

SPIN DIFFUSION AND MAGNETIC RELAXATION OF NUCLEI

G. R. KHUTSISHVILI

Institute of Physics, Academy of Sciences, Georgian S.S.R.

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Diffusion of a nuclear spin in crystals is studied theoretically with allowance for the presence of a diffusion barrier. An expression is obtained for the nuclear magnetic relaxation time in an ionic crystal containing paramagnetic atoms. The agreement between theory and experiment is improved by taking the diffusion barrier into account.

1. Bloembergen has shown that in many non-conducting solids nuclear magnetic relaxation is caused by paramagnetic ions.^[1] In the same paper he suggested a relaxation mechanism wherein the spin of the paramagnetic ion reverses direction by interaction with the lattice periodically, with a period on the order of τ (the spin-lattice relaxation time of the paramagnetic ion).¹⁾ The nuclear spin near the paramagnetic ion is therefore acted upon by a time-varying local magnetic field, which causes its re-orientation. It is clear that the nuclear spins near the paramagnetic ions soon enter into equilibrium with the lattice. This gives rise to a spin temperature gradient, which in turn causes diffusion of the nuclear spin (diffusion not of the nuclei but of the nuclear-spin direction,²⁾ which leads ultimately to an equilibrium between the nuclear spins and the lattice over the entire specimen.

Bloembergen calculated the time $T_1^{\text{dir}}(r)$ of direct relaxation of a nuclear spin situated a distance r from the paramagnetic ion. Calculation (for a nuclear spin equal to $1/2$) yields

$$T_1^{\text{dir}}(r) = r^6/C, \quad (1)$$

where

¹⁾ $\tau = \rho/2\pi$, where ρ is a quantity used in Bloembergen's paper^[1]. More accurately, τ is correlation time of the z component of the paramagnetic ion spin (z is the direction of the external magnetic field). In the case of sufficiently low paramagnetic-impurity concentration, the paramagnetic ions are independent of each other and τ coincides with the spin-lattice relaxation time. At large concentrations, on the other hand, τ coincides with the spin-spin relaxation time of the paramagnetic ion.

²⁾ This diffusion is connected with the simultaneous re-orientation of the spins of two neighboring nuclei, wherein the total spin projection on the external field is conserved. The re-orientation is caused by dipole-dipole interaction.

$$C = 2(\gamma_n g \beta)^2 S(S+1)\tau/5 [1 + (\tau\gamma_n H)^2], \quad (2)$$

γ_n is the gyromagnetic ratio of the nucleus, β is the Bohr magneton, g and S are respectively the Landé factor and the effective spin of the paramagnetic ion, and H is the external magnetic field. Averaging over the angles is already included in formula (2). Usually $\tau\gamma_n H \gg 1$.

Bloembergen then set up a differential equation for the z component of the nuclear magnetization $M(r, t)$,

$$\partial M/\partial t = D\Delta M - 2AM - C \sum_n |\mathbf{r} - \mathbf{r}_n|^{-6} (M - M_0). \quad (3)$$

Here M_0 —equilibrium value of M , A —probability per unit time of reorientation of a nuclear spin under the influence of the resonance exchange field, \mathbf{r}_n —radius vector of n -th paramagnetic ion; D —coefficient of nuclear-spin diffusion. An estimate yields

$$D \cong a^2/30T_2, \quad (4)$$

where T_2 is the transverse nuclear-relaxation time, a —distance between the nearest spin-possessing nuclei whose relaxation is being investigated.

Finally Bloembergen solved (3) numerically and determined the time-averaged nuclear magnetic relaxation.

2. We have obtained an analytic solution of (3) for the stationary case in the absence of a saturating alternating field.^[2] It follows from our analysis that the nuclear magnetic moment of the sample has a single relaxation time. We further obtained an expression for the relaxation time from the asymptotic expression for the solution.

Nuclear spin diffusion in the presence of a saturating alternating field was later investigated by De-Gennes^[3] (see also the detailed analysis in the book by Abragam^[4]) who obtained a solu-

tion of (3) for the stationary case. He derived for the relaxation time a formula that agreed with ours.

De-Gennes considered also the non-stationary problem of the restoration of the nuclear magnetic moment of a sample after the saturating field has been turned off. He showed that for times that are not too short the relaxation has an exponential character, and the expression obtained for the relaxation time again agreed with ours.

