Magnetic resonance in solids in a rotating coordinate frame

V. G. Pokazan'ev and L. I. Yakub

Urals Polytechnical Institute
(Submitted November 29, 1976)
Zh. Eksp. Teor. Fiz. 73, 221–227 (July 1977)

A theory of magnetic resonance in a rotating coordinate frame is developed by the method of the nonequilibrium statistical operator. It is shown that, not only for systems whose behavior is described satisfactorily by the Bloch equations, but also for systems for which the Bloch equations are certainly incorrect, the resonance in the effective field can be studied using the z-component of the magnetization in the laboratory coordinate frame, since this component experiences a resonance and modulation dependence at the frequency of precession of the spins in the effective field $H_e=\{(H_0-\omega/\gamma)^2+H_1^2\}^{1/2}$.

PACS numbers: 76.20.+q

INTRODUCTION

It is well known that the action on a system of spins I of a radio-frequency (rf) field $\mathbf{H}_1(t)$ rotating with frequency ω in a constant magnetic field $\mathbf{H}_0$ ($\parallel z$) leads to coherent precession of the spins in the field $\mathbf{H}_0$ if ω is equal to the resonance frequency $\omega_0=\gamma H_0$ (γ is the gyromagnetic ratio). In the coordinate frame rotating with frequency ω about $\mathbf{H}_0$ the spins experience the action of an effective field, constant in time,

$$\mathbf{H}_e=\mathbf{i}H_1+\mathbf{k}(H_0-\omega/\gamma),$$

which makes an angle

$$\theta=\mathrm{arctg}[H_1/(H_0-\omega/\gamma)]$$

with the z axis (cf. Fig. 1). In this field, however, the precession is not coherent, as is revealed by the absence of a component of the magnetization of the system perpendicular to $\mathbf{H}_e$. To introduce coherence into the motion of the spins in the rotating coordinate frame (RCF) or, in other words, to excite a magnetic resonance in the effective field $\mathbf{H}_e$, we can, for example, apply a second rf field, varying with a frequency Ω close to the spin resonance frequency $\omega_e=\gamma H_e$, in the plane perpendicular to $\mathbf{H}_e$. In practice this can be achieved by modulation, with frequency Ω, of the amplitude of the rotating field $\mathbf{H}_1(T)$, or by modulation of the field $\mathbf{H}_0$ by a field $\mathbf{H}_2(t)=\mathbf{k}H_2\cos\Omega t$ (cf. Fig. 1).

Basing his approach on the spin-temperature hypothesis, Redfield[1] attempted to detect magnetic resonance in the RCF by saturating the rf transitions by a second field $\mathbf{H}_2(t)$. As is well known, in an ordinary resonance (in the laboratory coordinate frame (LCF) the absorption of the rf energy by the spins is detected directly. In a resonance in the RCF, ω_e falls in the region of very low frequencies and the energy absorbed by the spins from the field $\mathbf{H}_2(t)$ is extremely small. However, these transitions can be detected from the change in the dispersion signal at the high frequency ω of the field $\mathbf{H}_1(t)$. This is due to the fact that this signal depends on the magnitude of the projection of the magnetization on the direction of $\mathbf{H}_e$, and this projection changes substantially when $\Omega=\omega_e$, in conditions of saturation.

To study the transitions at the frequency $\Omega=\omega_e$ in systems whose behavior in magnetic-resonance conditions is described satisfactorily by the Bloch equations, in our earlier papers[2] we proposed a new principle, based on the observation of the z-component of the magnetization in the LCF, modulated at frequencies that are multiples of Ω. In Refs. 2 we also reported the realization of this principle in a system of optically oriented Cs^{133} atoms, the z-component of the magnetization being measured from the light absorption. The object of the present paper is to investigate theoretically those resonance phenomena in the spin systems of solids in the RCF for which the Bloch equations are, in general, inapplicable.

