

Laboratori Nazionali di Frascati

LNF-69/35

G. Baldacchini and V. Montelatici : PROTON SPIN-LATTICE  
RELAXATION IN LANTHANUM NITRATE DOPED WITH NEODYMIUM

Estratto da : Lett. Nuovo Cimento 1, 649 (1969)

G. BALDACCHINI, *et al.*  
1° Maggio 1969  
*Lettere al Nuovo Cimento*  
Serie I, Vol. 1, pag. 649-652

## Proton Spin-Lattice Relaxation in Lanthanum Magnesium Nitrate Doped with Neodymium.

G. BALDACCHINI and V. MONTELATICI

*Laboratori Nazionali del CNEN - Frascati (Roma)*

(ricevuto il 15 Marzo 1969)

The spin-lattice relaxation time of protons in hydration water of diamagnetic crystals with paramagnetic impurities depends on the magnetic dipolar interaction between the protons and the paramagnetic ions.

The phenomenological shell-of-influence model <sup>(1)</sup> predicts the proton relaxation time,  $T_p$ , to be given by the expression

$$(1) \quad T_p^{-1} = \frac{3}{10} \left( \frac{g\beta}{H} \right)^2 \frac{1}{r_1^3 r_2^3} \operatorname{sech}^2 \left( \frac{g\beta H}{2KT} \right) T_e^{-1},$$

where  $r_1$  is the minimum distance between ion and proton,  $2r_2 \propto 2N^{-\frac{1}{3}}$  (ion/cm<sup>3</sup>)<sup>- $\frac{1}{3}$</sup>  the average distance between ions,  $g \simeq 2.7$ ,  $\beta$  the Bohr magneton,  $H$  the constant external magnetic field,  $T$  the heat bath temperature,  $T_e$  the ion spin-lattice relaxation.

Measurements performed <sup>(1)</sup> on the protons of the double lanthanum magnesium nitrate crystals [La<sub>2</sub>Mg<sub>3</sub>(NO<sub>3</sub>)<sub>12</sub>·24H<sub>2</sub>O] with 1% neodymium impurities are in agreement with formula (1) as far as the dependence on magnetic field and temperature is concerned. There is only a small number of experimental data on the crystals with different concentrations <sup>(2,3)</sup>.

In this letter we present measurements on the proton relaxation time performed with two different amounts of neodymium (1% and 3.5%) in order to verify the dependence of  $T_p$  on the concentration (these concentrations refer to grown solutions).  $T_p$  was measured by photographing the decaying signals of protons enhanced by the dynamic method <sup>(4,5)</sup>. The decaying signals are impressed on an optical storage oscilloscope at fixed times. The proton polarization was enhanced to about 100 times that of thermal equilibrium polarization. After switching off the microwave pumping power, the meas-

<sup>(1)</sup> T. J. SCHMUGGE and C. D. JEFFRIES: *Phys. Rev.*, **138**, A 1785 (1965).

<sup>(2)</sup> J. RAMAKRISHNA: *Proc. Phys. Soc.*, **92**, 520 (1967).

<sup>(3)</sup> G. M. VAN DEN HEUVEL, C. T. C. HEYNING, T. J. B. SWANENBURG and N. J. POULIS: *Phys. Lett.*, **27** A, 38 (1968).

<sup>(4)</sup> A. ABRAGAM: *The Principles of Nuclear Magnetism* (Oxford, 1961).

<sup>(5)</sup> O. S. LEIFSON and C. D. JEFFRIES: *Phys. Rev.*, **122**, 1781 (1961).

urements were taken after a time interval long enough (approximately 10% of the relaxation time) to permit thermalization of the crystal with the heat bath.

To detect the proton signal we used a conventional  $Q$ -meter detector modified by using a repetitive linear frequency sweep (<sup>6,7</sup>). The repetition rate was varied to not perturb the polarization when the proton relaxation times become very long at lower temperatures. Within the experimental errors one exponential decay was observed for all polarizations.