However, neither we nor De-Gennes took into consideration the presence of the so-called diffusion barrier due to the fact that the Zeeman frequencies of the nuclei located near the paramagnetic ion differ appreciably from each other,^[1] making the diffusion of the nuclear spin difficult. This apparently must be the reason for the discrepancy between our results and the experimental data. The role played by the presence of the diffusion barrier is emphasized by Bloembergen.^[5]

The purpose of the present paper is to derive an expression for the nuclear relaxation time with allowance for the diffusion barrier.

3. We assume the concentration of the paramagnetic ions to be sufficiently small (a criterion for the smallness of the concentration follows). In such a case the paramagnetic ions are independent of each other and the crystal can be regarded as made up of separate independent systems, each comprising a single paramagnetic ion surrounded by a large number of nuclear spins.

Let N be the concentration of paramagnetic ions and let $R = (3/4\pi N)^{1/3}$ be the radius of the sphere for each ion.

We can confine ourselves to one term in the sum of (3). We consider the stationary case in the absence of a saturating alternating field. If the origin is located at the center of the paramagnetic ion, Eq. (3) becomes

$$\Delta M - \beta r^{-6} (M - M_0) = 0, \quad (5)$$

where $\beta = C/D$.

A general centrally-symmetrical solution of (5) is

$$M = M_0 - M_0 r^{-1/2} [A I_{-1/2}(\beta^{1/2}/2r^2) - B I_{1/2}(\beta^{1/2}/2r^2)], \quad (6)$$

where A and B are integration constants and $I_p(x) = i^{-p} J_p(ix)$. Using the known expressions for Bessel functions of small arguments, we readily obtain an asymptotic form of (6) for $r \gg \beta^{1/4}$:

$$M = M_0 - M_0 \left[\frac{4\Gamma(\frac{5}{4}) A}{\pi\beta^{1/4}} - \frac{B\beta^{1/4}}{2^{1/2}\Gamma(\frac{5}{4}) r} \right].$$

In order for the problem to be stationary it is necessary to maintain M artificially constant at large r . We assume, in particular, that $M(\infty) = 0$.³⁾ This boundary condition makes it possible to determine the constant A and we obtain as a result⁴⁾

$$M = M_0 F/r, \quad F = B\beta^{1/4}/2^{1/2}\Gamma(\frac{5}{4}). \quad (7)$$

In order for our analysis to be valid, the following conditions must be satisfied

$$\beta^{1/4} \ll R, \quad F \ll R. \quad (8)$$

The first of these conditions is necessary to make the asymptotic form (7) valid over a certain range. The condition $F \ll R$ is necessary to make $M(R) \ll M_0$. Only then can we assume that the different paramagnetic ions act independently of each other.

4. According to (7) the nuclear moment flux through a sphere of radius r is (with $r \gg \beta^{1/4}$)

$$D4\pi r^2 |\text{grad } M| = 4\pi D F M_0.$$

For the total nuclear moment of a sphere of radius R we obtain [we use (7) over the entire sphere]

$$\mathfrak{M} = 2\pi M_0 F R^2 = (9\pi/2)^{1/2} F M_0 N^{-1/3}.$$

From the condition $F \ll R$ we get $FN^{1/3} \ll 1$. In this case \mathfrak{M} is negligible compared with its equilibrium value $\mathfrak{M}_0 = M_0 N^{-1}$. The nuclear moment flux through a sphere of radius R is therefore $4\pi D F N(\mathfrak{M} - \mathfrak{M}_0)$. We see therefore that \mathfrak{M} has a single relaxation time T_1 , given by the formula⁵⁾

$$T_1 = 1/4\pi D F N = R^3 \beta / 3CF. \quad (9)$$

This conclusion shows that the presence of a single relaxation time is due to the fact that M is inversely proportional to r when $r \gg \beta^{1/4}$, with T_1 expressed in terms of the factor F in the asymptotic formula (7).

The problem has thus been reduced to a determination of a quantity F , with the dimension of length. To determine this quantity we need the boundary condition for small r .

5. We use the derivation of formula (9) given by De-Gennes.^[3] At large values of r we can neglect the relaxation term, and in the presence

³⁾ The same result is obtained for the relaxation time if we assume $M(\infty) = M_1$ (see [2]).

⁴⁾ If we include the succeeding terms of the expansion, we obtain $M = M_0(F/r - \beta/12r^4)$.

