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Spin-Echo Measurement of the Spin-Lattice and Spin-Spin Relaxation in Ce^{3+} in Lanthanum Magnesium Nitrate*

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Fast-resolution time-pulsed microwave apparatus has been used to measure the spin-spin and spin-lattice relaxation in Ce^{3+} in lanthanum magnesium nitrate by spin-echo techniques. T_1, measured by a three-pulse sequence, varies as $T_1=6\times10^{-10}\exp(34/T)$ over a range of four orders of magnitude from 4°K to 1.8°K but changes less rapidly below this temperature. T_2, measured by the decay of the echo following a two-pulse sequence, is approximately 1 μsec at 1.4°K and drops very rapidly above 3°K.

The accuracy of the numerical values does not seem to be seriously affected by spectral diffusion within the line, but the echo envelope exhibits a striking amplitude modulation which we attribute to surrounding nuclear moments which makes accurate determination of T_2 quite difficult.

INTRODUCTION

THE use of spin-echo techniques as a tool for the investigation of electron spin systems has been limited by the difficulty of producing very short intense microwave pulses and of detecting the resultant relatively weak induction signals. The conditions which must be fulfilled[1] are not trivial and it is only recently that suitable apparatus for investigating a wide variety of paramagnetic systems has been available.[2,3]

We have observed spin echoes in a large number of dilute paramagnets and are reporting measurements made in Ce^{3+} in lanthanum magnesium nitrate in which the spin lattice relaxation takes place by a mechanism recently proposed by Finn, Orbach, and Wolf[4] and Orbach.[5,6] The results which we obtain agree with those obtained by Finn *et al.* using the Casimir–du Pré technique over the range of temperatures 1.9° to 3°K and those of Leifson and Jeffries[7] obtained by observing the change in Q of an electron spin resonance cavity following a saturating pulse.

We have also measured a T_2 which we attribute to the width of the homogeneous packet in the inhomogeneously broadened line. It agrees qualitatively with a calculation based on the theory of Kittel and Abrahams.[8]

Mims *et al.*[9] and Klauder[10] have recently proposed that spectral diffusion is important in the measurement of T_1 and T_2 by spin-echo techniques but, although we see evidence of such diffusion in our data, it does not appear to affect the results seriously.

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EXPERIMENTAL PROCEDURE

The microwave pulses are produced by a pair of Litton L3028B magnetrons driven by hard-tube modulators. The modulator-magnetron combination is capable of producing 100-watt pulses approximately 50×10^{-9} sec wide at the half-power points. The microwave pulses, at 9300 Mc/sec, are coupled through isolators and attenuators to the two side arms of a hybrid T junction, from the H arm through a ferrite circulator to the waveguide cavity which contains the sample. The echo signals are transmitted back through the circulator, to a traveling wave tube amplifier, detected and presented on a Tektronix 517 oscilloscope. (See Fig. 1.)

Since much of the experimental work has been performed at low temperatures and since the magnetrons are essentially fixed-frequency oscillators (9300±20 Mc/sec), it is necessary to be able to tune the cavity to compensate for frequency shifts due to the change in both cavity dimensions and sample properties with temperature. This has been accomplished by a rack-and-pinion gear driven by a stainless-steel tube which inserts a 0.2-in. pin into the center of the broad side of the cavity wall in a region of high electric field. The cavity operates in the TE_{102} mode but has been narrowed from 0.400 in. to 0.250 in. in the narrow dimension to allow room for the tuning pin in the Dewar.

The samples have been ground to fit the full cross section of the guide 0.250×0.900 in., and are approxi-

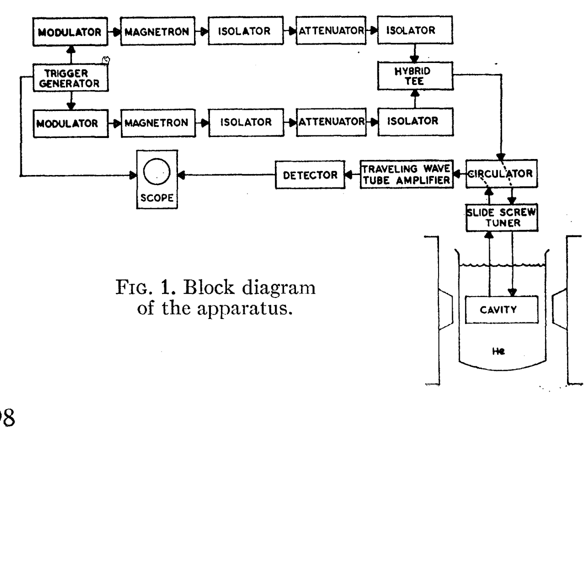


FIG. 1. Block diagram of the apparatus.