The experimental results at 6370 G and 9100 G are given in Fig. 1 and Fig. 2. They were obtained on two single crystals (size  $(3 \times 4 \times 6)$  mm<sup>3</sup>) with their optical axis at  $\simeq 90^\circ$  with the direction of the external magnetic field. The solid lines are given by the following relationships:

$$(2) \quad \left\{ \begin{array}{l} T_p^{-1}(1\%, \quad 9.1 \text{ kG}) = \left[ 5.03 \times 10^{-16} H^3 \operatorname{ctgh} x + \frac{9.87 \times 10^{11}}{H^2} \exp \left[ \frac{-47.6}{T} \right] \right] \operatorname{sech}^2 x, \\ T_p^{-1}(3.5\%, \quad 9.1 \text{ kG}) = \left[ 9.33 \times 10^{-15} H^3 \operatorname{ctgh} x + \frac{7.54 \times 10^{12}}{H^2} \exp \left[ \frac{-47.6}{T} \right] \right] \operatorname{sech}^2 x, \\ T_p^{-1}(1\%, \quad 6.37 \text{ kG}) = \left[ 8 \times 10^{-16} H^3 \operatorname{ctgh} x + \frac{1.14 \times 10^{12}}{H^2} \exp \left[ \frac{-47.6}{T} \right] \right] \operatorname{sech}^2 x, \\ T_p^{-1}(3.5\%, \quad 6.37 \text{ kG}) = \left[ 1.53 \times 10^{-14} H^3 \operatorname{ctgh} x + \frac{6.12 \times 10^{12}}{H^2} \exp \left[ \frac{-47.6}{T} \right] \right] \operatorname{sech}^2 x, \end{array} \right.$$

where  $x = g\beta H/2KT$ . These relationships represent the best fit of the experimental values obtained by using formula (1) in which  $T_e$  is given by the sum of a direct and an Orbach process (<sup>8</sup>) (<sup>\*</sup>).

The true ratio between neodymium concentrations in the two crystals was measured with a conventional bridge spectrometer (EPR at  $\simeq 34$  GHz); the value  $N(3.5\%)/N(1\%) = 2.5 (\pm 5\%)$  was found.

By using this value the proton relaxation time was found proportional to  $N^{-K}$  with  $K \simeq 3$ , in contrast with formula (1) in which  $K = 1$ . In the theory given in ref. (<sup>3</sup>) a value  $K = 3$  was derived for high concentrations, while a value  $K = 1$  was obtained for low concentrations.

Introducing the third power for  $N$  in (1), in our case we obtain

$$(3) \quad \frac{T_p(1\%)}{T_p(3.5\%)} = \left[ \frac{N(3.5\%)}{N(1\%)} \right]^3 \frac{T_e(1\%)}{T_e(3.5\%)}$$

for a given magnetic field.

(<sup>6</sup>) M. BORGHINI, P. ROUBEAU and C. RYTER: *Nucl. Instr. Meth.*, **49**, 259 (1967).

(<sup>7</sup>) G. BALDACCHINI and V. MONTELATICI: *Ricerca Scientifica*, **5**, 418 (1968).

(<sup>8</sup>) P. L. SCOTT and C. D. JEFFRIES: *Phys. Rev.*, **127**, 32 (1962).

(<sup>\*</sup>) An analysis of the coupled equations for the two spin species shows that the proton relaxation time is independent of the phonon bottleneck process which is relevant for the ion relaxation time (<sup>8</sup>). Hence one has the form  $T_e^{-1} = aH^3 \coth x + b \exp[-47.6/T]$  for Nd<sup>3+</sup> in nitrate.

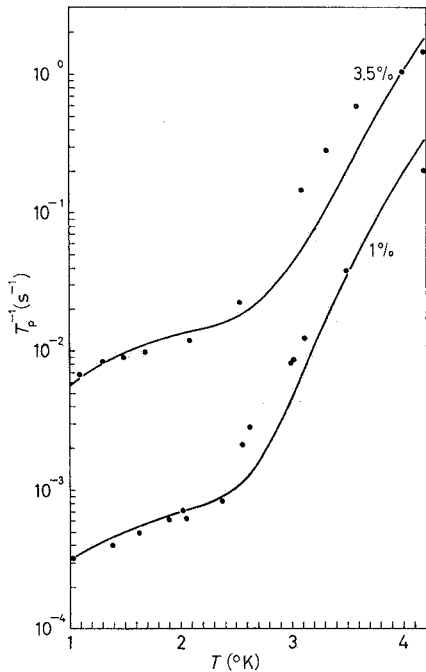


Fig. 1. - Proton spin-lattice relaxation times at 6370 gauss vs. °K for 1% and 3.5% impurities (maximum error 10%).