1. THE HAMILTONIAN OF THE SPIN SYSTEM IN THE EFFECTIVE FIELD

We suppose that a system of spins placed in a strong constant magnetic field $\mathbf{H}_0$($\parallel z$) is acted upon by an rf field $\mathbf{H}_1(t)$, rotating with frequency ω and amplitude H_1 about $\mathbf{H}_0$, and a field $\mathbf{H}_2\cos\Omega t$, oscillating parallel to $\mathbf{H}_0$. The frequency ω may be the resonance frequency in the field H_0; it belongs, therefore, to the high-frequency band, while Ω belongs to the low-frequency band.

The Hamiltonian of the system has the form

$$\mathscr{H}=\omega_0 I_z+{}^1/_2\omega_1(I_+e^{-i\omega t}+I_-e^{i\omega t})+\omega_2 I_z\cos\Omega t+\mathscr{H}_d, \quad (1)$$

where $\omega_j=\gamma H_j$ ($j=0, 1, 2$); $I_\pm=I_x\pm iI_y$ and I_i ($i=x, y, z$) are the components of the total spin; $\mathscr{H}_d$ is the dipole-dipole

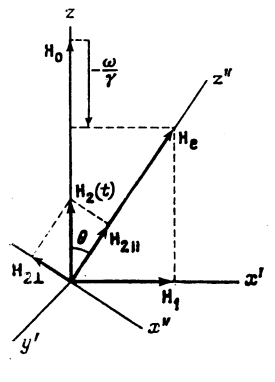

FIG. 1.

0038-5646/77/4601-0114$02.40

interaction energy. In (1) we have not taken into account the influence of the lattice, which will be assumed to be weak in comparison with the spin-spin interaction and will be taken into account phenomenologically in the following.

In the coordinate frame rotating with frequency ω about $\mathbf{H}_0$ the energy of the spins is described by the expression

$$\mathscr{H}_s=\Delta I_z+\omega_1 I_{x'}+\omega_2 I_z\cos\Omega t+\mathscr{H}_d^0,$$

$$\mathscr{H}_d^0=\sum_{i<j}a_{ij}(3I_z^iI_z^j-\mathbf{I}^i\mathbf{I}^j),\qquad a_{ij}=\frac{\gamma^2}{2r_{ij}^3}(1-3\cos^2\vartheta_{ij}),\tag{2}$$

where $\Delta=\omega_0-\omega$ and $\mathscr{H}_d^0$ is the secular part of the dipole-dipole interaction; we neglect the effect of the nonsecular parts, since they vary in time with frequencies ω and 2ω.

Performing the unitary transformation $T=\exp(iI_y, \theta)$, which is equivalent to a rotation of the RCF through an angle θ about the y' axis (i.e., the z'' axis will point along $\mathbf{H}_e$), we obtain

$$\mathscr{H}_T=\omega_e I_{z''}+\omega_2\cos\Omega t(I_{z''}\cos\theta-I_{x''}\sin\theta)+k\mathscr{H}_d^0,$$

$$k={}^1/_2(3\cos^2\theta-1),\quad \theta=\mathrm{arctg}(\omega_1/\Delta),\quad \omega_e=[\Delta^2+\omega_1^2]^{1/2}.\tag{3}$$

It is clear that in the rotated coordinate frame (x'', y'', z'') the field $\mathbf{H}_2(t)$ has, with respect to $\mathbf{H}_e$, a transverse component $H_{2\perp}$ ($H_2\sin\theta\cos\Omega t$) and a longitudinal component $H_{2\parallel}$ ($H_2\cos\theta\cos\Omega t$). Redfield[1] disregarded the effect of the longitudinal component, and attributed the appearance of the resonance in the effective field entirely to the action of the component $H_{2\perp}$. However, although the longitudinal component $H_{2\parallel}$ (unlike the field $H_{2\perp}$) does not induce resonance transitions of the spins in the field $\mathbf{H}_e$, it does exert an important influence on the character of the interaction of the spins with the field $H_{2\perp}$, leading to a number of interesting effects. With the aim of taking this influence into account we shall carry out a unitary transformation using the operator $U=\exp(iI_{z''}a\sin\Omega t)$, where $a=(\omega_2/\Omega)\cos\theta$. We then obtain

$$\mathscr{H}_U=\omega_e I_{z''}+k\mathscr{H}_d^0-\frac{\Omega\,\mathrm{tg}\,\theta}{2}\sum_{q=-\infty}^{\infty}qJ_q(a)\,(I_+e^{iq\Omega t}+I_-e^{-iq\Omega t}).\tag{4}$$