⁵⁾ The method used here to derive the formula for the relaxation time from the asymptotic expression for the magnetic moment flux was suggested to us by L. D. Landau.

of a saturating field the stationary equation assumes the form

$$\Delta M - L^{-2}M = 0, \quad L = (D/2A)^{1/2}. \quad (10)$$

This equation has a centrally symmetrical solution that vanishes at infinity:

$$M = M_0 \text{const } r^{-1} \exp(-r/L). \quad (11)$$

We find that $\beta^{1/4}/L \ll 1$ always. To reconcile (11) and (7) we therefore put $F = \text{const.}$ ⁶⁾ Thus, if we eliminate small spheres of radius on the order of $\beta^{1/4}$ centered on the paramagnetic ions, we can employ (3) without the relaxation term for the remainder of the crystal.

By finding the stationary solution (with account of all the paramagnetic ions), we obtain

$$\mathfrak{M}/\mathfrak{M}_0 = 4\pi NFD / (2A + 4\pi NFD), \quad (12)$$

We then determine T_1 from the formula

$$T_1 = 1/2A_{1/2}, \quad (13)$$

where $A_{1/2}$ is the value of A for which the nuclear magnetic moment of the specimen is equal to half its equilibrium value. A comparison of (12) with (13) again leads to (9).

Replacing A in (10) by $A_{1/2}$, we obtain

$$L_{1/2} = (DT_1)^{1/2} = (4\pi FN)^{-1/2} = (R^3/3F)^{1/2}. \quad (14)$$

$L_{1/2}$ is the distance covered by the nuclear spin through diffusion during the relaxation time T_1 .

De-Gennes believes that (11) is valid if the condition $R \ll L$ is satisfied in addition to (8). Accordingly, we must have $R \ll L_{1/2}$ for (9) to be valid. This condition, however, follows automatically from (8) and (9).

6. We proceed to calculate F (or B). For this purpose we need a second boundary condition for Eq. (5).

We introduce a quantity b with the dimension of length (see [2])

$$b = \pi\beta^{1/4}/2^{3/2} [\Gamma(5/4)]^2 = 0.68\beta^{1/4}. \quad (15)$$

The expressions (7) and (15) yield $B/A = F/b$.

In [2] we used the boundary condition $M(0) = M_0$. In this case, (6) yields $A = B$ or

$$F = b. \quad (16)$$

Then, according to (9)

$$T_1 = 1/4\pi ND b = R^3\beta^{3/4}/2C = 1.6 \cdot (bR)^3/C. \quad (17)$$

However, the derivation of (16) does not take into consideration the presence of the diffusion barrier.

⁶⁾In [3], as in [2], the formula for T_1 contains in lieu of F the quantity b [see (15) below].

Therefore expressions (16) and (17) are valid only if b is appreciably greater than the radius of the diffusion barrier.

7. The radius of the diffusion barrier d is defined as the distance from the paramagnetic ion, on which the difference of the Zeeman frequencies of the neighboring nuclei is equal to the nuclear-resonance line width (the broadening of the nuclear resonance is due to nuclear dipole-dipole interaction). This yields⁷⁾

$$d \sim (\mu_e/\mu_n)^{1/4} a \quad \text{if } \tau > T_2 \text{ or } \mu_e H/kT > 1, \quad (18a)$$

$$d \sim \left(\frac{\mu_e}{\mu_n} \frac{\mu_e H}{kT} \right)^{1/4} a \quad \text{if } \tau < T_2 \text{ or } \frac{\mu_e H}{kT} < 1, \quad (18b)$$

where μ_e and μ_n are the magnetic moments of the paramagnetic ion and of the nucleus, respectively.

We note that Blumberg^[5] introduces a quantity δ , defined as the distance from the paramagnetic ion, at which the Zeeman frequency shift is equal to the width of the nuclear resonance line. It is easy to see that δ is given by formulas (18), in which, however, the exponent $1/4$ is replaced by $1/3$.

Nuclei closer than δ to the paramagnetic ion barely participate in the resonance, since the displacements of their resonant frequencies are too large. Further, when the distance from the magnetic ion is less than d , the diffusion of the nuclear spin weakens, since simultaneous re-orientation of the neighboring nuclear spins with conservation of the total projection is made difficult by the difference in their Zeeman frequencies.

8. For an approximate calculation of the diffusion barrier we employ the boundary condition

$$dM/dr = 0 \quad \text{for } r = d. \quad (19)$$

In such a case we can obtain from (6)

$$\frac{F}{b} = \frac{2xI_{s/4}(x)}{2xI_{s/4}(x) + I_{1/4}(x)}, \quad x = \frac{\beta^{1/2}}{2d^2}. \quad (20)$$

Formulas (15) and (20) express F as a function of b and d . Substitution of F in (9) yields the relaxation time.

