

Laboratori Nazionali di Frascati

LNF-73/78

V. Montelatici :  
THE SPIN DIFFUSION IN THE DYNAMIC POLARIZATION BY  
SOLID EFFECT

Nuovo Cimento 17B, 129 (1973).

## The Spin Diffusion in the Dynamic Polarization by Solid Effect (\*).

V. MONTELATICI

*Laboratori Nazionali di Frascati del CNEN - Frascati*

(ricevuto il 5 Ottobre 1972; manoscritto revisionato ricevuto il 13 Febbraio 1973)

**Summary.** — By considering  $N$  electron spins  $S_i$  and  $n$  nuclear spins  $I_j$  ( $S_i = I_j = \frac{1}{2}$ ) coupled by a weak dipolar interaction which mixes the autostates by means of a coefficient  $|e_{ij}| = \frac{3}{2} \gamma_s \hbar H^{-1} R_{ij}^{-3} \sin \theta_{ij} \cos \theta_{ij}$  ( $R_{ij}$  is the distance between  $S_i$  and  $I_j$ ,  $\theta_{ij}$  the angle between  $S_{iz} - I_j$  and the direction of the magnetic field) it is possible to write the differential equations for the spin and the  $j$ -th spin. These microscope equations can be averaged on those nuclei and ions for which one can establish an isotropic distribution and a unique temperature on the nuclei at any time. By solving the differential-equation system one obtains the same particular result foreseen by the theory of spin diffusion.

### I. — Introduction.

The dynamic polarization by solid effects has been studied extensively by many authors. The phenomenon has been studied from two particular viewpoints, by using two types of approaches: those of JEFFRIES<sup>(1,2)</sup>, based on the Bloembergen method, and those of ABRAGAM and BORGHINI<sup>(4)</sup>, based on the Provotorov equations<sup>(5)</sup>. We notice that the more general method

---

(\*) To speed up publication, the author of this paper has agreed to not receive the proofs for correction.

(1) C. D. JEFFRIES and O. S. LEIFSON: *Phys. Rev.*, **122**, 1781 (1961).

(2) T. J. SCHUMUGGE and C. D. JEFFRIES: *Phys. Rev.*, **138**, A 1785 (1965).

(3) T. E. GUNTER and C. D. JEFFRIES: *Phys. Rev.*, **159**, 290 (1967).

(4) M. BORGHINI and A. ABRAGAM: *Proceedings in the Low Temperature Physics*, Vol. 4 (Amsterdam, 1964).

(5) B. N. PROVOTOROV: *Sov. Phys. JETP*, **14**, 1126 (1962).

of ABRAGAM and BORGHINI contains the first as a particular case. The former method is valid in the case that the spectral ionic lines are well resolved and extremely sharp.

Both methods assume a unique relaxation time for all protons, or in other words the nuclear spin diffusion <sup>(6)</sup> is postulated to explain the polarization transport towards the distant nuclei from the paramagnetic ion. The theory of spin diffusion has been developed up to the general formulation given by KHUTSISHVILI <sup>(7-10)</sup> after the work of BLOEMBERGEN in 1949. Indeed the experimental measurements, in a sample of  $\text{La}_2\text{Mg}_3(\text{NO}_3)_{12} \cdot 24\text{H}_2\text{O} + 1\% \text{Nd}$ , which contains  $n \simeq 10^3 N$  protons in the water of hydration and  $N$  neodymium atoms, show a unique proton relaxation time.

But it is known that a few protons «near» the neodymium ion interact with the paramagnetic impurity more strongly than with each other, and are relaxed directly by dipolar coupling with the ion at a rate  $T_{\text{near}}^{-1} \propto r_{ij}^{-6}$ , where  $r_{ij}$  is the distance of the proton  $j$  from the ion  $i$ . The greater number of the «distant» protons, beyond a certain distance from the ion, reach an internal thermal equilibrium via the spin diffusion and they have a unique relaxation time which is measured in the conventional experiments.

Some authors <sup>(2,3)</sup> by introducing a phenomenological cross-relaxation between the «near» and the «distant» protons have been able to write a system of differential equations in the  $n$  (distant),  $n$  (near),  $N$  (ion) variable.

