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# SPIN DIFFUSION, MAGNETIC RELAXATION, AND DYNAMIC POLARIZATION OF NUCLEI

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The role of nuclear spin diffusion in magnetic relaxation and dynamic polarization of nuclei in nonconducting crystals containing paramagnetic impurities in investigated. The presence of a diffusion barrier due to the fact that the Zeeman frequencies of nuclei located near paramagnetic ions differ strongly from each other, thereby impeding diffusion, is taken into account. During dynamic polarization the diffusion barrier should be important for not too powerful microwave fields and should diminish the nuclear polarization.

1. Nuclear spin diffusion plays an important role in magnetic relaxation and dynamic polarization of nuclei in nonconducting crystals containing paramagnetic impurities. The role of spin diffusion in nuclear relaxation has been considered in a number of papers,[1-5] in which[2,3] an expression has been obtained for the relaxation time of the total nuclear magnetic moment of a sample without, however, taking into the account the so-called diffusion barrier. The diffusion barrier is caused by the fact that the frequencies of nuclei situated near paramagnetic ions differ strongly from each other thereby impeding diffusion.

In a previous paper[5] (which will henceforth be referred to as I) we considered spin diffusion, taking into account the presence of a diffusion barrier. The final result obtained in I for the relaxation time did not agree well with experiments at low temperature, however.

2. In I, a solution was sought for the differential equation for the z component (z axis directed along the constant external field) of the nuclear magnetization M in steady state and in the absence of a saturating alternating field [see Eq. (5) in I]. A solution was found satisfying the boundary condition $M(\infty) = 0$. In particular, for the asymptotic form of this solution we have

$$M(r) = M_0 F / r \tag{1}$$

where $M_0$ is the equilibrium value of M.

In order to determine the constant F, a second boundary condition for small values of r is required.

The relaxation time $T_n$ of the total nuclear magnetic moment of the sample is expressed through F:

$$T_n = 1 / 4\pi NDF, \tag{2}$$

where N is the concentration of paramagnetic centers and D is the nuclear spin diffusion coefficient. Actually, the nuclear spin diffusion coefficient is a function of the distance r from the nearest paramagnetic center. The functional form of D(r) can be determined if use is made of the theory of cross relaxation. The asymptotic form of M(r) will again be given by Eq. (1) since the value of D(r) is constant for large r. In what follows we shall let D stand for the constant value of D(r) for large r.

In order to determine the constant F accurately it is necessary to proceed as follows: one must find a solution to Eq. (5) in I, with a diffusion coefficient depending on r, that satisfies the conditions $M(0) = M_0$ and $M(\infty) = 0$. By comparison of the asymptotic form of this solution with Eq. (1) we find F.

We assumed in I that the dependence D(r) could be approximated by the step function

$$D(r) = 0 \quad \text{for } r < d,$$
$$D(r) = D \quad \text{for } r > d. \tag{3}$$

In this case it is necessary to solve Eq. (5) in I with the boundary conditions $dM/dr = 0$ for $r = d$ and $M(\infty) = 0$. This gives us the function F(b, d) expressed by Eq. (20) in I. In the limiting cases we have

$$F = b \qquad \text{for } d \ll b, \tag{4a}$$
$$F = C / 3Dd^3 = 1{,}6 b^4 / d^3 \quad \text{for } d \gg b; \tag{4b}$$

b is equal to the distance from the paramagnetic ion to which direct relaxation of the nuclear spin (by means of dipole-dipole interaction with the spin of the paramagnetic ion) plays a greater role than spin diffusion (in the case of no diffusion barrier); $C/2r^6$ is the probability (per unit time) of a relaxation reorientation of the nuclear spin located a distance r from the paramagnetic ion. The magnitude of b is given by the formula

$$b = 0.68\,(C/D)^{1/4}. \tag{5}$$

Thus, by applying the model of a step function for D(r) the problem comes down to a determination of an effective radius d for the diffusion barrier. If $d \ll b$, the result does not depend on d and coincides with the result[2,3] given in previous work by the author and de Gennes.

