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Preliminary study of dynamic polarization in LaMN

GIUSEPPE BALDACCHINI (*) & VINICIO MONTELATICI
Laboratori Nazionali di Frascati (CNEN) – Frascati (Roma)

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1 – Dynamic nuclear orientation.

In this article we report some measurements on the dynamic polarization of protons in the hydration water of $La_2Mg_3(NO_3)_{12} \cdot 24\ H_2O$(LaMN) doped with paramagnetic impurity of Nd^{3+}. The enhancement of normal polarization, which occurs when a microwave source saturates the transitions that simultaneously flip a proton and a Nd^{3+} ion, is based on the so-called ' effet solide '. This effect is a consequence of the dipole-dipole coupling in a system containing two kinds of spins. We shall describe it qualitatively and refer to the pertinent literature for a deeper understanding [1-4].

Our system, LaMN crystal, may be represented, from a magnetic point of view, as formed by paramagnetic ions S of neodimium and by protons I of the crystallization water molecules. The Nd^{3+} ion has an angular momentum $\hbar \boldsymbol{S}$ with ' effective spin ' $|\boldsymbol{S}| = 1/2$ and magnetic moment $\gamma_s \hbar \boldsymbol{S}$. This model may be assumed to be adequate in the range temperature of liquid helium [5]. The gyromagnetic ratio γ_s, because of the spin-orbit-crystal field coupling, depends on the angle, θ, between the axis of the crystal and the magnetic field direction [5]. The energy levels for the (S, I) pair in an external field H_0, neglecting dipolar magnetic interaction, are:

$$E(M_s, m_I) = |\gamma_s| \hbar H_0 M_s - \gamma_I \hbar H_0 m_I \tag{1}$$

This situation is represented in Fig. 1 where n_i are the mean occupation numbers of the levels E_i and N, n refers to electrons and protons respectively. Fig. 1-*a* shows the allowed transitions for which $\Delta m_I = 0$ $\Delta M_s = \pm 1$ and $\Delta m_I = \pm 1$ $\Delta M_s = 0$. The dipolar magnetic coupling between S and I mixes partially the energy levels through its non-diagonal terms so that there is a relaxation probability $w = \alpha\, w_s$ (w_s electron transition probability and $\alpha \simeq H_0^{-2}$) between levels, Fig. 1-*b*, for which $\pm \Delta m_I = \pm 1$ $\Delta M_s = \pm 1$. Thus the resonance spectrum

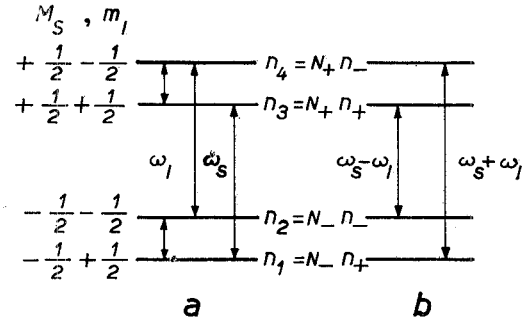

FIG. 1 – Energy levels of (I, S) system.

(*) (CNR) fellowship 1966.

of the crystal, in our scheme, has a finite intensity at the frequencies $\omega_{1,2} = \omega_s \pm \omega_I$, $\omega_3 = \omega_s$, $\omega_4 = \omega_I$.

Supposing the lines ω_1, ω_2, ω_3, completely resolved, an electromagnetic field of frequency, e.g. ω_1, may induce transitions between the levels 4, 1 and change the level population from the Boltzmann equilibrium. If, moreover, the nuclear relaxation process is slower than the electronic one, the electronic population ratio is not modified from its Boltzmann equilibrium. When the saturation condition, $n_4 = n_1$, is satisfied, the nuclear population ratio is:

$$\frac{n_+}{n_-} = \left(\frac{N_+}{N_-}\right)_0 = \exp\left(-\frac{\hbar\omega_s}{kT}\right) \tag{2}$$

which corresponds to a polarization defined as $p = (n_+ - n_-)/(n_+ + n_-)$, $(\gamma_s)/\gamma_I \simeq 660$ times greater than the static value. Generally there is not complete saturation and if W is the transition probability induced by the electromagnetic field, proportional to the microwave power, one obtains [6, 7]

$$p = \pm \tanh\left\{-\frac{hH_0}{2kT}\left[Z\left(|\gamma_s| + \gamma_I\right) - \gamma_I\right]\right\} \tag{3}$$

in which $Z = W/(W + w)$ is a saturation parameter and the lower sign applies to the case of pumping at frequency ω_2. Obviously this formula represents an ideal case because our simple model does not consider some effects which reduce the polarization.