As a consequence, by solving such a system, the relaxation time of the «distant» protons as well as the proton polarization is determined. This model is insensitive to the value of the diffusion barrier, although the effect of the diffusion is important to establish a unique temperature for the «distant» protons. The different results of the relaxation time expressions are the most important differences between this model and the spin diffusion theory.

In this article, we want to show that under the hypothesis of an isotropic distribution of the protons and ions the rate equation gives the same result as the diffusion theory.

## 2. - The coupled equations of the solid effect.

The coupled equations which give the time evolution of the polarizations of protons  $p(t)$  and of ions  $P(t)$  (protons and ions with spin  $I = \frac{1}{2}$  and  $s = \frac{1}{2}$

<sup>(6)</sup> N. BLOEMBERGEN: *Physica*, **15**, 386 (1949).

<sup>(7)</sup> P. G. DE GENNES: *Journ. Phys. Chem. Sol.*, **3**, 345 (1958).

<sup>(8)</sup> W. E. BLUMBERGEN: *Phys. Rev.*, **119**, 79 (1960).

<sup>(9)</sup> G. R. KHUTSISHVILI: *Sov. Phys. Usp.*, **8**, 743 (1966) (original Russian edition: *Usp. Fiz. Nauk*, **87**, 211 (1966)).

<sup>(10)</sup> H. E. RORSCHACH jr.: *Physica*, **30**, 38 (1964).

respectively) are <sup>(11)</sup>

$$(1) \quad \begin{cases} \dot{p}(t) = -(p - p_0)w\beta \frac{N}{n} \left( \frac{1}{P_0} - P_0 \right) - W \frac{N}{n} \beta (p \mp P), \\ \dot{P}(t) = -(P - P_0) \frac{w}{P_0} (\alpha + \beta) - W\beta (P \mp p), \end{cases}$$

where the gyromagnetic ratios of ions and protons are  $\gamma_s < 0$  and  $\gamma_I > 0$ .  $W$  is the transition probability induced by an electromagnetic field at frequency  $\nu_s$ , which is central with respect to the frequencies  $\nu_{\pm} = \nu_s \pm \nu_I$ . The terms in (1) which have the double sign must be understood as a sum of two terms: that with the upper sign refers to the pumping frequency  $\nu_+$ , the lower one refers to the pumping frequency  $\nu_-$ .  $(w/P_0)^{-1}$  is the relaxation time of the ions. We suppose that the lattice is always at thermal equilibrium with the heat bath, so that the coefficient of the phonon bottle-neck is zero.  $N$  is the number of ions and  $n$  is the number of protons in the volume  $V$  of the sample. The coefficients  $\alpha$  and  $\beta$  are related to the distance  $r_{ij}$  between the  $i$ -th ion and the  $j$ -th proton by the relations

$$(2) \quad \alpha = \frac{\left(1 - \sum^n \varepsilon_j^2\right)^2}{\left(1 + \sum^n \varepsilon_j^2\right)^2}, \quad \beta = \frac{4 \sum^n \varepsilon_j^2}{\left(1 + \sum^n \varepsilon_j^2\right)^2} \equiv \sum^n A_j,$$

where

$$\varepsilon_j^2 = \frac{3}{40} \left( \frac{\hbar \gamma_s}{H} \right)^2 r_{ij}^{-6}$$

is a coefficient due to the mixing of the autostates of the  $i$ -th ion and  $j$ -th proton by means of the dipolar magnetic interaction between them.

The values  $p(t)$  and  $P(t)$  represent average values over all protons and ions, that is

$$(3) \quad p(t) = \frac{\sum^n p_j(t)}{n}, \quad P(t) = \frac{\sum^N P_i(t)}{N}.$$

From the expression of the average value it is possible to go back to the values for one proton and one ion. In this way it should be possible to deduce the conditions under which the average is done.

---

<sup>(11)</sup> G. BALDACCHINI and V. MONTELATICI: *Nuovo Cimento*, **68** B, 253 (1970).