Our treatment is correct for the fulfillment of the condition

$$a \ll \max(b, d) \ll R = (3/4\pi N)^{1/3}, \tag{6}$$

where a is the distance between nearest-neighbor nuclear spins and R is the radius of a sphere fitting around one paramagnetic ion. If a nuclear relaxation independent of the paramagnetic ion also occurs, with a partial relaxation time $T_d$, the total nuclear relaxation time $T_n$ will be given by

$$T_n^{-1} = T_d^{-1} + 4\pi NDF. \tag{7}$$

3. We introduce the quantity δ:

$$\delta \sim (\gamma_e/\gamma_n)^{\alpha} a \quad \text{for } \tau > T_2, \tag{8a}$$
$$\delta \sim (\gamma_e \hbar \gamma_e H/\gamma_n kT)^{\alpha} a \quad \text{for } \tau < T_2, \tag{8b}$$

where τ is the spin-lattice relaxation time of the paramagnetic ion, $T_2$ is the nuclear transverse relaxation time, $\gamma_e$ and $\gamma_n$ are the absolute values of the gyromagnetic ratios of the paramagnetic ion and the nucleus, and $\alpha = 1/4$ to $1/3$.[1)]

In I we took d = δ. At the temperatures of liquid hydrogen and helium (where $b \ll d$), this leads to values of $T_n$ markedly in excess of the experimental data of Bloembergen.[1] Further, when the diffusion barrier is not taken into account the temperature dependence of $T_n$ is $T_n \sim \tau^{1/4}$. With account taken of the diffusion barrier in the step-function model with d = δ we obtain $T_n \sim \tau$ in the limiting case of low temperatures. But according to experiment at low temperatures $T_n \sim \tau^{\beta}$, where $\beta = 0.5$ to $0.7$. Thus, by taking the diffusion barrier into account according to the step-function model the theoretical result is changed in the required direction, but by too great an amount.

This discrepancy can be analyzed. Let us assume the inequality $b \ll \delta$. For distances r satisfying the condition $b < r < \delta$, the effect of direct relaxation is weak (since $r > b$), and hence it is impossible to neglect the role of diffusion (although D(r) does diminish, beginning with values of r of the order of δ). It is clear from this that by applying the step-function model with d = δ, we tend to overestimate the role of the diffusion barrier at low temperatures (leading to values of $T_n$ that are too large and to too strong a temperature dependence). Hence, strictly speaking, it is necessary to solve Eq. (5) in I with a function D(r) calculated with the aid of the theory of cross relaxation. It is obvious that the value of F for $b < \delta$ obtained in this way will be greater than the expression obtained from Eq. (4b) by means of the substitution d = δ, and thus the agreement between theory and low-temperature experiments will be improved. However, the analytical solution of Eq. (5) in I with a variable diffusion coefficient presents great difficulties. It makes sense to solve Eq. (5) of I numerically for values of the parameters corresponding to the conditions of an actual experiment.

We note, however, the following fact: we shall use the model of Eq. (3) but take

$$d = \min[\delta, (b\delta)^{1/2}], \tag{9}$$

which gives

$$d = (b\delta)^{1/2} \quad \text{for } b < \delta. \tag{9a}$$

Then, applying Eqs. (2) and (4b) we obtain agreement between theory and experiment both with respect to the temperature dependence ($T_n \sim \tau^{5/8}$), and with respect to the order of magnitude of $T_n$ at liquid hydrogen and helium temperatures. Qualitatively, Eq. (9a) can be understood in the following manner: $b < \delta$, then as b decreases diffusion must be taken into account up to smaller distances.

4. Samples containing polarized protons are of great interest for nuclear physics and the physics of elementary particles. The most promising method for polarizing protons appears to be the method of forced dynamic polarization (the so-called solid effect).[6-10]

Consider a crystal with a small concentration of paramagnetic ions (e.g., a dilute paramagnetic salt or a crystal containing free radicals) to which is applied a strong constant magnetic field H. The principal interaction between the electron spins (for brevity we mean by "electron spin" the spin of the electron shell of the paramagnetic ion) and the nuclei will be dipole-dipole. In this case, as

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[1)] If we take $\alpha = 1/3$, then δ will be of the order of the distance from the paramagnetic ion at which the shift of the nuclear Zeeman frequency equals the nuclear resonance line width. If we take $\alpha = 1/4$, then δ will be of the order of the distance at which the difference in the Zeeman frequencies of neighboring nuclei (situated along one radius) equals the line width of the nuclear resonance. In view of the approximate nature of our treatment there is no point in distinguishing between these two lengths; we can use their mean, i.e., take $\alpha = 7/24$.

is known, the Overhauser effect is not operative, i.e., the nuclei are not polarized when the electron paramagnetic resonance is saturated.

