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Abstract. Nuclear relaxation arising from spin–spin interactions in the crystal unit cell is
described by the model approach. The analytical expression for the free-precession signal
(FPS) is obtained for an arbitrary velocity of the reciprocal spin flips. An excellent agreement
with experimentally observed FPS in CaF_2 is obtained. The fundamental possibility to observe
the critical slowing down of the phase relaxation in resonant magnetic fields is revealed.

The problem of the phase relaxation of spin systems in solids is still not resolved, although
there have been continuous discussions over the last forty years. In many cases the NMR
and EPR line shapes, arising from the processes of spin phase relaxation, are described
by means of the method of moments, either by some modification of the perturbation
theory or by various numerical methods. The matter seems to be rather difficult because
it is necessary to solve an essentially many-body problem, which remains a fundamental
question in solid state physics. The problem arises from the dipole–dipole interactions
between the spins, ordered in the crystal. This interaction excites the reciprocal spin
flips (a flip–flop (f–f) process) disturbing the phase of an individual particle without
energy loss in the entire spin system. Nevertheless, different approaches exist that
provide an exact solution of the problem, but within an ideal model. In this model the
problem is converted to the statistical analysis of random fields, seen by the selected spin
in the crystal. One of these approaches has been developed in [1], where the local field
$H_{z0}(t)$ seen by a selected spin is considerd as the sum of two statistically independent
fields

$$H_{z0}(t) = H_{z0}^{(1)}(t) + H_{z0}^{(2)}(t)$$

having an essentially different nature. This is stipulated by the existence of two spheres
(one near and one remote) for the selected spin in the crystal, where the orientations
of the spins and hence the fields created by them are correlated and uncorrelated,
respectively, with the selected spin orientation. In [1] the equations that describe the
decay of the total transverse component of the spins, produced by the random fields
resulting from the f–f processes, have been obtained. The Laplace transform of the
solution of the equations has been found, but a comprehensive analysis of the solution
has not been performed. The objective of the present paper is to deduce and to analyse
the solution of the equations, analogous to those in [1], and to investigate the influence

of the resonantfield on the kinetics of the transverse component of the nuclear magnetization of atoms with spins of $\frac{1}{2}$ in a simple cubic lattice.

Let us consider the spin system described by the following Hamiltonian:

$$\mathcal{H} = \mathcal{H}_z + \mathcal{H}_d^0 + \mathcal{H}_1(t)$$

$$\mathcal{H}_z = \gamma \hbar H_0 \sum_j \hat{S}_{zj} \qquad \mathcal{H}_1(t) = \gamma \hbar H_1 \sum_j \hat{S}_{xj} \cos \omega t$$

$$\mathcal{H}_d^0 = \frac{\gamma^2 \hbar^2}{2} \sum_{i \neq j} \frac{1 - 3\cos^2\theta_{ij}}{r_{ij}^3} (\tfrac{3}{2}\hat{S}_{zi}\hat{S}_{zj} - \tfrac{1}{2}\hat{S}_i \cdot \hat{S}_j)$$

where $\mathcal{H}_z$ and $\mathcal{H}_1(t)$ are the Hamiltonians of the interaction with constant field H_0 and alternating magnetic field $H_1 \cos \omega t$, respectively, $\mathcal{H}_d^0$ is the secular part of the dipole-dipole interactions (see [2]), r_{ij} is the distance between spins i and j, θ_{ij} is the angle contained by the direction of the constant magnetic field H_0 and the internuclear vector, connecting the spins i and j and γ is the gyromagnetic ratio.

We confine ourselves to consideration of the first (the nearest) sphere, that is to the analysis of the influence of the field $H_{z0}^{(1)}(t)$. The spins, for which the probability of the f–f process is large, are correlated with the selected spin. They are contained in the sphere of radius r. According to [1] we also call this sphere a 'cell'. Two parameters, characterizing the cell, may be introduced: the correlation time τ_c and the mean spread in the random fields H_c. For a simple cubic lattice of spins $\frac{1}{2}$ the distribution function of the random fields $F(\Delta)$ is supposed to be close to the uniform one (the rectangular distribution function) [1]:

$$F(\Delta) = \begin{cases} \tau_c/2C & \text{when} \quad |\Delta\tau_c| < C \\ 0 & \text{when} \quad |\Delta\tau_c| > C \end{cases}$$

$$\tfrac{1}{3}(C/\tau_c)^2 = (\gamma H_c)^2 \qquad \Delta = \gamma H_{z0}^{(1)}$$