By introducing the sums in (1) one has

$$(4) \quad \begin{cases} \frac{1}{n} \sum_{j=1}^n \dot{p}_j(t) = -\frac{w}{n} \sum_{j=1}^n \sum_{i=1}^N A_{ij} \left( \frac{1}{P_{0i}} - P_{0i} \right) (p_j - p_{0j}) - \frac{W}{n} \sum_{j=1}^n \sum_{i=1}^N A_{ij} (p_j \mp P_i), \\ \frac{1}{N} \sum_{i=1}^N \dot{P}_i(t) = -\frac{w}{N} \sum_{i=1}^N \left[ \sum_{j=1}^n A_{ij} + \frac{\left( 1 - \sum_{j=1}^n \varepsilon_j^2 \right)^2}{\left( 1 + \sum_{j=1}^n \varepsilon_j^2 \right)^2} \right] \left( \frac{P_i}{P_{0i}} - 1 \right) - \\ - \frac{W}{N} \sum_{i=1}^N \sum_{j=1}^n A_{ij} (P_i \mp p_j). \end{cases}$$

From the differential-equation system (4) by multiplying by  $n$  and  $N$  and by dropping the corresponding sums in the first and in the second equation respectively one obtain a system for the  $j$ -th proton and  $i$ -th ion <sup>(12)</sup>.

From these coupled equations for the pair  $j$ - $i$  one goes back to (1) by performing the average over all protons and ions when the following conditions are satisfied:

- I)  $p_1 = p_2 = p_3 = \dots = p_n \equiv p$ ,  $p_{01} = p_{02} = \dots = p_{0n} \equiv p_0$ ,
- II)  $A_{1j} = A_{2j} = \dots = A_{Nj}$ ,
- III)  $P_1 = P_2 = \dots = P_N \equiv P$ ,  $P_{01} = P_{02} = \dots = P_{0N} \equiv P_0$ .

Hypothesis III) is reasonable. Hypothesis I) means that at any time all protons have the same polarization, that is to say, the same relaxation time. Hypothesis II) means that around each ion all protons are distributed isotropically. If, moreover, an isotropic distribution of the ions is supposed then each ion sees the same number of protons distributed in  $N$  spheres of influence, and each sphere contains  $n/N$  protons. Thus, an explicit calculation of the relaxation time, after performing the averages, gives

$$(5) \quad T_I^{-1} = \frac{w}{P_0} \frac{N}{n} \beta (1 - P_0^2), \quad T_s^{-1} = \frac{w}{P_0} (\alpha + \beta) = \frac{w}{P_0}.$$

By introducing a continuous distribution one has

$$(6) \quad \begin{aligned} \frac{N}{n} \sum_{j=1}^n A_j &= \frac{3}{10} \left( \frac{\hbar \gamma_s}{H} \right)^2 \frac{N}{n} \left[ \sum_{j=1}^{n_R} r^{-6} + \sum' r^{-6} \right] \left[ 1 + \sum_{j=1}^n \varepsilon_j^2 \right]^{-2} = \\ &= \frac{3}{10} \left( \frac{\hbar \gamma_s}{H} \right)^2 \frac{\int_{R_i}^R r^{-6} dn + \int_{R_i}^{R^*} r^{-6} dn}{\int_{R_i}^R dn} \left[ 1 + \sum_{j=1}^n \varepsilon_j^2 \right]^{-2} = \end{aligned}$$

<sup>(12)</sup> M. BORGHINI: *Phys. Rev. Lett.*, **16**, 318 (1966).

$$\begin{aligned}
&= \frac{3}{10} \left( \frac{\hbar\gamma_s}{H} \right)^2 \frac{1}{R_1^3 R^3} \left[ 1 + \frac{1 - R^3/R_*^3}{R^3/R_1^3 - 1} \right] \left[ 1 + \sum_{j=1}^n \varepsilon_j^2 \right]^{-2} \simeq \\
&\simeq \frac{3}{10} \left( \frac{\hbar\gamma_s}{H} \right)^2 \frac{1}{R_1^3 R^3} \left[ 1 + \left( \frac{R_1}{R} \right)^3 \left( 1 - \frac{R^3}{R_*^3} \right) \right],
\end{aligned}$$

where the apex indicates a sum over the external protons to the sphere of the radius  $R$ ,  $R_1$  is the minimum distance from the ion which is about a factor 10 less than  $R$ ,  $dn = n^* 4\pi r^2 dr$ , and  $n^*$  is the proton density. Moreover, the following approximation is made:

$$\begin{aligned}
(7) \quad 1 + \sum_{j=1}^n \varepsilon_j^2 &= 1 + \frac{(n/N) \sum_{j=1}^n \varepsilon_j^2}{n/N} = \\
&= 1 + \frac{4\pi}{10} n^* \left( \frac{\hbar\gamma_s}{H} \right)^2 \frac{1}{R_1^3} \left( 1 - \frac{R_1^3}{R^3} \right) \left[ 1 + \frac{R_1^3}{R^3} \left( 1 - \frac{R^3}{R_*^3} \right) \right] \simeq 1.
\end{aligned}$$

The approximation (7) is better when the external magnetic field is higher: one has  $\gamma_s \simeq 2 \cdot 10^7 \text{ cm}^{-1} \text{ G}^{-1}$ ,  $n^* \simeq 4 \cdot 10^{23} \text{ cm}^{-3}$ ,  $R_1 \simeq 4 \text{ \AA}$ , then  $1 + \sum \varepsilon_j^2 = 1 + \pi \cdot 10^5 H^{-2}$ .

The term due to protons external to the sphere with radius  $R$  is less than unity and decreases rapidly as  $R_*$  increases. Therefore one approximates the sum over all protons by means of the sum over  $n/N$  protons. Then (6) represents the average value of the mixing coefficient over the protons in the spherical shell defined by the radii  $R_1 \leq r \leq R$ . By using (5) and (6) the relaxation time of the proton is

$$(8) \quad T_I^{-1} = (1 - P_0^2) T_s^{-1} \frac{3}{10} \left( \frac{\hbar\gamma_s}{H} \right)^2 \frac{1}{R_1^3 R^3}.$$

This expression is that given by JEFFRIES<sup>(3)</sup> and co-workers. It is deduced by supposing hypothesis I) satisfied for all protons in the sphere of radius  $R$ .

### 3. - The relaxation time given by the diffusion theory.

Qualitatively we observe that the protons sufficiently near the ion have a high probability to be flipped by the ion-proton dipolar interaction. On the contrary, at greater distances, the protons are mutually coupled by proton-proton dipolar interaction. Therefore, at any time, the near protons have polarization depending on the distance. Consequently the hypothesis I) is not satisfied. Thus, it is necessary to discriminate between the near protons and the distant ones. Only the distant protons satisfy the condition I). After averaging

over these protons and ions, it is possible to take the common factors  $p(t) - P_0$  and  $P(t) - P_0$  outside the sums. The possibility of discriminating between near and distant protons is given by the theory of spin diffusion.

The theory, in the form given by KHUTSISHVILI<sup>(9)</sup>, assumes an isotropic distribution of the ions and protons. Each ion sees a sphere of radius  $R$  containing  $n/N$  protons. The protons in such a sphere are divided by a sphere of radius  $\delta$  into two groups. The near protons at distances  $0 < r < \delta$ , the distant ones at distances  $\delta < r < R$ . The diffusion barrier  $\delta$  is defined as the distance from the ion for which the difference of the Zeeman frequencies of two neighbouring protons is of the order of the width of the proton magnetic line,  $\delta \simeq \simeq (\gamma_s/\gamma_I)^{\frac{1}{2}} a$  ( $a$  is the distance between neighbour protons) (\*).

The study of the transport equation, which describes the behaviour of the spin diffusion, introduces a parameter  $b$ . Its value with respect to the value of the diffusion barrier  $\delta$  gives rise to two different expressions of the relaxation time.

Particularly: if  $b < \delta$ , the distant protons reach an internal equilibrium in a short time, so that the magnetization is a function of the time only. The near protons, at distances  $0 < r < b$ , are under the retarded direct influence of the ion in the region  $b < r < \delta$ .

This case is called rapid spin diffusion, since the process of diffusion (that is the thermalization of the distant proton) is more rapid than the rate due to the ion.