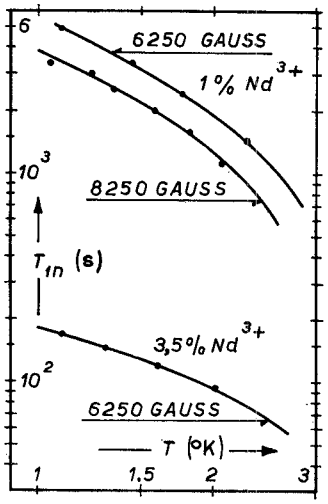

FIG. 2 – Proton relaxation time.

Often the three lines of the electronic spectrum are not resolved so that one cannot saturate a given line without simultaneously interfering with the others. The optimum condition is $\omega_I > \Delta\omega_{1/2}$, where $\Delta\omega_{1/2}$ is the electronic line width, and this may be obtained with the highest possible high magnetic fields.

A more rigorous treatment [4] shows a dependence of p on the 'leakage factor' $(1 + nT_s/NT_I)^{-1}$ where, T_I and T_s are the spin-lattice relaxation time. In a typical case where $T = 2$ °K, 1 % concentration of Nd^{3+}, $n/N \simeq 10^4$, $T_s \simeq 10^{-2}$ s and $T_I = 10^3$ s one has a factor $\simeq 0.9$; with a concentration of 3.5 %, T_I decreases more than an order of magnitude, Fig. 2, and the factor becomes $\simeq 0.7$. Another effect, the phonon bottleneck, limits the polarization. This phenomenon depends on the low number of phonons at low temperatures; they are not able to transfer the energy received from paramagnetic ions to the heat bath, consequently the lattice temperature, which is of importance for the protons, reaches a value higher than the heat bath temperature.

All these effects and others, which limit the value of polarization, have been considered theoretically by many authors [8, 9]. Generally there is not a good quantitative agreement with the experimental results but only a qualitative one.

2 – Measurements and experimental apparatus.

The measurements are performed in magnetic fields of 8.250 gauss and 6.250 gauss corresponding to the Larmor frequency of 23.990 Mc/s, $\theta \simeq 56^{\circ}$, and 23.300 Mc/s, $\theta \simeq 85^{\circ}$, for electrons and 35.500 kc/s and 26.500 kc/s for protons on two crystals doped respectively with 1 % and 3.5 % of Nd^{3+}.

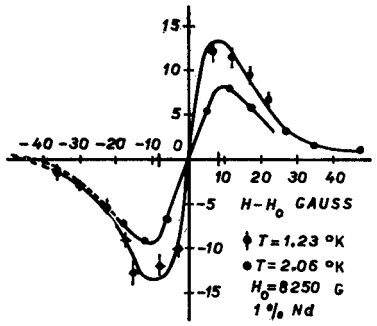

FIG. 3 – Dynamic polarization versus magnetic field.

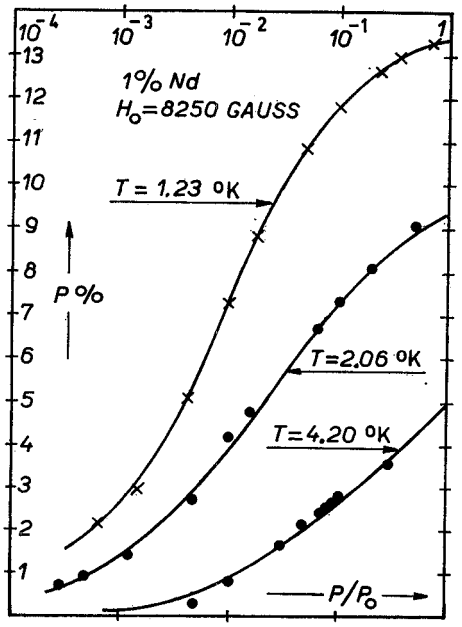

FIG. 4 – Dynamic polarization versus pumping power.