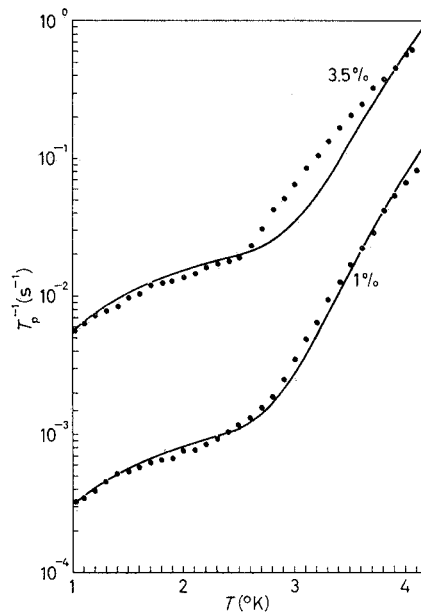
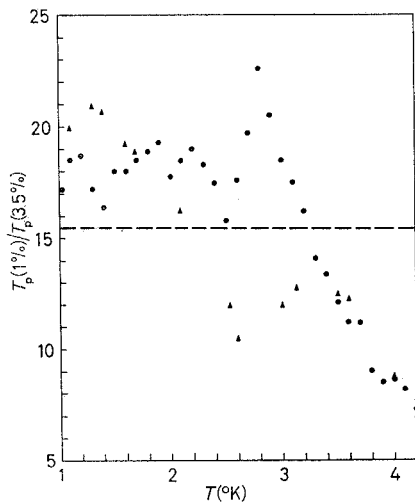


Fig. 2. - Proton spin-lattice relaxation times at 9100 gauss vs. °K for 1% and 3.5% impurities (maximum error 10%).



Measurements of the ion relaxation time<sup>(9-11)</sup> have been performed by other authors. Their results are in disagreement about the dependence on the concentration below  $\approx 2.5^\circ\text{K}$ . Above  $2.5^\circ\text{K}$ , in the Orbach region, they found similar results, independent of the concentration. The disagreement is within  $(20 \div 30)\%$  at low temperature for small differences of concentration, as in the present case. Hence the ratio (3) should be essentially constant in the range of liquid-helium temperature. Figure 3 shows the ratios of the experimental relaxation times and the  $(2.5)^3$  value. The agree-

Fig. 3. - Proton spin-lattice relaxation time ratios vs. °K; the dashed line is the  $(2.5)^3$  value:  $\blacktriangle$   $H_0 \approx 6370$  gauss,  $\bullet$   $H_0 \approx 9100$  gauss.

(9) R. H. RUBY, H. BENOIT and C. D. JEFFRIES: *Phys. Rev.*, **127**, 51 (1962).  
 (10) J. RAMAKRISHNA: *Indian Journ. Pure Appl. Phys.*, **5**, 565 (1966).  
 (11) E. J. VERWEY: *Phys. Lett.*, **28 A**, 152 (1968).

ment is fairly good for temperature below  $\simeq 3^\circ\text{K}$  with the exception of the results obtained at 6370 G. Above  $\sim 3^\circ\text{K}$  the proton relaxation time is not consistent with the best fit, especially for higher concentrations.

We wish to remark that in this last case a certain number of satellite lines on both sides of the main EPR neodymium line was observed (their overall area corresponds to approximately 8% of that of the main line). Such lines were not observed in the crystal having 1% of Nd impurities.

By now no attempt has been done to understand the influence of these lines on the ion relaxation time. However it is probable that these satellites influence directly the proton relaxation by means of a cross-relaxation between them and the proton line.

Therefore formula (1) should be completed by considering the presence of a cross-relaxation term depending on the ion concentration. Summarizing our results, we can conclude that the shell-of-influence model is valid at least at low temperatures ( $\lesssim 3^\circ\text{K}$ ) regarding the constancy of the ratio of relaxation times. At higher temperatures measurements with various concentrations and different magnetic fields are needed to explain results still not understood.

G. BALDACCHINI, *et al.*

1° Maggio 1969

*Lettere al Nuovo Cimento*

Serie I, Vol. 1, pag. 649-652