If  $b > \delta$  the spin diffusion is important for the protons at a distance  $b < r < R$ , while the protons for which  $r < b$  are under the direct influence of the ion. This case is called limited spin diffusion. The ratio of the relaxation times in the two cases is

$$(9) \quad \frac{T(b > \delta)}{T(b < \delta)} = 1.6 \left(\frac{b}{\delta}\right)^3$$

and

$$T(b < \delta) = \frac{3}{10} T_s \left(\frac{H}{\hbar\gamma_s}\right)^2 (\delta R)^3,$$

the parameter  $b$  is related to the diffusion constant  $D$  by the relation

$$b = 0.68 \left[ \frac{10}{3} \left(\frac{\hbar\gamma_s}{H}\right)^2 D^{-1} T_s^{-1} \right]^{\frac{1}{2}}.$$

In the case of the neodymium salt one has  $b < \delta$  for temperatures less than 4 °K. One can calculate  $b \simeq 1 \text{ \AA}$ ,  $\delta \simeq 10 \text{ \AA}$ .

---

(\*) For a detailed analysis of the diffusion barrier see ref. (10).

#### 4. - The relaxation time in the coupled equations.

By averaging the equations for the pair  $j$ - $i$  over the distant protons  $n_d$  and over  $N$  ions, one obtains the relaxation time.

The near protons  $n_r$  are excluded from the average since they have different values of  $p(t) - P_0$ , which implies that hypothesis I) is not satisfied.

By calling the distant protons of the sample  $n^+ = n_d N$  we have the expression of the relaxation time

$$(10) \quad T^{-1} = T_s^{-1}(1 - P_0^2) \frac{3}{10} \left( \frac{\hbar\gamma_s}{H} \right)^2 (\delta R)^{-3},$$

where we have used (6) with the substitution  $n \rightarrow n^+$ .

The ratio of the two expressions (10) and (8) is  $(\delta/R_1)^3$  since we have excluded the protons inside the sphere of radius  $\delta$ .

The near protons are governed by a number of equations equal to the number of those protons that, among  $n_r$ , have a unique relaxation time and a unique polarization. This choice can be made by dividing the sphere of radius  $\delta$  into many concentric spheres all containing the same number of protons.

The smaller the thickness of these spherical shells is the more exactly the inside protons have the same relaxation time at any time. If we choose  $R_0 < \delta$  as the radius of the first sphere with radius less than  $\delta$ , the spheres of radii

$$R_K = [\delta^3 - K(\delta^3 - R_0^3)]^{\frac{1}{3}} < R_{K-1} = [\delta^3 - (K-1)(\delta^3 - R_0^3)]^{\frac{1}{3}}$$

determine a shell of thickness  $R_{K-1} - R_K$  containing  $\bar{n}$  protons as does the shell of thickness  $\delta - R_0$ .

All the  $N$  spheres, having the same  $K$ , contain  $\bar{n}_K = \bar{n}N$  protons with the same value of polarization. By averaging over  $\bar{n}_K$  and  $N$  one finds

$$(11) \quad \begin{cases} \dot{p}_K = -(p_K - p_0) \frac{w}{P_0} \sum_{j=1}^{\bar{n}_K} A_j \frac{N}{\bar{n}_K} (1 - P_0^2) - \frac{N}{\bar{n}_K} W \sum_{j=1}^{\bar{n}_K} A_j (p_K \mp P) , \\ \dot{P} = -(P - P_0) \frac{w}{P_0} - W \sum_{j=1}^{\bar{n}_K} A_j (P \mp p_K) . \end{cases}$$

The relaxation time of these protons is

$$(12) \quad T_K^{-1} = T_s^{-1} \frac{N}{\bar{n}_K} \sum_{j=1}^{\bar{n}_K} A_j (1 - P_0^2) \simeq T_s^{-1} \frac{3}{10} \left( \frac{\hbar\gamma_s}{H} \right)^2 (1 - P_0^2) (r_K r_{K-1})^{-3},$$

where approximations analogous to those performed in (6) are made.



If  $r_K \simeq r_{K-1}$  one has  $T_K^{-1} \propto r_K^{-6}$ , a result in agreement with the general theory of the relaxation <sup>(13)</sup>.