The crystals are grown from a saturated solution of magnesium nitrate (analytical), lanthanium nitrate (purity 99.997) and neodynium nitrate (purity 99.9) in a temperature bath at about 0 °C. The Nd ions appear not to crystallize as readily as La ions and it is estimated (private communication from Gilbert Shapiro) that the crystals grown from 1 % doped solution contain only about 0.2 % Nd. Fig. 3 shows the dynamic polarization as a function of the magnetic field at different temperatures with constant frequency and microwave power; in the same figure are drawn the position of the two normally forbidden transitions ω_1 and ω_2, the electronic one is at the center. The dependence of the maximum positive polarization on the pumping power is shown in Fig. 4 for a few temperatures; such a dependence is observed to be in agreement with the formula (3). The curves of Fig. 5 give the highest polarization obtainable with the available power as a function of temperature. It can be noted that at the higher field the polarization is lower. This is due to a less resolved spectrum at 8.250 gauss than that at 6.250 gauss, because of

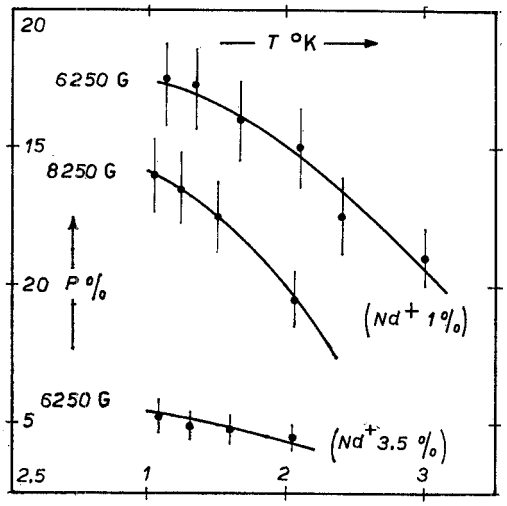

FIG. 5 – Dynamic polarization versus temperature.

a wider line at $\theta = 56^{\circ}$ compared with the corresponding line at $\theta = 85^{\circ}$ at 6.250 gauss. The polarization does not follow the $1/T$ dependence and this is caused primarily by the onset of phonon bottleneck. Moreover, the leakage factor certainly is responsible for the low polarization of the 3.5 % Nd crystal. The maximum polarization value, of 18 % must be compared with the ideal value of 55 % for $T = 1$ °K and $f_s = 24.000$ Mc/s. However, our measurements indicate that the higher polarization may be obtained with 1 % Nd crystals.

The crystal samples are put in a tunable microwave cavity [10] immersed in a

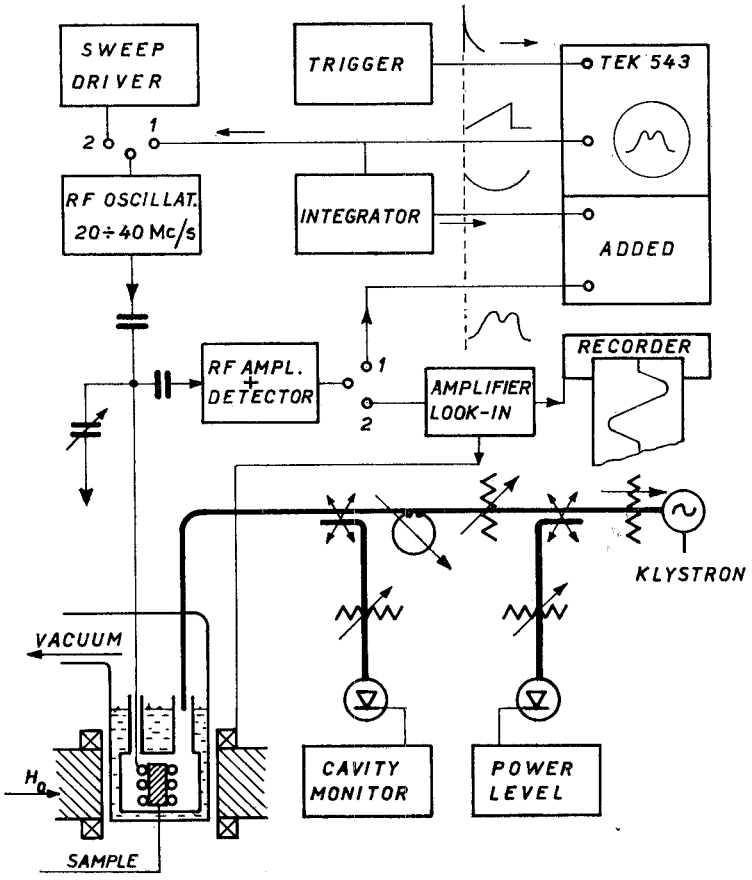

FIG. 6 – Block diagram of experimental apparatus.

