Laboratori Nazionali di Frascati

V. Montelatici and G. Tomassetti: EXPERIMENTAL OBSERVATION ON LMN OF AN EFFECT RELATED TO THE NUCLEAR DYNAMIC- POLARIZATION

Experimental Observation on LMN of an Effect Related to the Nuclear Dynamic Polarization.

V. MONTELATICI and G. TOMASSETTI

Laboratori Nazionali del CNEN - Frascati

The magnetic interaction among nuclear spins and few paramagnetic ions is the mechanism through which the nuclear polarization can be enhanced by about three orders of mangitude, and through which the nuclear spins relax.

In the case of the dynamic polarization by solid effect observed in the diamagnetic crystal LMN $\equiv La_2Mg_3(NO_3)\cdot24H_2O$ doped with 1% of paramagnetic ions N_d^{+3f}, it seems appropriate to use the phenomenological shell-of-influence model developed by JEFFRIES and coworkers [1]. Particularly, if the average distance between the paramagnetic ions is $2R_3$, the protons around the ion can be treated as follows: the protons within the shell $R_1 < R < d$ are under the direct influence of the ion, while the n'' protons in the shell $d < R < R_3$ do not interact directly with the ion. The n'' « distant protons » rapidly come into internal equilibrium with a caracteristic time, t_d, by means of mutual spin flips, that is by diffusion of proton polarization [2,3]; the near protons strongly interact with the ion and the mutual spin flips are hindered. R_1 is the minimum distance between the central ion and the nearest proton. By using the X-ray data of the crystal structure JEFFRIES and coworkers give the following figures: $R_1 = 4.4$ Å, $R_3 = 30$ Å, while typical value of the diffusion barrier is $d = 10$ Å, and $t_d = 0.1$ s. Furthermore, they show that the protons being within the distance of 7 Å do not contribute to the proton resonance as a consequence of the effect of the local ion field. The relatively few n' « near protons » in the shell 7 Å $< R < d$, under the direct influence of the ion have a relatively fast average relaxation rate T_n^{-1}.

This is actually not strictly true since these protons have a relaxation rate proportional to r^{-6}, but however their fast relaxation rate is faster than that one of the distant protons.

In order to observe the solid effect by pumping at a microwave frequency $v_- = v_s - v_I$ on the forbidden line of the ion spectrum, an enhanced proton polarization is build up at a negative temperature; an enhanced proton signal at a positive temperature can be also obtained by pumping at frequency $v_+ = v_s + v_I$. After a maximum enhanced proton polarization is obtained, for example, by pumping at the frequency v_+, pumping

[1] T. J. SCHMUGGE and C. D. JEFFRIES: *Phys. Rev.*, **139**, A 1785 (1965).
[2] T. E. GUNTER and C. D. JEFFRIES: *Phys. Rev.*, **159**, 290 (1967).
[3] G. R. KHUTSISHVILI: *Sov. Phys. Uspekhi*, **8**, 5, 743 (1966).

can be changed at the frequency ν_-; then the proton polarization decreases and reaches the maximum at negative temperature passing through zero polarization.

Since the two groups of protons, n' and n'', have different relaxation rate, the « near protons » reach the maximum negative polarization in a short time whereas the « distant protons » always stay at positive polarization.

Thus at time t^*, when zero polarization is observed, one has n' protons polarized at a negative temperature and n'' protons polarized at positive temperature, both having the same absolute value. Now at time t^* the pumping power can be swicthed off, and the two groups of protons must reach an internal equilibrium at a common temperature through an effective cross relaxation rate $T_x^{-1} \ll t_d^{-1}$; that is they obey the coupled equation

(1)
$$\begin{cases} \dot{p}' = -(p' - p_0')\, T_{n'}^{-1} - \dfrac{n''}{n' + n''}\,(p' - p'')\, T_x^{-1}\,, \\[2mm] \dot{p}'' = -(p'' - p_0'')\, T_{n''1}^{-1} - \dfrac{n'}{n' + n''}\,(p'' - p')\, T_x^{-1}\,, \end{cases}$$

where $T_{n''1}^{-1}$ is a relaxation rate due to spurious relaxation, in our case $T_{n''1}^{-1} = 0$. The solution of eq. (1) gives the time evolution of $p'(t)$ and $p''(t)$. With a fast time constant $\tau_f^{-1} \simeq T_x^{-1} + T_{n'}^{-1}$ they reach the common value $p''(t^*)$ and subsequently, with a slow time constant $\tau_s^{-1} \simeq (n'/n'')\, T_{n'}^{-1}$, they reach the thermal equilibrium value at the temperature of the heat bath. As a consequence of this process after the time t^* one must observe a growing signal over zero proton polarization, and a subsequent decay.