The stationary value of the polarization is

$$\begin{aligned}
 (13) \quad p_K^{(s)} &= \frac{\mp (N/\bar{n}_K) \sum_{j=1}^{\bar{n}_K} A_j W P_0}{1 + (1 + (\bar{n}_K/N)(T_s/T_K)) T_K (N/\bar{n}_K) \sum_{j=1}^{\bar{n}_K} A_j W} = \\
 &= \frac{\mp P_0}{1 + (1 - P_0^2) \sum_{j=1}^{\bar{n}_K} A_j} \frac{W}{W + T_s^{-1} \frac{1 - P_0^2}{1 + (1 + P_0^2) \sum_{j=1}^{\bar{n}_K} A_j}},
 \end{aligned}$$

where  $\sum_{j=1}^{\bar{n}_K} A_j$  is a quantity much less than unity as one can verify by substituting  $R_1, R, n$  in (7) by  $r_K, r_{K-1}, \bar{n}_K$  respectively.

We note that the stationary value of the polarization, that is, of the magnetization, is independent of the position to a good approximation. On the contrary, as the time interval increases, the magnetization depends on  $r_K$  as one finds by taking the solution of (11) as a function of time.

As a consequence the stationary value of the magnetization of the near protons of the sample is

$$(14) \quad M(\text{tot}) = N\bar{n} \sum p_K^{(s)} = N n_r p_K^{(s)},$$

where the sum is over all the spherical shells. The evolution of  $M(t)_{\text{tot}}$  is not a unique exponential, but a distribution of exponentials. Clearly it is actually impossible to detect in conventional experiments such a distribution during the growth of magnetization since the number  $n_r$  is a fraction of  $n_d$ . If one does not take into account the effect of the local field of the ion, one has the maximum number of near protons

$$(15) \quad \frac{n_r}{n_d} = \frac{\delta^3}{R^3(1 - \delta^3/R^3)};$$

for  $\delta \simeq 10 \text{ \AA}$ ,  $R \simeq 30 \text{ \AA}$  one obtains  $n_r/n_d \simeq 0.03$ .

## 5. - Discussion.

First we summarize the results of the diffusion theory when it is applied to the dynamic polarization <sup>(9)</sup>. The mathematical development of the transport equation introduces a new parameter  $b^*$ , which is related to the parameter  $b$ ,

---

<sup>(13)</sup> A. ABRAGAM: *The Principles of Nuclear Magnetism* (Oxford, 1961).

via a function of the pumping power, by the relation

$$b^* = b(1 + WT_s)^{\frac{1}{2}}.$$

This new parameter has the same physical meaning as the parameter  $b$ , to which it reduces when the induced transition probability  $W$  is zero.

Then one can deduce different cases with  $b^* \geq \delta$  where  $b > \delta$  or  $b < \delta$ . The value of the stationary polarization is always the same in all cases. These cases are summarized in Table I.

TABLE I.

Relaxation $W = 0$ , $b^* = b$	Build-up $W \neq 0$ , $b^* = b(1 + WT_s)^{\frac{1}{2}}$
$b < \delta$ $T(b < \delta) = (10/3)(H/\hbar\gamma_s)^2 T_s (\delta R)^3$	$\tau^{-1}(b^* > \delta) = (1/1.6)(\delta/b)^3 T(b < \delta)^{-1} (1 + WT_s)^{\frac{1}{2}}$ $\tau^{-1}(b^* < \delta) = T(b < \delta)^{-1} (1 + WT_s)$
$b > \delta$ $T(b > \delta) = (16/3)(H/\hbar\gamma_s)^2 T_s (bR)^3$	$\tau^{-1}(b^* > \delta) = T(b > \delta)^{-1} (1 + WT_s)^{\frac{1}{2}}$
$b = 0.68 [(3/10)(\hbar\gamma_s/H)^2 D^{-1} T_s^{-1}]^{\frac{1}{2}}$ , $p^{(s)}/p_0 - 1 = (P_0/p_0 - 1) WT_s / (1 + WT_s)$	

One sees that the differential system of equations (1) gives the same results as the theory of spin diffusion, with the exception of the factor  $1 - P_0^2$ , only in the case  $b < b^* < \delta$ .

We note the different behaviour of the build-up time constant as the value  $b^*$  becomes greater than the value  $\delta$  (as the power increases).