where $H_c^2 = \langle (H_{z0}^{(1)})^2 \rangle$ is the dispersion of the random fields, and the parameter C characterizes the velocity of the random process of the field fluctuations. This is confirmed by the proximity between the ratio of the fourth-line moment M_4 to the square of the second moment M_2 (M_4/M_2^2) and the same ratio for the rectangular distribution function [2]. According to [1, 3, 4] let us divide the dipole–dipole interaction into two parts: $\mathcal{H}_{zz}$ is the interaction of the Z-components of spins and $\mathcal{H}_{ff}$ is the interaction responsible for the f–f process. Then the correlation time τ_c will correspond to the mean time value of about W_d^{-1}, during which the reciprocal flips in the spin pairs occur owing to the $\mathcal{H}_{ff}$ part. The field $H_{z0}^{(1)}(t)$ seen by the selected spin is created by the z-components of all spins in the cell arising from the $\mathcal{H}_{zz}$ part. Since it is supposed that this field is not correlated with the field $H_{z0}^{(2)}(t)$, created by the other spins in the crystal, the influences of these fields on the selected spin may be considered separately.

The field $H_{z0}^{(1)}(t)$ induces random changes of the resonant frequency of the selected spin in the cell. This process may be described in terms of spectral diffusion, in which all spins are divided into spectral packets, and a frequency change of the separate spin is considered as its transition from one spectral packet to another. Let us utilize the approximation of the resonant frequency change of a spin by an abrupt Markovian process (the strong-redistribution model). Under this approach the magnetization components

$M_x(\Delta)$, $M_y(\Delta)$, $M_z(\Delta)$ of spectral packets with frequency deviation of $\Delta = \gamma H_{z0}^{(1)}$ from the resonant frequency $\omega_0 = \gamma H_0$ satisfy the following equations of motion in the rotating frame [5, 6]:

$$\frac{dM_x(\Delta)}{dt} = \Delta M_y(\Delta) - \frac{1}{\tau_c} M_x(\Delta) + \int W(\Delta', \Delta) M_x(\Delta')\, d\Delta'$$

$$\frac{dM_y(\Delta)}{dt} = -\Delta M_x(\Delta) - \omega_1 M_z(\Delta) - \frac{1}{\tau_c} M_y(\Delta) + \int W(\Delta', \Delta) M_y(\Delta')\, d\Delta'; \qquad (1)$$

$$\frac{dM_z(\Delta)}{dt} = \omega_1 M_y(\Delta) - \frac{1}{\tau_c} M_z(\Delta) + \int W(\Delta', \Delta) M_z(\Delta')\, d\Delta'$$

where $\omega_1 = \gamma H_1$; $\langle \Delta \rangle = 0$; $\omega = \omega_0$. Here the terms with the factor $1/\tau_c$ (the 'out' terms) describe the spin loss in the packet Δ occurring from the f–f processes, which induce the change of the local field $H_{z0}^{(1)}$. The integral terms on the right-hand side of equations (the 'in' terms) describe the particles coming into the packet considered out of all the others. This process is determined by the conditional probability $W(\Delta', \Delta)$. Let us assume that this probability does not depend on the initial state Δ', that is $W(\Delta', \Delta) = \tau_c^{-1} F(\Delta)$. This uncorrelated stationary process permits us to use a simple scheme in solving the equations (1). By Laplace transformation (in terms of non-dimensional variables) of

$$M(p) = \int_0^\infty \exp[-(p-1)t/\tau_c] M(t)\, \frac{dt}{\tau_c}$$

equation (1) is converted to the set of algebraic equations, the solution of which has the form

$$M(p, \Delta) = \phi(\Delta, p, \omega_1; M(0, \Delta); \langle M(p) \rangle)$$

where $M(0, \Delta) = F(\Delta) m(0)$ is the magnetization vector of the packet at the initial moment;

$$\langle M(p) \rangle = \int M(p, \Delta)\, d\Delta$$

is the summary magnetization vector of all the packets, the components of this vector are connected with initial values of $m_x(0)$, $m_y(0)$, $m_z(0)$ as follows:

$$\langle M_x(p) \rangle = m_x(0)\, \frac{K(p)}{1 - K(p)} \qquad (2a)$$

$$\langle M_y(p) \rangle = \frac{[(p-1)m_y(0) - \varepsilon m_z(0)]p^2 K(p)}{(p^2 + \varepsilon^2)(p-1) + p[\varepsilon^2 - p(p-1)]K(p)} \qquad (2b)$$

$$K(p) = \frac{(p^2 + \varepsilon^2)^{1/2}}{Cp} \tan^{-1} \frac{C}{(p^2 + \varepsilon^2)^{1/2}} \qquad \varepsilon = \omega_1 \tau_c. \qquad (2c)$$