Let us examine some limiting cases. If $d \ll b$, (20) yields $F = b$, and we again obtain (16) and (17). On the other hand, if $d \gg b$, (20) yields⁸⁾

$$F = \beta/3d^3 = 1.6b^4/d^3, \quad (21)$$

$$T_1 = \frac{0.05}{NDb} \left(\frac{d}{b} \right)^3 = \frac{(dR)^3}{C}. \quad (22)$$

⁷⁾When $\tau > T_2$, the nuclear spin is acted upon by a static local magnetic field, brought about by the magnetic moment of the paramagnetic ion. This field averages out when $\tau < T_2$.

⁸⁾We can obtain (21) by imposing boundary condition (19) on the function mentioned in footnote 4).

A comparison of (17) and (22) shows that the presence of a diffusion barrier slows down the relaxation, as expected.

From (2), (15), (17), and (22) we obtain for the dependence of T_1 on N , H , and T , for $\tau\gamma_N H \gg 1$,

$$T_1 \sim N^{-1} \tau^1 H^{1/2} \quad d < b, \quad (23a)$$

$$T_1 \sim N^{-1} \tau d^3 H^2 \quad d > b. \quad (23b)$$

9. It is easy to show that if $b > d$, then diffusion plays a larger role than direct relaxation when the distance from the paramagnetic ion is larger than b . Indeed, when $r > b$, Eq. (5) reduces to $\Delta M = 0$ and its solution is given by (7). However, to determine the factor F we must know the values of M for small r . On the other hand, when $r < b$, the role of diffusion is small compared with the role of direct relaxation.

Furthermore, the quantity d was defined as the radius of a sphere inside which the nuclear spin diffusion coefficient is small. It is clear that the introduction of d is meaningful only if $d > b$.

Thus, we see that the nuclear spin diffusion plays an appreciable role when $r > l$, where l is the greater of the two quantities b and d . It is clear therefore that in order for the macroscopic description of the spin diffusion to be valid it is essential to have $l \gg a$.

Furthermore, for our analysis to be correct it is essential to have $d \ll R$. We take additional account of (8) and of the fact that $F < b$ in accord with (16) and (21). We then obtain finally the following conditions under which our analysis is valid:

$$a \ll l \ll R. \quad (24)$$

10. We now consider the extent to which the boundary condition (19) takes correct account of the presence of the diffusion barrier.

To allow correctly for the diffusion barrier it is first necessary to determine the dependence of the diffusion coefficient D on r . Calculation shows that for small r (starting with $r \sim d$) D decreases with decreasing r . The reason for this decrease is that the resonances of the neighboring nuclei do not coincide at small values of r . Using further the obtained dependence D on r , we must then solve (5) with the boundary conditions $M(0) = M_0$ and $M(\infty) = 0$.

The dependence of D on r can be determined approximately, using the theory of crossing relaxation (see [6]). Recognizing that the difference of the Zeeman levels of neighboring nuclei is proportional to r^{-4} , we obtain

$$D(r) = D(\infty) \exp(-\text{const } r^{-8}), \quad (25)$$

where $\text{const} \sim d^8$.

It is, however, very difficult to solve (5) with variable D . It is therefore desirable to replace this procedure with a solution of (5) with constant D for $r > d$, and with a corresponding boundary condition for $r = d$. The boundary condition (19) which we use follows from the continuity of the flux of the nuclear moment, if it is assumed that the nuclear spin diffusion coefficient vanishes when $r < d$.

The case $d > b$ signifies that the diffusion of the nuclear Zeeman energy to the paramagnetic ion (up to distance on the order of d) is faster than the transfer of this energy from the paramagnetic ion to the lattice.

We note that the result (22) which we obtained for the limiting case $d \gg b$ agrees with the result obtained by Blumberg [5] in a non-stationary analysis of the problem.

11. We see that the diffusion of the nuclear spin is significant when $r > l$. Our results will therefore be valid only if the following condition is fulfilled

$$T_1 = R^3 / 3DF \gg T_1^{\text{dir}}(l), \quad (26)$$

which yields $l^6 \ll R^3 b^4 / F$. This condition, however, is automatically fulfilled if $l \ll R$.