The protons in a sample with  $b < \delta$  can exhibit two different behaviours of the build-up time constant as a function of the power. They relax to the heat bath in a unique way which is given by eq. (1) and by the diffusion theory. Measurements of  $\tau$ ,  $T_I$ ,  $p_s/p_0$  as functions of the pumping power at various temperatures should give useful information about such processes<sup>(14)</sup>. Until now they have not been performed in a systematic way.

The value of the relaxation time (10) is in disagreement with the experimental data, which are in agreement with the expression<sup>(3)</sup> (8). That is (10) gives a relaxation time longer by a factor  $\simeq 10$ , exactly following the ratio  $(\delta/R_1)^3$ . On the other hand, the expression (8) is obtained by performing an average operation which is not justified from the logical viewpoint.

The eqs. (1) are valid under the conditions I), II), III). These conditions are not satisfied in the complex nature of the sample. Moreover, there are other reasons for which we find a shorter relaxation time.

<sup>(14)</sup> V. MONTELATICI and G. TOMASSETTI: *Lett. Nuovo Cimento*, **5**, 285 (1972).

Thus it seems to us that there is no possibility of finding an exact agreement with the experimental data. Moreover, if it is not possible to perform the average operation over the near protons, then the introduction of a phenomenological cross-relaxation between them and the distant protons is not possible. Indeed, the mixing equations (\*) between  $n_r$  and  $n_d$  give a relaxation time of the distant protons as

$$T_d \simeq \frac{n_d}{n_r} T_r$$

with

$$T_r^{-1} = \frac{3}{10} \left( \frac{\hbar \gamma_s}{H} \right)^2 \langle r^{-6} \rangle n_r T_s^{-1} (1 - P_0^2),$$

where  $\langle r^{-6} \rangle n_r = (R_1 \delta)^{-3}$ , then  $T_d^{-1}$  is expressed by (8) since  $n_r \simeq n_d (\delta/R)^3$ . On the other hand, the introduction of such a thermal mixing does not give an explanation for the transient effect observed<sup>(15,16)</sup>.

## 6. - The transient effect in the dynamic polarization.

This effect, which we will discuss below, was performed in two different magnetic fields of 2.3 kG and of 9.1 kG.

The solid effect is observed by pumping at a side frequency  $\nu_{\pm} = \nu_s \pm \nu_I$  with respect to the central ion frequency  $\nu_s$ . We assume to reach the stationary state of the maximum enhancement of the proton polarization, for example, at a frequency  $\nu_-$ . We have an emission proton signal since the protons reach a negative temperature. Now we change the pumping power to the frequency  $\nu_+$  where we have an absorption proton signal since the protons reach a positive temperature. The proton magnetization goes from the initial stationary state

---

(\*) The differential equations given in ref. (3) with the phenomenological cross-relation between  $n_r$  and  $n_d$  are

$$\dot{p}_r = -(p_r - p_{0r}) T_r^{-1} - (p_r - p_d) T_x^{-1} - W(p_r \mp P),$$

$$\dot{p}_d = -(p_d - p_{0d}) T_d^{-1} - \frac{n_r}{n} (p_d - p_r) T_x^{-1},$$

$$\dot{P} = -(P - P_0) T_s^{-1} - W \frac{n_r}{N} (P \mp p_r),$$

with cross-relaxation rate  $T_x^{-1} \gg T_r^{-1}$ .

(15) J. RAMAKRISHNA and F. N. A. ROBINSON: *Proc. Phys. Soc.*, **87**, 945 (1967).

(16) V. MONTELATICI and G. TOMASSETTI: *Lett. Nuovo Cimento*, **3**, 391 (1972).

to the final state crossing zero, with a time constant directly proportional to the proton relaxation time. The distant protons take a longer time to reach the final stationary state than the near ones. The latter ones stay in the various shells with decreasing relaxation time as the distance from the ion decreases.

When we observe zero signal at time  $t^*$ , that is zero magnetization, the protons are divided into two groups having equal but opposite magnetization.

Now at time  $t^*$ , we switch off the pumping power. The two groups of protons gradually reach thermal equilibrium with the heat bath with their respective relaxation times: the distant protons with their long unique relaxation time; the near protons with their different relaxation times shorter than the former. The observed signal is the total magnetization which is the algebraic sum of the magnetization of the distant and of the near protons.