The behaviour of the transverse component of the summary magnetization may be obtained by applying the inverse Laplace transformation

$$\langle M_{x,y}(t) \rangle = \frac{1}{2\pi i} \exp(-t/\tau_c) \int_{a-i\infty}^{a+i\infty} \langle M_{x,y}(p) \rangle \exp(pt/\tau_c)\, dp. \qquad (3)$$

We shall first be concerned with the free induction decay. The $\pi/2$ pulse rotates the

spins of all the packets through 90°. Then, because of the spread of the eigenfrequencies and mixing of packets, the dephasing process (i.e. the spread of the spin packets in the x–y plane) occurs. This process may be described if we put $\omega_1 = 0$ ($\varepsilon = 0$); $M_x(0, \Delta) = F(\Delta)m_0$; $M_y(0, \Delta) = M_z(0, \Delta) = 0$ in (2). Then the solution of the problem is reduced to finding the object function of the Laplace transform

$$\langle M_x(p) \rangle = m_0 \tan^{-1}(C/p)/[C - \tan^{-1}(C/p)]. \tag{4}$$

The latter has a pole $p = p_1 = C \cot C$ at $C \leqslant \pi/2$ and two logarithmic branch points $p = \pm iC$ for arbitrary values of the parameter C. The inverse Laplace transformation of (4) according to the formula (3) gives the following expression for the free-induction decay signal:

$$\langle M_x(t) \rangle = m_0 \exp(-t/\tau_c)\left[\theta\left(\frac{\pi}{2} - C\right)\frac{C^2}{\sin^2 C}\exp[(t/\tau_c)C \cot C] + Q(t)\right] \tag{5a}$$

$$Q(t) = \frac{1}{2\pi}\int_{-\Omega_K}^{\Omega_K} G(\Omega)\,e^{i\Omega t}\,d\Omega \qquad \theta(x) = \begin{cases} 1, & x \geqslant 0 \\ 0, & x < 0 \end{cases} \tag{5b}$$

$$G(\Omega) = \pi C \tau_c \frac{[C^2 - (\pi/2)^2 - N^2] + i2CN}{[C^2 - (\pi/2)^2 - N^2]^2 + 4C^2N^2} \tag{5c}$$

$$N = \frac{1}{2}\ln\frac{C - \Omega\tau_c}{C + \Omega\tau_c} \qquad \Omega_K = C/\tau_c = \sqrt{3}\,\gamma H_c \tag{5d}$$

where the first exponential term appears owing to the pole contribution and the second (integral term) is a result of going around the logarithmic branch points. It should be pointed out that the Q-function has this form at all values of the parameter C, with the exception of $C = \pi/2$, since at this value, the pole $p_1 = 0$ falls on the branch cut in the complex plane $(-iC; +iC)$. Therefore $Q(t)$ must be calculated in another way at $C = \pi/2$. The expression (5) for $C \ll 1$ is essentially simplified:

$$\langle M_x(t) \rangle \simeq m_0 \exp(-t/T_2)$$
$$T_2^{-1} = (\gamma H_c)^2\tau_c. \tag{6}$$

This case corresponds to a fast process leading to motional narrowing and consequently to the exponential relaxation with time T_2. Expression (5) at $C \gg 1$ (the slow process) has another asymptote, that is

$$\langle M_x(t) \rangle \simeq m_0[\sin(Ct/\tau_c)/(Ct/\tau_c)]\exp(-t/\tau_c). \tag{7}$$

This is an inverse Fourier transform of the static rectangular distribution function multiplied by the time exponent. Transition from the exponential relaxation (6) to the non-exponential comes about as follows. The solution (5) consists of two parts—pure exponential and non-exponential. The first one exists at $0 < C \leqslant \pi/2$, that is when the Laplace transform (4) has a pole. The second exists at all values of C and it is stipulated by logarithmic branch points. Let us name $C = C_{cr} = \pi/2$ by a critical point, since when passed the relaxation becomes non-exponential. The case $C > C_{cr}$ is of the most interest, as the velocity of the f–f process in a pair (τ_c^{-1}) is much smaller than the precession frequency of a spin in a local field of the cell $H_{z0}^{(1)}$, that is $C = \sqrt{3}\,\gamma H_c\tau_c > \pi/2$ or