helium bath able to reach and maintain a temperature of 0.9 °K. The lower end of the glass dewar is placed between the pole pieces of a magnet, which gives a field with a total stability of 1 part in 10^4 and a homogenity on the sample volume better than 10^{-4}. The electronic resonance is observed with a wide band detection spectrometer, Fig. 6, which is driven by a klystron OKI24V11 with a maximum output power of 0.5 watts. The nuclear magnetic resonance is detected by using two methods, Fig. 6, a narrow (position 2) and a wide band (position 1) system. Both systems enable detection of the variations of potential at the end of an L C parallel circuit (a wire envelops the crystal) which is tuned at the Larmor frequency; it is fed by a constant

current oscillator. This spectrometer, known in the literature as a Q-meter is very versatile because of its linearity, essential in this kind of measures. The sensibility of the narrow band method (or lock-in amplifier) is by far better. Therefore we have used it to detect the signal at the thermal equilibrium buried in the noise; $p_0 = 0.08$ % for 1 °K and 8.000 gauss. On the other hand the periodic method is sufficient to detect signals amplified over $p \simeq 0.5$ % and has the advantage of monitoring continuously and does not saturate the signal. Fig. 7 shows the photos, taken every 10 minutes, of the decay of the proton signal, detected with the periodic method. From these we have obtained the relaxation time of Fig. 2. The quoted values of the polarization are determined from the formula:

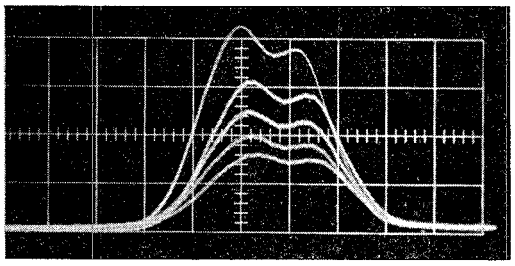

FIG. 7 – Oscilloscope photography of proton signals.

$$(4) \qquad p = p_0 \frac{S}{S_0} \left(1 \pm 1/2 \left| \frac{\Delta V}{V_0} \right| \right)$$

in which $p_0 = 2.36 \times 10^{-5} f_0$ (Mc/s)$/T_0$ (°K), S_0 is the area of the natural signal, S the area of the amplified signal and $|\Delta V/V_0|$ ($\leqslant 0.2$) the maximum percentage variation of the Q-meter voltage when crossing the resonance, with the upper sign for $p < 0$ and the lower one for $p > 0$. The small correction $\Delta V/V_0$ is due to the non linearity of the Q-meter, because of the high absorption (or emission) of the proton signal.

In closing we would note the importance of the methods of dynamic polarization (other than in the experiments of high energy particles) in the study of properties of solid state physics, such as relaxation time, spin diffusion, phonon bottleneck, F-center and correlated effects.

REFERENCES

[1] ABRAGAM, A. & PROCTOR, N. G.: *Compt. rend.*, **246**, 2253 (1958).

[2] UBERSFIELD, J.; MOTCHANE, J. L. & ERB, E.: *Colloques intern. Recherche scientifique, LXXXVI Sur la résonance magnétique (Centre National de la Recherche Scientifique*, Paris, 1958) p. 49.

[3] ABRAHAM, M.; CAUSLAND, M. A. H. & ROBINSON, F. N. H.: *Phys. Rev. Letters*, **2**, 449 (1959).

[4] LEIFSON, O. S. & JEFFRIES, C. D.: *Phys. Rev.*, **122**, 1781 (1961).

[5] SCOTT, P. L. & JEFFRIES, C. D.: *Phys. Rev.*, **127**, 32 (1962).

[6] BALDACCHINI, G. & MONTELATICI, V.: Laboratori Nazionali di Frascati, LNF-67/64 (1967).

[7] MONTELATICI, V.: *Nuovo Cimento*, **47**, 104 (1967).

[8] BORGHINI, M.: *Phys. Letters*, **20**, 228 (1966).

[9] GUNTER, C. T. E. & JEFFRIES, C. D.: *Phys. Rev.*, **159**, 290 (1967).

[10] BALDACCHINI, G. & MONTELATICI, V.: Laboratori Nazionali di Frascati, LNF-65/32 (1965).