12. We now proceed to compare the theory with experiment. The first experiments on spin diffusion were set up by Bloembergen. [1] The dependence of the proton relaxation time on the temperature, external field intensity, and chromium atom concentration was measured in potassium chrome alum highly diluted with aluminum. The relative concentration of the chromium atoms ranged from 2×10^{-6} to 3×10^{-2} . The measurements were made in the temperature interval 300–1°K. The condition $\tau\gamma_N H \gg 1$ was fulfilled in all these experiments. The dependence of T_1 on the paramagnetic-atom concentration, given by (9), was experimentally confirmed. The temperature dependence obtained was $T_1 \sim \tau^\alpha$, with $\alpha = 0.5-0.7$ for different N . This result is intermediate between (23a) and (23b).

Blumberg experimented with a solution of $(\text{NH}_4)_2\text{CrO}_4$ in NH_4HSO_4 , and measured the time dependence of the proton resonance signal. The results obtained with some specimens do not agree with the theory that does not allow for the diffusion barrier; allowance for this barrier improves the agreement. It was found further that for certain specimens the proton-resonance signal is proportional to $t^{1/2}$ at small values of t .

Leifson and Jeffries^[7] measured the proton relaxation time in lanthanum-magnesium double nitrate, in which a small fraction of the lanthanum atoms was replaced by cerium atoms. The concentration of cerium varied in the interval 0.05–10%. The measurements were made in the temperature interval 1.6–4.2°K. The experiment consisted of measuring the dependence of the proton relaxation T_1 on the concentration of the cerium atoms, on the external field, and on the temperature. The external field was applied in these experiments perpendicular to the axial-symmetry axis of intracrystalline electric field.

The results of the measurements yielded $T_1 \sim N^{-2}$, which is in sharp disagreement with (9).⁹⁾

Leifson and Jeffries^[7] obtained $T_1 \sim T^{-7}$ (in the temperature interval 1.9–2.7°K), and in accordance with their data $\tau \sim T^{-14}$. Thus, $T_1 \sim \tau^{1/2}$, which is intermediate between (23a) and (23b).

Scott measured T_1 in the same specimens as Leifson and Jeffries, except that the external field was applied parallel to the axial-symmetry axis of the intracrystalline electric field. He found that $T_1 \sim N^{-1.3} T^{-12}$. Assuming $\tau \sim T^{-14}$, we find this result to be quite close to (23b).

We see therefore that an account of the diffusion barrier improves the agreement between theory and experiment.

We do not make a detailed comparison between theory and experiment for the following reasons. First, the numerical values of certain quantities (for example, the diffusion coefficient D) are known only very approximately. Second, formulas (18) for the radius of the diffusion barrier d are accurate only to order of magnitude. Furthermore, our analysis itself, in which we assume that the diffusion terminates abruptly at $r = t$, is of course

⁹⁾The spin-spin relaxation time of a paramagnetic ion is on the order of $\hbar\mu_e^2 R^3$. It is proportional to N^{-1} and is practically independent of the temperature. Consequently, at sufficiently low temperatures or at sufficiently high concentrations it will be smaller than the spin-lattice relaxation of the paramagnetic ion. In this case, we must take τ to mean the spin-spin relaxation time in all our formulas. According to (23a) and (23b), this yields $T_1 \sim N^{-1.25}$ when $d < b$ and $T_1 \sim N^{-2}$ when $d > b$. But then T_1 should depend only weakly on the temperature, in contradiction to the results of Leifson and Jeffries^[7]. We note that the greatest concentrations employed by these authors are too large to allow the use of our results.

a crude approximation. All these circumstances do not influence, however, the correctness of (23a) and (23b), which give the dependence of T_1 on T , N , and H in two limiting cases.

The foregoing shows that to confirm the theory we need experimental data on the dependence on T_1 and τ on N , H , and T . It is desirable here to carry out experiments in one of the two limiting cases $d \gg b$ or $d \ll b$, and to satisfy conditions (24).¹⁰⁾

We note, finally, that the nuclear magnetic relaxation which we investigated in crystals containing paramagnetic centers should have considerable anisotropy in the case of a single crystal, i.e., the relaxation time T_1 should depend on the direction of the external field relative to the crystallographic axes. Indeed, the diffusion coefficient D is in fact a tensor. Furthermore, C and the diffusion barrier become anisotropic.

Note added in proof. (20 April 1962). Substitution of (18a) in (22) leads, at hydrogen and helium temperatures, to relaxation times T_1 that exceeds Bloembergen's experimental data^[1]. It must be concluded that at low temperatures the effective radius of the diffusion barrier is less than given by (18a).

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¹⁰⁾We note that according to (2), (15), and (18) b decreases with decreasing temperature while d increases.