$\gamma H_c > 0.9 W_d$. In this domain of C-values free-induction decay is described by the expression

$$\langle M_x(t)\rangle = m_0 Q(t)\exp(-t/\tau_c).$$

The function $Q(t)$ may be interpreted as a Fourier integral of the spectral function, which coincides with $G(\Omega)$ in the interval $(-\Omega_K, \Omega_K)$ and equals zero when $|\Omega| \geqslant \Omega_K$. Such a form of the solution enables us to reconstruct the line shape function $f(\omega)$, since the Fourier transform of the free-precession signal is known [2] to be proportional to $f(\omega)$. Taking into account the Borel convolution theorem we obtain

$$f(\omega) = \frac{1}{2\pi}\int_{-\Omega_K}^{\Omega_K} G(\Omega)g(\omega - \Omega)\,\mathrm{d}\Omega \qquad (8a)$$

$$g(\omega - \Omega) = \tau_c \frac{1 - \mathrm{i}(\omega - \Omega)\tau_c}{1 + (\omega - \Omega)^2\tau_c^2} \qquad (8b)$$

where $g(\omega - \Omega)$ is the Fourier transform of the function $\exp(-t/\tau_c)$. This expression is correct in the region beyond the critical value of $C\,(C > C_{cr})$. When C is smaller than C_{cr} it is transformed as follows:

$$\tilde{f}(\omega) = f(\omega) + \frac{T_2 C^2}{\sin^2 C}\frac{1 - \mathrm{i}\omega T_2}{1 + (\omega T_2)^2}$$

$$T_2 = \tau_c(1 - C\cot C)^{-1}.$$

The real part of the function $G(\Omega)$ has a specific dependence on the process velocity $(\sim C^{-1})$. When $C \to \infty$ (the slow process) it coincides with the rectangular distribution function. When C decreases to its critical value (the velocity of the process increases) this function transforms to the bell-shaped function. In figure 1 the dependence of Re $G(\Omega)$ on the frequency Ω and the parameter C is presented. In the region beyond the critical value of $C\,(C > C_{cr})$ the function Re $G(\Omega)$ admits the approximation of

$$\text{Re } G(\Omega) = \frac{\pi\tau_c C}{C^2 - (\pi/2)^2}\left[1 - \left(\frac{\Omega}{\Omega_K}\right)^2\right]^{\nu_1} \qquad (9)$$

where the index ν_1 is connected with C as follows:

$$C = \frac{\pi}{2}\left(1 - \frac{\sqrt{\pi}}{2}\frac{\Gamma(\nu_1 + 1)}{\Gamma(\nu_1 + \frac{3}{2})}\right)^{-1/2}.$$

When $C \to \infty$ the index ν_1 tends to zero, while for $C \to C_{cr}$ it tends to infinity. For example, the index ν_1 takes the values 1 and 1/2 when C is equal to 2.72 and 3.39, respectively.

The imaginary part of the function $G(\Omega)$ at large values of C is a gently sloping curve (proportional to $-\Omega$), assuming zero values at the boundaries $(-\Omega_K, \Omega_K)$. The parameter C approaching C_{cr}, this curve transforms into that similar to an ordinary
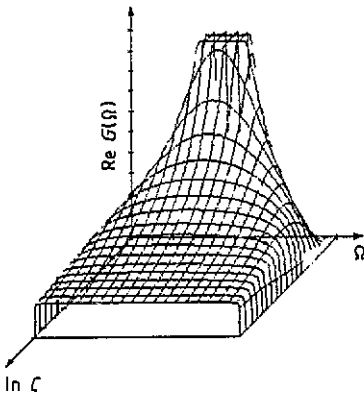
Figure 1. The real part of the spectral function $G(\Omega)$ is plotted against frequency Ω and parameter C.
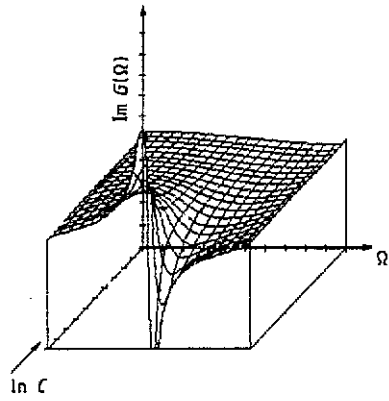

Figure 2. The imaginary part of the spectral function $G(\Omega)$ is plotted against frequency Ω and parameter C.

dispersion curve $\chi'(\Omega)$. In figure 2 Im $G(\Omega)$ is shown plotted against Ω and C at $C > C_{cr}$. In this region of C-values the function Im $G(\Omega)$ permits the following approximation:

$$\text{Im } G(\Omega) = -\frac{2\pi\tau_c}{C(C - \pi/2)}\left(\frac{\Omega}{\Omega_K}\right)\left[1 - \left(\frac{\Omega}{\Omega_K}\right)^2\right]^{\nu_2}$$

$$C = \frac{\pi}{2}\left(1 - \frac{\sqrt{\pi}}{2}\frac{\Gamma(\nu_2 + 1)}{\Gamma(\nu_2 + \frac{3}{2})}\right)^{-1}.$$

(10)

Approximations (9) and (10) allow one to obtain a simple analytical expression for the induction signal at $C > C_{cr}$:

$$\langle M_x(t)\rangle = m_0 \exp(-t/\tau_c)\frac{\sqrt{\pi}}{C - \pi/2}\left(\frac{C^2\Gamma(\nu_1 + 1)}{C + \pi/2}\frac{J_{\nu_1+1/2}(\Omega_K t)}{2(\Omega_K t/2)^{\nu_1+1/2}}\right.$$

$$\left. + \Gamma(\nu_2 + 1)\frac{J_{\nu_2+3/2}(\Omega_K t)}{(\Omega_K t/2)^{\nu_2+1/2}}\right)$$

(11)

where $J_\nu(z)$ is the Bessel function.