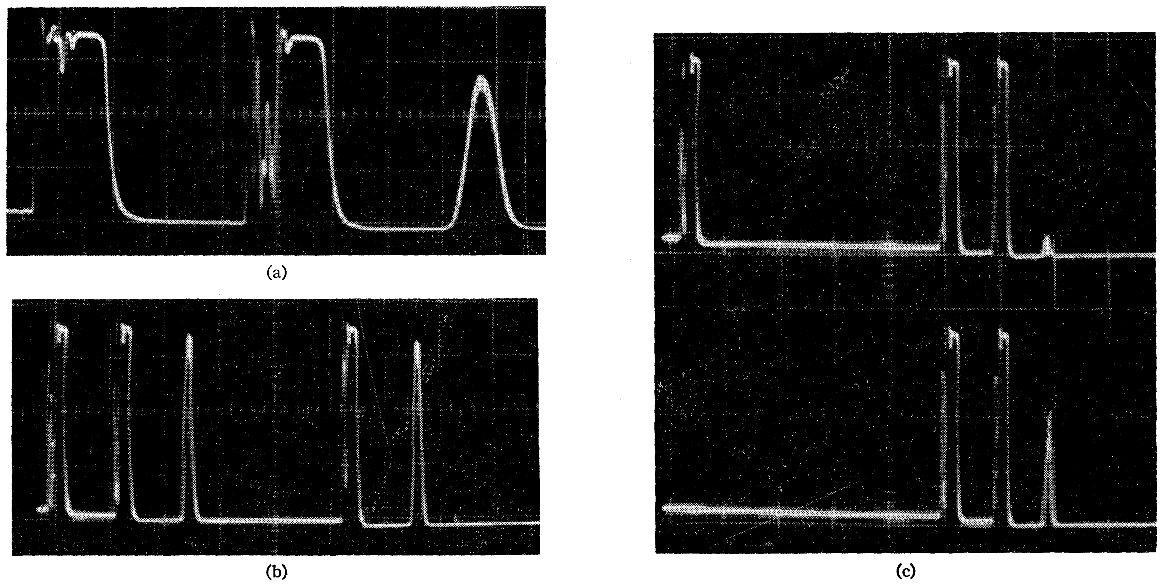


FIG. 2. (a) Two-pulse sequence and echo (sweep rate 0.2 μsec/cm). (b) Three-pulse sequence and stimulated echo (1 μsec/cm). (c) Echo measuring recovery from $\pi/2$ pulse (1 μsec/cm).

mately 0.06 in. thick, weighing 0.2 to 0.6 g. To insure good thermal contact of the samples with the helium bath (for measurements made between 4.2°K and 1.6°K), two small holes have been drilled in the cavity wall on either side of the sample which is placed in the region of high rf magnetic field.

The system of trigger pulses allows three types of spin-echo measurements:

(a) A two-pulse ($\pi/2$, then π) sequence giving an echo decaying in time T_2, the spin-spin relaxation time, [Fig. 2(a)].

(b) A three-pulse sequence ($\pi/2$, θ, then $\pi/2$) which produces, among others, a stimulated echo decaying with a time determined by T_1 and diffusion [Fig. 2(b)].

(c) A three-pulse sequence ($\pi/2$, then $\pi/2$, π) which produces an echo following the second pair of pulses whose amplitude represents M_z and which, to a good approximation, measures T_1 as determined by the recovery of the spin system following the first $\pi/2$ pulse [Fig. 2(c)].

The data plotted in Fig. 3 were taken using both type (a) and type (c) pulse sequences. At the highest temperature where $T_1 \simeq T_2$, the only quantity which could be measured was T_2 as given by the two-pulse sequence, and even this lay just within the time resolution limits of the apparatus. At lower temperature the data were taken using type (c) pulse sequence which gives accurate results so long as $T_1 > \tau$, the time between the sampling pulses.

T_1's from 50×10^{-9} sec to 20×10^{-3} sec may be determined, being limited on the low end by the time resolution of the apparatus and on the high end by diffusion effects giving rise to cross relaxation. The data were taken on crystals nominally containing 0.2% Ce^{3+} and were taken with the applied magnetic field perpendicular to the c axis.