Now if we apply to the crystal an alternating field of frequency $\omega_e + \omega_n$ or $\omega_e - \omega_n$ ($\omega_e$ and $\omega_n$ are the electronic and nuclear Zeeman frequencies), then a quantum of the alternating field will cause a simultaneous reorientation of the electronic and nuclear spins. These "forbidden" transitions are possible because of the mixing of the wave functions caused by the static part of the dipole-dipole interaction between the electronic and nuclear spins. In practice, one usually operates with a fixed microwave frequency and varies the magnitude of the main field H. "Forbidden" transitions occur for values of H equal to $H_+$ or $H_-$, where

$$H_\pm = H_0 \pm \gamma_n H_0 / \gamma_e; \tag{10}$$

$H_0$ is the resonance value of the field, corresponding to ordinary electron resonance:

$$H_0 = \omega / \gamma_e. \tag{11}$$

The electronic spin interacts strongly with the lattice. Therefore the Boltzmann excess of electron spins directed oppositely to the external field will be constantly re-established. From this it is clear that each electronic spin can bring about the reorientation of a rather large number of nuclear spins, effecting a polarization of the nuclei. This polarization interferes with the nuclear relaxation by which equilibrium between the nuclear spins and the lattice is re-established. The role of relaxation becomes relatively less important as the amplitude of the alternating field is increased. In the absence of nuclear relaxation for a forbidden transition corresponding to the field $H_+$, the nuclear magnetization increases $\gamma_e/\gamma_n$-fold; for a forbidden transition corresponding to the field $H_-$, the magnetization increases in absolute magnitude by the same factor but changes sign.

The probability of a forbidden transition decreases with increasing r (the distance between a nucleus and a paramagnetic ion) as $r^{-6}$ in view of the fact that the state-mixing by the dipole-dipole interaction is proportional to $r^{-3}$. Hence for small concentrations of paramagnetic impurity only those nuclei situated close to paramagnetic ions will be polarized. Because of the emergence of a gradient of nuclear magnetization (or a nuclear spin temperature), diffusion of the excess nuclear spins will occur, resulting in a distribution of the nuclear polarization over the entire crystal.

A calculation of spin diffusion in dynamic polarization has been carried out by Winter.[11] He did not account for a diffusion barrier, however. We shall now do this, treating the case of nuclear spin ½, since all the experiments have been done on protons or $F^{19}$ nuclei. We shall also limit ourselves to the case of effective ionic spin of ½.

5. The z component of the nuclear magnetization $M(\mathbf{r},t)$ satisfies the equation[8,11]

$$\frac{\partial M}{\partial t} = \frac{1}{T_d}(M_0 - M) + D\Delta M - C\sum_n |\mathbf{r} - \mathbf{r}_n|^{-6}(M - M_0)$$
$$- \Gamma_\pm \sum_n |\mathbf{r} - \mathbf{r}_n|^{-6}\left(M \mp \frac{\gamma_e}{\gamma_n} M_0\right) - 2AM. \tag{12}$$

Here $\mathbf{r}_n$ is the radius vector of the n-th paramagnetic ion, and A is the probability (per unit time) for the reorientation of the nuclear spin by the alternating field at a frequency equal to the nuclear Larmor frequency. Moreover, C and $\Gamma_\pm$ are given by the formulas

$$C = 3(\hbar\gamma_e)^2 / 10\tau H^2, \quad \Gamma_\pm = \pi\gamma_e H_1^2 \tau G(H - H_\pm)\, C, \tag{13}$$

where $2H_1$ is the amplitude of the alternating field exciting the forbidden transitions, applied perpendicular to the dc field, and $G(H - H_0)$ is a function giving the line shape of the electronic resonance line, normalized to unity. It is to be noted that we are considering the case for which the transitions at $H_+$, $H_0$, and $H_-$ do not overlap, i.e., when the nuclear Larmor frequency significantly exceeds the width of the electron resonance. In Eq. (12) the upper sign is chosen for the case of the $H_+$ transition and the lower sign for the $H_-$ transition.

By W we symbolize the probability (per unit time) of an allowed electronic transition in an alternating field of amplitude $2H_1$ and with the same departure from the corresponding condition for exact resonance as for the forbidden transition we are considering. Then we can write

$$\Gamma = 2W\tau C = sC,$$

where s is a parameter characterizing the degree of saturation of the resonance:

$$s = 2W\tau = \pi\gamma_e H_1^2 \tau G(H - H_\pm).$$

From now on we omit the ± sign on Γ.