At large values of the parameter C the order of the first Bessel function $(\nu_1 + \frac{1}{2})$ tends to a half and this part of the solution transforms to the asymptote (7). The second component of the solution with the Bessel function of the order of $\nu_2 + \frac{3}{2}$ gives a small correction of the order of $1/C$. Such FPS behaviour is typical of the CaF$_2$ single crystal that was considered in [2]. At $C = 3.339$ the order of the first Bessel function is equal to unity and this part of the solution gives the time dependence of FPS, coinciding with that suggested in [7] for solidified nH$_2$ at 4.2 K. The second part, proportional to $J_{\nu_2+3/2}(\Omega_K t)$, is equal to zero at $t = 0$. The other zeros of $J_{\nu_2+3/2}(\Omega_K t)$ nearly replicate those of the first Bessel function, and at $C = 2.37$ the zeros coincide strictly, since $\nu_1 + \frac{1}{2} = \nu_2 + \frac{3}{2}$. At $C > 2.37$ the zeros of the second Bessel function lag behind and at $C < 2.37$ they are slightly ahead of the zeros of the first Bessel function. Furthermore, it may be shown that in the expansion of the function $\langle M_x(t)\rangle$ into a power series of t, the term of the first power is absent. This is because of the fact that the expansion of the second part of the solution without the exponential factor begins from the term t/τ_c, and

of the first part starts from unity, so as a result we have: $m_0(1 + t/\tau_c + \ldots)$. The exponential multiplier has in its turn a power series expansion of the form $1 - t/\tau_c + \ldots$, and finally the function proportional to $J_{\nu_2 + 3/2}(\Omega_K t)$ influences the solution $\langle M_x(t)\rangle$ so that it leads to slowing down of the FPS decay. It is especially noticeable at the initial stage of evolution, when due to the second term the derivative of $\langle M_x(t)\rangle/m_0$ at $t = 0$ equals zero but not $-1/\tau_c$.

In order to illustrate the method suggested let us describe the FPS in CaF_2 using solution (5). The detailed experimental data on free-induction decay in this single crystal have been given in [8] with the indication of eight zeros of the $\langle M_x(t)\rangle$ function for the magnetic field parallel to the crystalline direction [100]. In order to compare the theory with experiment it is necessary to know two parameters, that is C and τ_c. In order to determine them the function $f(t) = \langle M_x(t)\rangle/m_0$ will be expanded in a power series of t in the vicinity of $t = 0$:

$$f(t) = 1 - \frac{M_2}{2!}t^2 + \ldots = 1 - \frac{1}{2!}\left(1 + \frac{C^2}{3 + 2\nu_1}\right)\left(\frac{t}{\tau_c}\right)^2 + \ldots$$

where according to [2] M_2 is the second moment of the line. From this it is easy to obtain the connection of the parameter C with a well known quantity M_2:

$$C = [(3 + 2\nu_1)(M_2\tau_c^2 - 1)]^{1/2}. \tag{12}$$

The second parameter τ_c defines the probability of the f–f process stipulated by the 'flip–flop' part of the dipole–dipole interactions:

$$(\mathcal{H}_{ff})_{ij} = -\gamma^2\hbar^2[(1 - 3\cos^2\theta_{ij})/4r_{ij}^3](\hat{S}_i^+\hat{S}_j^- + \hat{S}_i^-\hat{S}_j^+).$$

Therefore it may be presented as

$$\left(\frac{1}{\tau_c}\right)^2 = \frac{1}{\hbar^2}\sum_{j=1}^{6}|\langle\pm\mp|(\mathcal{H}_{ff})_{ij}|\mp\pm\rangle|^2 \tag{13}$$

where i is the index of a selected spin, and the summation over j means the sum over the six nearest-neighbour spins. The influence of the local field $H_{z0}^{(2)}(t)$, created by the distant spins (i.e. by spins out of the cell) on a selected spin, because of the statistical independence of $H_{z0}^{(1)}(t)$, leads to the factor $\exp(\frac{1}{2}a^2t^2)$ appearing in the function $\langle M_x(t)\rangle$ (see [1]). The factor decreases monotonically with time and consequently does not influence the FPS zero positions. However this should be taken into account when calculating the C parameter, since the value of a contributes to M_2.