DISCUSSION

In the ideal spin-echo experiment, the pulse width is short compared to the reciprocal of the linewidth,

$$T_2^* = 1/\gamma\Delta H_{\text{inhomogeneous}},$$

and the rf magnetic field, h_1, is large compared to the linewidth ΔH_{inho}. Under these conditions the entire line is saturated and the measured T_2 and T_1 will be determined in the usual manner. The inhomogeneous lines which we are investigating have widths from 2 to 20 oersteds, corresponding (at $g=2$) to 0.2 μsec$\leq T_2^*$ ≤ 0.02 μsec. Usually our pulses do not span the line and therefore the $\pi/2$ pulse "burns a hole" in the line. This gives rise to two phenomena. The free-precession tail following the pulse, and consequently the echo shape, is determined by the width of the hole rather than the real linewidth. More important is the fact that the unsampled portion of the line perturbs the decay of the saturated portion.

This occurs in two ways: (1) The decay of the excited "A" spins proceeds by mutual spin flips with the unexcited "B" spins as well as by the spin lattice process. This manifests itself in the case of long T_1's by a fast initial decay and a slower asymptotic decay. The asymptotic value is taken to be T_1. (2) The flipping of the B spins shortens the phase memory time of the A spins, and therefore the T_2 which we measure is perturbed. This would be a very important process if our T_2 data were good enough for accurate measurement. As it is, the modulation of the echo envelope by the surrounding nuclei makes it possible to obtain only

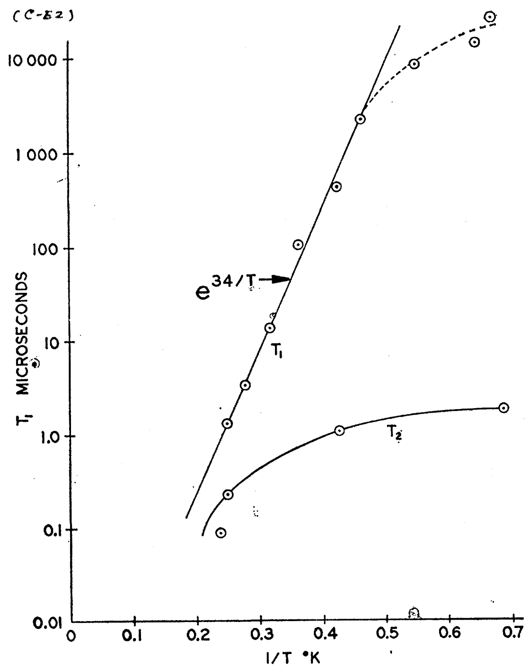


FIG. 3. Temperature dependence of the spin-spin and spin-lattice relaxation time in Ce^{3+} in lanthanum magnesium nitrate.

relative numbers and this diffusion does not seem to be critical. Mims has considered the problem in detail and has shown that it is very important under the conditions of his experiment. Our pulses are considerably stronger and it appears that they more nearly approach the conditions of an ideal spin-echo experiment.

THEORY AND RESULTS

Spin-lattice relaxation in rare-earth salts has been a subject of much interest, although until recently the relaxation process has been poorly understood. Finn *et al.* and Orbach have postulated a two-step relaxation process which applies to cerium in the following way.

If the J multiplet is split so that the first excited crystal field level lies an energy Δ above the ground state, relaxation may take place by a two-step process through this real level—each step conserving energy. In order for this to occur, phonons of energy Δ must be available, which imposes the condition that Δ be less than the Debye temperature. Orbach's theory shows that there will be a resonance between the phonons of every Δ and the crystalline field levels, so that relatively few phonons very effectively carry on the relaxation process. This will go on so long as there are some phonons of this energy and gives rise to a temperature dependence:

$$T_1 = C \exp(\Delta/kT).$$

When the temperature is lowered to the point where the phonon population is depleted, the direct process dominates the relaxation.

