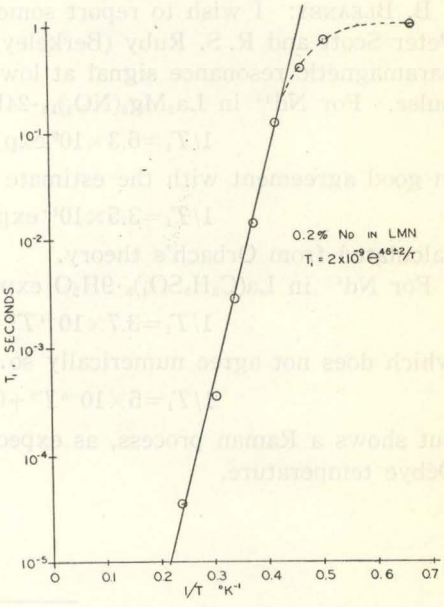

Fig. 3. Temperature dependence of T_1 for Nd^{+++} in LMN.

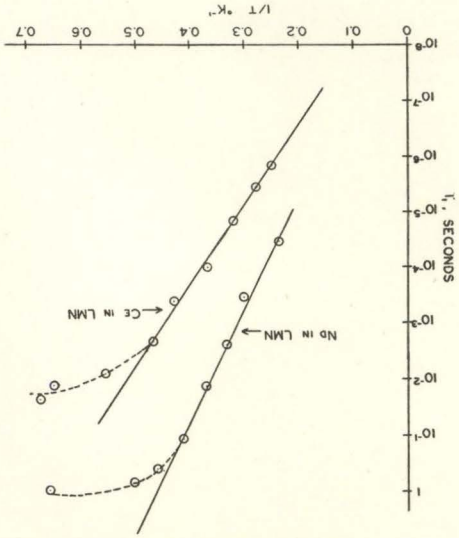

Fig. 2. Temperature dependence of T_1 for Nd^{+++} and Ce^{+++} in LMN.

that there would be no phonon modes to carry out the indirect relaxation. There must also be non vanishing matrix elements between the excited state and the ground state for such relaxation to take place.

We feel that these results demonstrate the usefulness of the spin echo technique and that it may well prove as fruitful a tool in the analysis of electron spin systems as it has for nuclear spin systems.

We would like to acknowledge many valuable discussions with Prof. C. D. Jeffries of the University of Calif., and the assistance of Mr. B. McDonough in construction of the apparatus and taking the data.

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DISCUSSION

B. BLEANEY: I wish to report some measurements of T_1 by Professor C. D. Jeffries, Peter Scott and R. S. Ruby (Berkeley) obtained from the exponential recovery of the paramagnetic resonance signal at low power following the application of a saturating pulse. For Nd^{3+} in $La_2Mg_3(NO_3)_{12}\cdot 24H_2O$ experiment gives ($H\perp c$-axis: $\nu=9000$ Mc/sec)

$$1/T_1=6.3\times10^9 \exp(-47.6/T)+0.30 \coth(0.23/T)$$

in good agreement with the estimate

$$1/T_1=3.5\times10^{10} \exp(-47.6/T)+0.37 \coth(0.23/T)$$

calculated from Orbach's theory.

For Nd^{3+} in $La(C_2H_5SO_4)_3\cdot 9H_2O$ experiment gives

$$1/T_1=3.7\times10^{-4}T^9+7.6T$$

which does not agree numerically so well with the calculated

$$1/T_1=5\times10^{-6}T^9+0.15T$$

but shows a Raman process, as expected since the excited levels lie higher than the Debye temperature.