The best coincidence with the experimentally observed zeros of the function $f(t)$ was obtained when $\sqrt{M_2} = 3.614$ G; $a = 0.6$ G; $\tau_c = 92\ \mu s$. According to the expression (12) the matching parameters are $C = 14.29$ and $\nu_1 = 0.02$. The correlation time of $92\ \mu s$ gives the square of the f–f process probability $W_{ff}^2 = (1/\tau_c)^2$ to be 1.75 times smaller than the sum (13). In figure 3, $f(t)$, obtained by numerical integration of the expression (5) with given parameters C and τ_c, is plotted. Comparison of the zeros calculated with the ones observed in the [100] field direction [8] is adduced in table 1, second column. For two other directions, [110] and [111], calculations have not been performed, since we believe that when the magnetic field H_0 changes its direction the values of M_2 and the correlation time τ_c change also, the magnitude of C remaining almost constant. This is confirmed by the fact that the ratio of times at which the nth zero is observed (t_n) for different orientations of H_0, is nearly not changed with n. In other words the relation
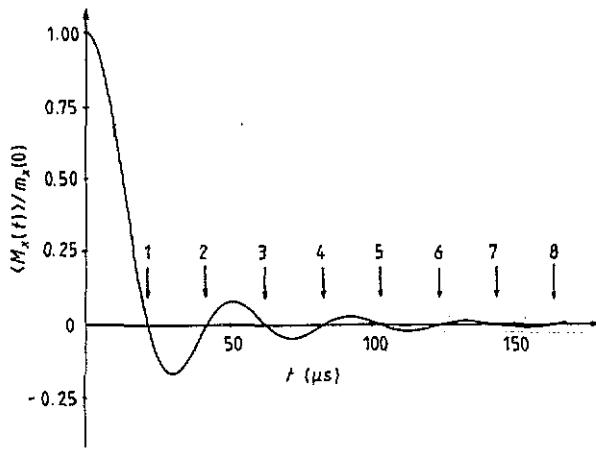
Figure 3. The time dependence of free precession signal, stipulated by the spin fluctuations in a cell, for a single crystal of CaF_2 with $H_0\|[100]$ when $\tau_c = 92\ \mu s$, $C = 14.29$. The arrows indicate the FPS zeros (on a microsecond scale).

Table 1. The zeros of the free precession signals on the microsecond scale. In the first column the zeros observed experimentally [8] are presented. The second column demonstrates the best agreement with the experimental data, obtained within the theory with a correlation time 32% longer than that calculated according to the expression (13). The theoretical results utilizing expression (13) are shown in the third column. The results of the theory with a correlation time calculated in the appendix are presented in the fourth column.

	FPS zeros (μs)			
Number	Experiment [8]	Theory, $C = 14.29$ $\tau_c = 92\ \mu s$	Theory, $C = 10.95$ $\tau_c = 69.5\ \mu s$	Theory, $C = 8.56$ $\tau_c = 54.95\ \mu s$
1	21.38 ± 0.01	21.43	21.53	22.1
2	42.15 ± 0.02	42.0	41.9	42.6
3	62.26 ± 0.03	62.42	62.1	62.92
4	82.75 ± 0.06	82.79	82.23	83.15
5	103.4 ± 0.15	103.14	102.3	103.3
6	122.96 ± 0.6	123.46	122.4	123.45
7	144.5 ± 1.5	143.77	142.44	143.56
8	165 ± 4.0	164.07	162.48	163.65

$t_n^i = \phi_n(C)\tau_c^i$ is fulfilled with an accuracy of a few per cent, where i is one of the three directions; therefore

$$\frac{t_n^i}{t_n^j} \approx \frac{\tau_c^i}{\tau_c^j} \approx \frac{(\sqrt{M_2})_j}{(\sqrt{M_2})_i} = \begin{cases} 1.625 \text{ at } i = [110] \\ 2.465 \text{ at } i = [111] \end{cases}$$

where $j = [100]$.

Thus, free-induction decay in CaF_2 is described by a Bessel function of the order of 0.502, by two hundredths differing from the order of the Bessel function suggested by Abragam:

$$(\sqrt{\pi}/2)J_{1/2}(bt)/(bt/2)^{1/2} = (\sin bt)/bt.$$

Comparison of the experimental results [8] with our theoretical predictions, which employ the correlation time τ_c calculated by the method described in [9], is presented in the appendix.