The data which we have taken are best fitted by

$$T_1 = 6\times10^{-10} \exp(34/T)$$

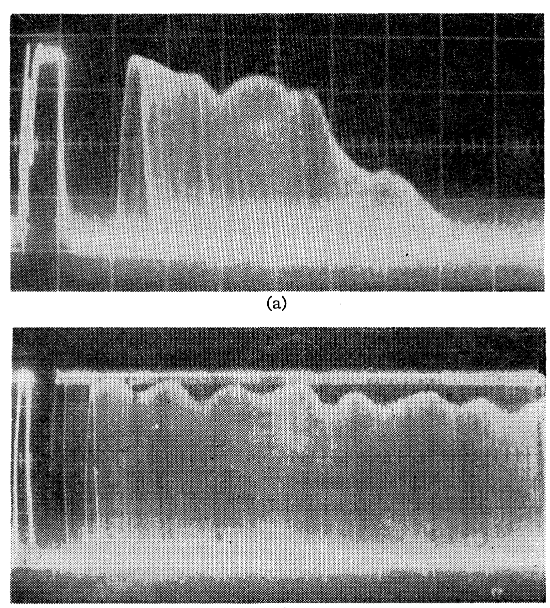
at the higher temperatures but T_1 changes less rapidly below 1.8°K where the direct process is taking over. This agrees well with the theoretical predictions as well as with the data taken by Finn *et al.* using the Casimir–du Pré technique and by Leifson and Jeffries obtained by observing the recovery of an electron spin resonance cavity following a saturating pulse.

The echoes observed as a function of time using both the two-pulse sequence and the three-pulse stimulated echo sequence exhibit a modulation of the echo envelope which we attribute to the nuclei surrounding the paramagnetic ion, (Fig. 4). The modulation exhibits a double period of 2.3 μsec and 1.2 μsec at $\theta = 90°$ and is strongly anisotropic. There are four nuclei present in significant abundance which, at 3650 gauss, at which the experiments were performed, would exhibit the following nuclear resonance periods:

Nucleus	Percent abundance	Nuclear resonance period (μsec)
La^{139}	99.9	0.6
N^{14}	99.6	1.2
H^1	100.0	0.08
Mg^{25}	10.0	1.4

There are six nitrate groups surrounding each cerium site so that the total modulation may be due solely to nonequivalent nitrogen nuclei. This technique should prove useful for investigating nuclear-electron coupling.

The values of spin-spin relaxation time obtained by observing the decay of the echo following a two-pulse



(a)

(b)

FIG. 4. (a) Envelope of two-pulse echo (0.5 μsec/cm). (b) Envelope of three-pulse echo (1 μsec/cm).

sequence are not very accurate because of this modulation. At the same time, an order-of-magnitude calculation using the equation of Kittel and Abrahams gives a few microseconds for T_2. As the temperature is increased, diffusion presumably becomes more important, giving the observed temperature dependence of T_2.

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Degenerate Germanium. II. Band Gap and Carrier Recombination

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The data bearing on the band structure of degenerate germanium have been abstracted from the literature and intercompared. A variety of effects are described in terms of a voltage characteristic of each. It is found that all the voltages have essentially the same value and show a striking independence of the carrier concentrations. The conclusion is drawn that this voltage closely represents the band gap of degenerate germanium. It is shown that the thermal current at low temperature must be carried by recombination in the junction, which gives the proper barrier if the recombination centers lie near the band edge. This model of recombination explains the thermal current, the minority carrier lifetime, the excess current, and the emission spectrum. The reflectivity peak at 2.2 ev is also consistent if the bands at the [111] edge are roughly parallel to each other. The barrier found from the transition capacitance is not understood. The recombination centers lie close to the band edge. Assuming they are donors and acceptors, their capture cross section at room temperature is about 10^{-15} cm^2 per neutral atom. On the basis of this model, the thermal gap of highly degenerate germanium is about 30 mv less than for the unperturbed lattice. The shrinkage is independent of temperature.

I. INTRODUCTION

THIS paper studies the change of the band gap of germanium doped to degeneracy and the change in carrier recombination processes for diodes of degenerate germanium by a comparison of information contained in several recent publications. It offers an interpretation of the effects found and in particular of the studies of the forward admittance of germanium tunnel diodes by Meyerhofer *et al*,[1] to which it is a sequel.