We introduce the following quantities[2)]:

$$\bar{b} = 0.68\left(\frac{C + \Gamma}{D}\right)^{1/4} = b\left(\frac{C + \Gamma}{C}\right)^{1/4}, \quad \bar{F} = F(\bar{b}, d). \tag{14}$$

Finally, we symbolize by $\mathfrak{M}$ the total nuclear magnetic moment of the sample

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[2)] More generally, if the step-function model for D(r) is not used, we understand by $\bar{F}$ the result obtained by the exchange $b \to \bar{b}$ in the dependence of F on b.

$$\mathfrak{M} = \int M dV.$$

Let the condition

$$a \ll \max(\bar{b}, d) \ll R$$

be fulfilled. Then, according to I, it follows from Eq. (12) that $\mathfrak{M}$ satisfies the equation

$$\frac{\partial \mathfrak{M}}{\partial t} = 4\pi N D \bar{F} \left[ \frac{C \pm \gamma_e \Gamma / \gamma_n}{C + \Gamma} \mathfrak{M}_0 - \mathfrak{M} \right] + \frac{\mathfrak{M}_0 - \mathfrak{M}}{T_d} - 2A\mathfrak{M}. \tag{15}$$

6. Since we are interested in dynamic polarization of the nuclei, we consider the case A = 0. Equation (15) gives for the stationary value of the magnetic moment $\mathfrak{M}_s$ and for the time $T_s$ for the establishment of the stationary state the following expressions:

$$\frac{\mathfrak{M}_s}{\mathfrak{M}_0} = \frac{T_d^{-1} + 4\pi N D \bar{F} (C + \Gamma)^{-1} (C \pm \gamma_e \Gamma / \gamma_n)}{T_d^{-1} + 4\pi N D \bar{F}}.$$

$$T_s^{-1} = T_d^{-1} + 4\pi N D \bar{F}. \tag{16}$$

Introducing the enhancement factor for nuclear polarization

$$\eta = \mathfrak{M}_s / \mathfrak{M}_0 - 1$$

and using Eq. (7), we can rewrite Eqs. (16) in the following way:

$$\frac{T_n}{T_s} = \frac{T_d^{-1} + 4\pi N D \bar{F}}{T_d^{-1} + 4\pi N D F}, \qquad \eta = \eta_m \frac{\Gamma}{C + \Gamma} \frac{4\pi N D \bar{F}}{T_d^{-1} + 4\pi N D \bar{F}},$$

$$\eta_m = \pm \gamma_e / \gamma_n - 1. \tag{17}$$

Equation (17) shows that $\eta$ increases with decreasing C and increasing $T_d$; this is easy to see: a decrease in C means a diminution in the role of nuclear relaxation due to paramagnetic ions, and an increase in $T_d$ means a decrease in the role of relaxation not caused by paramagnetic ions. Such a decrease in the role played by nuclear relaxation should enhance the dynamic polarization effect.

In the limiting case $d \ll \bar{b}$, we have the result obtained earlier[8,11]:

$$\eta = \eta_m \frac{\Gamma}{C + \Gamma} \frac{8.5\, N (C + \Gamma)^{1/4} D^{3/4}}{T_d^{-1} + 8.5\, N (C + \Gamma)^{1/4} D^{3/4}},$$

$$T_s^{-1} = T_d^{-1} + 8.5\, N (C + \Gamma)^{1/4} D^{3/4}. \tag{18}$$

Since $\Gamma$ increases with increasing microwave power, b will significantly exceed d for sufficiently high powers, and the diffusion barrier will cease to be important. When the microwave power is not too high, the diffusion barrier will become important and will diminish the nuclear polarization.

Note added in proof (November 24, 1962). According to the preliminary results of new measurements by Jeffries (private communication), $T_n$ is proportional to $\tau$ at helium temperatures. This is in agreement with our results [Eqs. (2) and (4a)] for a step function with a radius of the diffusion barrier given by Eq. (8a). Thus, if these preliminary results are confirmed, there is no necessity for carrying out the numerical calculations we referred to in Sec. 3 of this paper in order to obtain agreement between theory and experiment (particularly, to obtain the correct temperature dependence for $T_n$).

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