We consider the influence of the resonant field $H_1(t)$ on the relaxation of the transverse magnetization components: $\langle M_x(t)\rangle$ and $\langle M_y(t)\rangle$. The variation of the kinetics of the $\langle M_x(t)\rangle$ component can be detected by a 'spin-locking' technique, when the 90° phaseshift of the RF field follows the 90° pulse immediately, the magnetization in the rotating frame being parallel to the effective field H_1. The kinetics of the $\langle M_y(t)\rangle$ component can be observed without the following phaseshift of the continuously operating RF field of an intensity other than the pulse field.

In the case of a slow process ($C \ll 1$) the motion of the magnetization $\langle M(t)\rangle$ is described by the Bloch equations:

$$d\langle M_x\rangle/dt = -\langle M_x\rangle/T_{2x} \tag{14a}$$

$$d\langle M_y\rangle/dt = -\omega_1\langle M_z\rangle - \langle M_y\rangle/T_{2y} \tag{14b}$$

$$d\langle M_z\rangle/dt = \omega_1\langle M_y\rangle - (\langle M_z\rangle - M_{z0})/T_1. \tag{14c}$$

Its solution at $\langle M(0)\rangle = (m_x(0), 0, 0)$ has the form

$$\langle M_x(t)\rangle = m_x(0)\exp(-t/T_{2x}).$$

The time T_{2x} may be found by the inverse Laplace transformation (3) of the expression (2). In the strong RF field ($\omega_1\tau_c \gg 1$) the main contribution to the behaviour of the x-component is given by the pole at the extreme right:

$$p_r = 1 - C^2/3(\varepsilon^2 + 1) + \dots.$$

From this it follows that

$$T_{2x} = \tau_c[1 + (\omega_1\tau_c)^2]/(\gamma H_c\tau_c)^2.$$

This is a typical slowing down of the relaxation for 'viscous' liquids [2, 10–12] ($\gamma H_c\tau_c \ll 1$).

At $\langle M(0)\rangle = (0, m_y(0), 0)$ the solution of equation (14), when $\omega_1 T_{2y} \gg 1$; $M_{z0} = 0$; $T_1 \to \infty$, has the following form:

$$\langle M_y(t)\rangle = m_y(0)\exp\left(-\frac{t}{2T_{2y}}\right)\cos\left[\omega_1\left(1 - \frac{1}{8(\omega_1 T_{2y})^2}\right)t\right].$$

In the strong field ($\omega_1\tau_c \gg 1$) the main contribution in the behaviour of the y-component is determined in accordance with (2) by the two poles at the extreme right:

$$p_r = 1 \pm i\varepsilon \pm i(C^2/6\varepsilon) - (C^2/6\varepsilon^2)(1 + \tfrac{2}{15}C^2) + \dots.$$

From this it follows that $T_{2y} = T_{2x}$. Furthermore, it may be shown that the Rabi frequency increases as a result of the modification of the kinetics as follows: $\tilde{\omega}_1 = \omega_1[1 + \tfrac{1}{2}(H_c/H_1)^2]$.

When the velocity of the process is smaller than the critical value: $C^{-1} < C_{cr}^{-1}$, the relaxation becomes non-exponential and cannot be described by the Bloch equations

(14). This arises from the fact that the Laplace transform (2) has no poles. Switching on even a weak RF field ($\omega_1\tau_c \ll 1$) leads to a pole revival: $p_r = C_{cr}\varepsilon/(C^2 - C_{cr}^2)^{1/2} + \ldots$, owing to this in the $\langle M_x(t)\rangle$ component kinetics the long exponential 'tails' appear, characterized by the time

$$T_{exp} \simeq [1 + (C_{cr}/C)\gamma H_1 \tau_c]\tau_c \tag{15}$$

at $C \gg C_{cr}$. The latter is essentially longer than the time scale of non-exponential relaxation ($\sim(\gamma H_c)^{-1}$). The contribution of the exponential component to solution (3) increases with the field amplitude. In a strong field ($\omega_1\tau_c \gg C^2$) the relaxation becomes essentially exponential and may be described by the Bloch equations (14) with times:

$$T_{2x} = \tau_c(H_1/H_c)^2 \qquad T_{2y} = \tfrac{5}{2}\tau_c(H_1/\gamma H_c^2\tau_c)^2.$$

It may be shown that in the case of a slow process ($C \gg 1$) a significant slowing down of the x-component relaxation (the value of T_{2x} increases from a value of the order of $(\gamma H_c)^{-1}$ to several units of τ_c) already occurs when $H_1 \sim H_c$. In this process the relaxation rate of the y-component changes slightly. This difference in the times T_{2x} and T_{2y} remains up to very large field amplitudes, $H_1 \sim CH_c$.