Evidence is accumulating that the onset of degeneracy produces important modifications of the energy bands of germanium and the recombination processes. Reflection measurements by Cardona and Sommers[2] and emission[3] and absorption[4] measurements by Pankove show that doping to degeneracy has a significant effect on the band edges of *n*-type germanium. In forward-biased tunnel diodes, there occurs a carrier transport process which is associated with neither the normal Zener effect nor with the thermal current.[5] Meyerhofer *et al.*[1] found that the potential barrier controlling the flow of the thermal current in forward-biased tunnel diodes does not change with doping in the way predicted by the theory of Shockley[6] which has been so successful in explaining the forward current for germanium diodes of nondegenerate material. Finally, the injection efficiency of the emitter junctions of germanium transistors no longer changes with doping and with temperature as expected from the treatment of Shockley[6] when the emitter is degenerate.[7]

The large number of phenomena whose changes with doping in the region of degeneracy seem to be at variance with each other and with experience at lower dopings has pointed to the need of an analysis of the more striking discrepancies. In this paper we compare the findings of researches of two types; optical measurements on tunnel diodes[3] or homogeneous materials,[2] and studies of classical conduction[1,8] or tunneling[1,9] in junction diodes.

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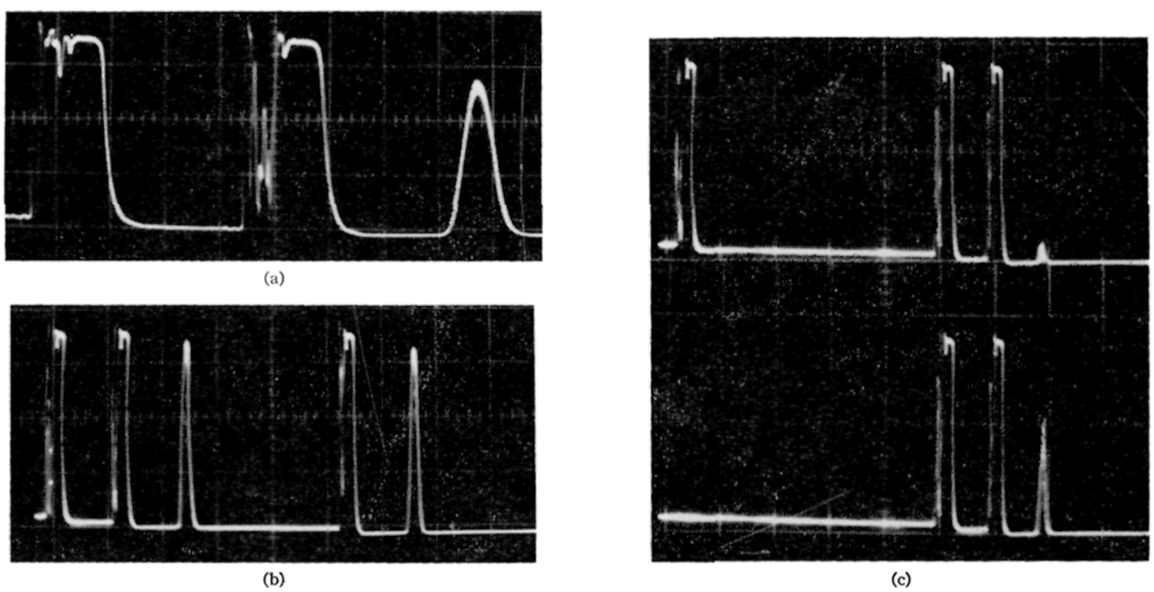

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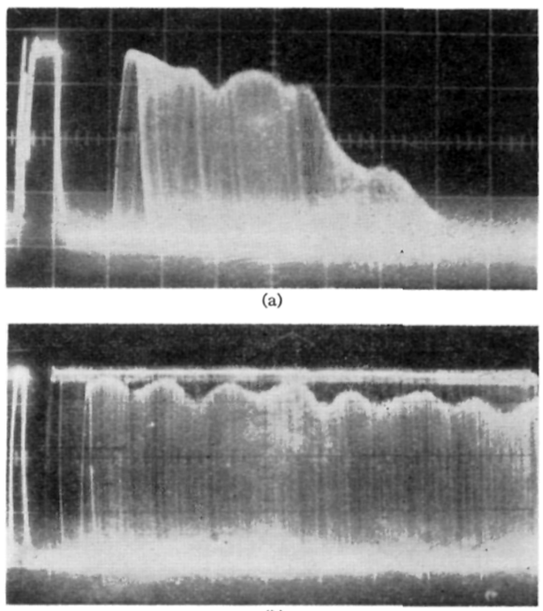

FIG. 4. (a) Envelope of two-pulse echo (0.5 μsec/cm). (b) Envelope of three-pulse echo (1 μsec/cm).