We observe a growing signal superimposed on the zero signal, and after its decay. Indeed the experiments show such a type of signal. The experimental<sup>(15)</sup> data at 2.3 kG first show a distribution of relaxation times, and in this time interval we observe an increasing signal due to the near protons relaxing to the heat bath temperature. Subsequently we observe the distant protons relaxing with a unique time constant.

Now we suppose that a thermal mixing exists between the near and the distant protons. At the time  $t^*$  the magnetization is zero; that is

$$M_{\text{tot}} = n_r p_r + n_a p_a = \frac{\hbar \gamma_I}{2K} \left( \frac{n_r}{T_r} + \frac{n_a}{T_a} \right) = 0.$$

The new temperature reached after mixing is

$$T_x^{-1} = \left( \frac{n_a}{T_a} + \frac{n_r}{T_r} \right) (n_a + n_r)^{-1} = 0,$$

where  $T_a$  and  $T_r$  are the initial temperatures of the distant and near protons respectively. This means that there is no observed growing signal since the protons are equally distributed among the energy levels. After mixing one should observe a growing signal due to all the protons which gradually return to the thermal equilibrium with the heat bath. But we observe a growing signal which is 4–6 times the thermal equilibrium signal. Thus it is not possible to invoke the thermal mixing.

In the calculation related to the experiment performed<sup>(16)</sup> at 9.1 kG equal polarization is assumed at time  $t^*$ . However on the ground of the above discussion this is wrong since, if  $p_r = p_a$ , one must have  $n_r = n_a$  in order to have  $M_{\text{tot}} = 0$ , whereas we know that  $n_r < n_a$ .

● RIASSUNTO

Si considerano  $N$  spin elettronici  $S_i$  e  $n$  spin nucleari  $I_j$  ( $S_i = I_j = \frac{1}{2}$ ) accoppiati da una debole interazione dipolare che mescola gli autostati per mezzo del coefficiente  $|\varepsilon_{ij}| = \frac{3}{4} \gamma_s \hbar H^{-1} R_{ij}^{-3} \sin \theta_{ij} \cos \theta_{ij}$  ( $R_{ij}$  è la distanza tra  $S_i$  ed  $I_j$ ,  $\theta_{ij}$  è l'angolo tra  $S_i - I_j$  e la direzione del campo magnetico), è allora possibile scrivere le equazioni differenziali per lo spin  $i$  e lo spin  $j$ . Queste equazioni microscopiche possono essere mediate su quei nuclei e ioni per i quali si può stabilire una distribuzione isotropa ed un'unica temperatura per i nuclei ad ogni istante. Risolvendo il sistema di equazioni differenziali si ottiene lo stesso risultato particolare previsto dalla teoria della diffusione di spin.

Диффузия спина при динамической поляризации из-за объемного эффекта.

Резюме (\*). — Рассматривая  $N$  электронных спинов  $S_i$  и  $n$  ядерных спинов  $I_j$  ( $S_i = I_j = \frac{1}{2}$ ), связанных слабым дипольным взаимодействием, которое перемешивает собственные состояния при помощи коэффициента  $|\varepsilon_{ij}| = \frac{3}{4} \gamma_s \hbar H^{-1} R_{ij}^{-3} \sin \theta_{ij} \cos \theta_{ij}$  (где  $R_{ij}$  — расстояние между  $S_i$  и  $I_j$ ,  $\theta_{ij}$  — угол между  $S_i - I_j$  и направлением магнитного поля), оказывается возможным записать дифференциальные уравнения для спина и  $j$ -ого спина. Эти микроскопические уравнения могут быть усреднены по тем ядрам и ионам, для которых можно установить изотропное распределение и единую температуру по ядрам в любой момент времени. Решение этой системы дифференциальных уравнений приводит к тому же результату, который был предсказан в теории диффузии спина.

(\*) *Переведено редакцией.*

<p>V. MONTELATICI  11 Settembre 1973  <i>Il Nuovo Cimento</i>  Serie 11, Vol. 17 B, pag. 129-140</p>
--