In order to detect this growing signal with high sensitivity, we used an improved version of the repetitive method of ref. ([4,5]). Figure 1 shows the schematic diagram of the apparatus used to detect the thermal equilibrium signal of the protons at 1.6 °K and 9100 G.
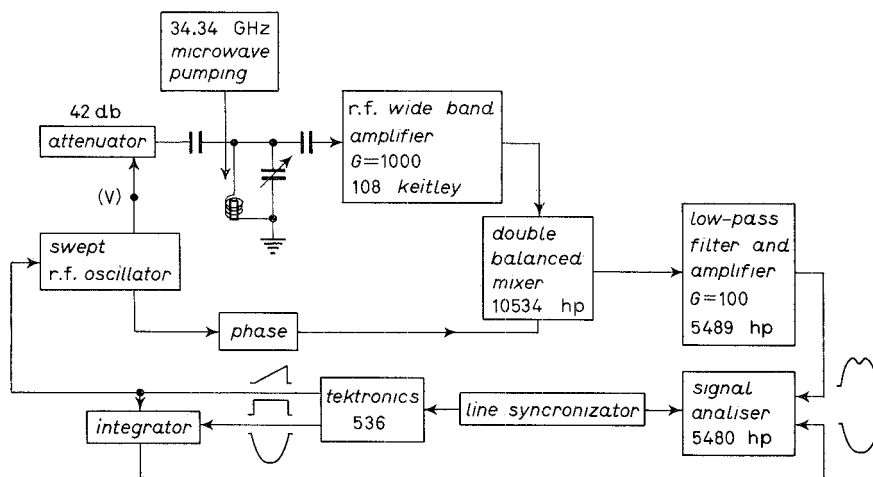

Fig. 1. – Skecth of the improved apparatus to detect the proton magnetic resonance; at point (v.) there is a radiofrequency voltage $\simeq 2$ V peak to peak.

([4]) M. BORGHINI, P. ROUBEAN and C. RYTER: Nucl. Instr. and Meth., 49, 259 (1967).
([5]) G. BALDACCHINI and V. MONTELATICI: Nuovo Cimento, 68 B, 253 (1970).

The radiofrequency oscillator was swept for about 250 kHz at the top of the voltage of the LC tuned circuit by means the saw tooth of an oscilloscope. This saw tooth was integrated and added to the LC signal to give an approximately straight line on which the proton resonance signal can be observed. The repetition time was 20 ms, each sweep was 10 ms long, the number of signals averaged to destroy the noise was 2^8. Not to saturate the resonance proton signal the voltage level of the radiofrequency oscillator was strongly reduced in the tuned LC circuit. After amplification, the amplitude modulated carrier at 39.75 MHz with a 250 kHz band width was mixed with a reference signal at the same frequency in a double balanced mixer working as a phase detector, Fig. 1.

The detected growing signal, normalized respect to the thermal equilibrium proton signal, is shown in Fig. 2. The sample ($\simeq 3 \times 4 \times 6$ mm³) was a LMN crystal, whose optical axis was at an angle of about 90° with the direction of the magnetic field.

Firstly the separation in Gauss between the maximum proton enhancements was determined and then measurements where done by shifting the magnetic field rather than the pumping frequency at 34.34 GHz. The maximum enhancement, determined as a function of the pumping microwave power, was about 450 in the range from 0 to 3 db of the full power available from the microwave oscillator.
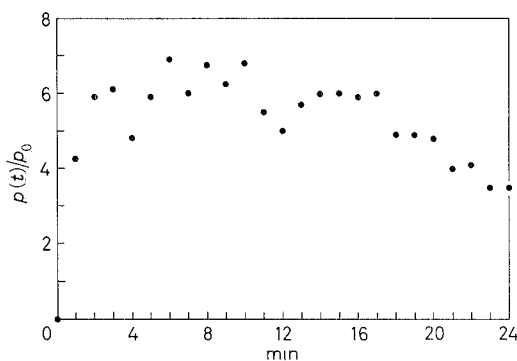

Fig. 2.   Fig. 3.

Fig. 2. – Ratio of the area of the enhanced proton resonance to the area of the thermal equilibrium proton signal, after time t^*. Maximum error 20%: $P_0 = 2.40 \cdot 10^{-5}(39.75 \text{ (MHz)}/1.6 \text{ (°K)}) = 5.956 \cdot 10^{-4}$, $H_0 \simeq 9100$ G, $T = 1.6$ °K.
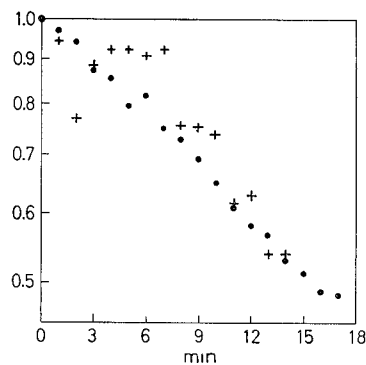
Fig. 3. – Decay of the proton signal area taken from the enhanced polarization (● dot), maximum error 6%; decay of the proton signal area taken after ten minutes the time t^* (+ cross).

In Fig. 3 the decay of the maximum enhancement, after pumping power at frequency ν_+ is switched off, is shown also the decay of the growing signal represented after it has reached the maximum value. The two decays display the some relaxation time within the experimental error.

From Fig. 2 one see that the growing signal reaches its maximum after a few minutes and then begins to decay. Unfortunately, our measurements do not permit to observe any possible presence of various growing times. However, one can observe that more than the half maximum is reached with a time shorter than the time to reach the maximum.

The time constant, τ_f, can be evaluated to be some tenths of seconds.

Furthermore, we observe that the enhanced maximum signal at frequency ν_+ takes a time of about 120 s to reach zero polarization when the pumping power is changed

to the frequency ν_-, that is the n' and n'' protons reach the same temperature in a time shorter than that occurring to reach zero polarization. This result seems to rule out the possibility of introducing a mechanism of cross relaxation between n' and n'' protons during the build up time of the polarization [2]. Indeed, the cross relaxation should take the two groups of protons to the same temperature in a shorter time than the relaxation time and not growing effect should be observable after the pump is swiched off at time t^*. The temperature of all protons should be infinite and only the growing of the proton signal to the thermal-equilibrium value should be observed. On the contrary, we observe an enhanced proton signal about 6.5 times the thermal-equilibrium value.