Our investigations show that in the liquid phase ($C < C_{cr}$) relaxation of the magnetization in the x–y plane is symmetric ($T_{2x} = T_{2y}$). Its slowing down depends on the relation of the Rabi frequency ω_1 and the correlation time τ_c. In the solid phase ($C > C_{cr}$) under a strong field ($H_1 > H_c$) the asymmetry in relaxation times appears ($T_{2x} \gg T_{2y}$). The slowing down of the x-component relaxation becomes significant when the RF field amplitude H_1 is comparable with the local field H_c. This result confirms the Redfield hypothesis [13] about the existence of the spin temperature in the rotating frame, according to which the spins at $H_1 > H_c$ are quantized in the effective field H_1 and relaxation of the x-component of magnetization slows down since it becomes an energy relaxation, while the y-component relaxation remains a phase relaxation. Asymmetry of relaxation times is assumed within the framework of this hypothesis, but follows directly from our theory.

In conclusion it should be noted that it is difficult to detect the moment of the process velocity crossing its critical value C_{cr}^{-1} (when τ_c decreases as a result of a sample heating) owing to the smooth character of the crossing. However, this point may be determined by the spin-locking technique in a weak continuously operating RF field ($\omega_1\tau_c \ll 1$), when T_{exp} (15) against the amplitude H_1 is analysed. At $C \gg C_{cr}$ this dependence is linear in H_1. In the vicinity of the critical point:

$$2(C - C_{cr})/C_{cr} \ll (\omega_1\tau_c)^2 \ll 1$$

and just at the point this dependence becomes non-linear:

$$T_{exp} = \tau_c[1 + (C_{cr}\omega_1\tau_c/\sqrt{2})^{2/3}].$$

The degree (index) of non-linearity depends on the form of the local field distribution. In a three-dimensional spin system, with typical distribution functions with gently sloping peaks and abrupt wings, for example, rectangular or Gaussian forms, the index of the power with which the field amplitude enters the expression for T_{exp} is two thirds. Distribution functions of one-dimensional spin systems have, on the contrary, gently

sloping wings and sharp peaks. For example, the Laplace distribution function possesses these properties

$$F(\Delta) = (\tau_c/2C) \exp(-|\Delta \tau_c|/C) \, d\Delta.$$

The deviation from the linear dependence of T_{exp} against H_1 in the vicinity of C_{cr} is smaller for this function because of the appearance of the extra logarithmic dependence:

$$T_{exp} = \tau_c \left[1 + \left(-\frac{3(C_{cr}\varepsilon)^2}{4 \ln(C_{cr}\varepsilon/\sqrt{2})} \right)^{1/3} \right]$$

where $\varepsilon = \omega_1 \tau_c$; $|\ln \varepsilon| \gg 1$.

Appendix

In [9] the probability of reciprocal spin flips in a pair ij is estimated as follows:

$$W_{ij} = (2\pi/\hbar^2)|\langle \pm\tfrac{1}{2}, \mp\tfrac{1}{2}|(\mathcal{H}_{ff})_{ij}|\mp\tfrac{1}{2}, \pm\tfrac{1}{2}\rangle|^2 \, \bar{T}_2/\pi$$

where $\bar{T}_2 = \pi F(0)$. In this expression in contrast to that adduced in [9] there is no multiplier $1/\sqrt{2}$, since the uniform distribution function is taken as $F(0)$. Therefore when the f–f transition in a pair of identical nuclei takes place the number of finite states per unit frequency interval is equal to $\bar{T}_2/\pi$. It is known that for $S = 1/2$:

$$M_2 = \tfrac{9}{16}\hbar^2 \gamma^4 \sum_j{}' r_{ij}^{-6} (1 - 3 \cos^2 \theta_{ij})^2.$$

Therefore the expression for the correlation time τ_c may be expressed as

$$\tau_c^{-1} = \sum_j{}' W_{ij} = \tfrac{2}{9} M_2 \bar{T}_2 = \pi M_2 \tau_c/9C$$

which gives an additional correlation between the following theoretical parameters τ_c, M_2 and C

$$M_2 \tau_c^2 = 9C/\pi.$$

Using this expression and the condition (12) one can obtain C and τ_c from M_2. Thus for the value of $\sqrt{M_2} = 3.614$ G the corresponding parameters of the theory are equal to $C = 8.56$; $\nu_1 = 0.0575$ and $\tau_c = 54.95 \, \mu$s. The zeros of the FPS at these values of the theoretical parameters are shown in the fourth column of table 1. The zeros of the FPS for τ_c, calculated from the expression (13) and with $\sqrt{M_2} = 3.614$ G, are listed in the third column, the corresponding parameters being equal to $\tau_c = 69.5 \, \mu$s, $C = 10.951$ and $\nu_1 = 0.0375$.

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