Here the third term is the energy of the interaction of the spins with an infinite set of rf fields that have amplitudes $\Omega qJ_q(a)\tan\theta$ and rotate with frequencies $q\Omega$ about the direction of $\mathbf{H}_e$.

If Ω is greater than the linewidth of the magnetic resonance in the field $\mathbf{H}_e$, then, obviously, the greatest influence on the state of the spins is exerted by the field with frequency $p\Omega\approx\omega_e$. To take this into account we transform by means of the unitary operator $R=\exp$ $R=\exp(ip\Omega I_{z''}t)$ to the coordinate frame rotating with frequency $p\Omega$ about $\mathbf{H}_e$:

$$\mathscr{H}_R=(\omega_e-p\Omega)I_{z''}-\frac{\Omega\,\mathrm{tg}\,\theta}{2}\sum_{q=-\infty}^{\infty}qJ_q(a)\,[I_+e^{i(p+q)\Omega t}+I_-e^{-i(p+q)\Omega t}]+k\mathscr{H}_d^0.\tag{5}$$

If $|qJ_q(a)\tan\theta|\ll 1$, we can retain only the zeroth harmonic (the secular approximation) in the second term of this relation and $\mathscr{H}_R$ goes over into the expression

$$\mathscr{H}_R^{(r)}=(\omega_e-p\Omega)I_z+p\Omega\,\mathrm{tg}\,\theta\,J_{-p}(a)I_x+k\mathscr{H}_d^0.\tag{6}$$

(The primes on z and x have been omitted for convenience.)

The quantity $\mathscr{H}_R^{(r)}$ is a static Hamiltonian, which permits us, in principle, to analyze the behavior of the spin system in the doubly rotating coordinate frame by the methods familiar in the statistical theory of magnetic resonance.

2. THE MAGNETIC-RESONANCE SIGNAL IN THE ROTATING FRAME IN THE CASE OF A WEAK RF FIELD (PROVOTOROV'S CASE)

Depending on the relative magnitudes of the energies described by the separate terms in (6), substantially different physical situations can be realized. In this section we consider the first of these possibilities, when the second term in (6) is small compared with the others and can be treated as a perturbation. In this case the spin system can be approximately decomposed into two subsystems (reservoirs) - the Zeeman and the dipole reservoir, the internal equilibrium of which can be characterized by the inverse temperatures β_z and β_d, respectively.

The evolution of the spin system can then be described by Zubarev's method of the nonequilibrium statistical operator (NSO).[3] Denoting this operator by ρ, for our case we write

$$\rho=Q^{-1}\exp\left\{-\beta_z\mathscr{H}_z-\beta_d\mathscr{H}_d'+(\beta_z-\beta_d)\int_{-\infty}^{0}dt\,e^{\epsilon t}K_z(t)\right\},\tag{7}$$

where

$$\mathscr{H}_z=(\omega_e-p\Omega)I_z,\quad \mathscr{H}_d'=k\mathscr{H}_d^0,$$
$$K_z(t)=\exp[i(\mathscr{H}_z+\mathscr{H}_d')t]K_z\exp[-i(\mathscr{H}_z+\mathscr{H}_d')t],$$
$$K_z=p\Omega(\omega_e-p\Omega)\,\mathrm{tg}\,\theta J_{-p}(a)I_y,\quad Q=\mathrm{Sp}\,\rho.$$

By means of calculations analogous to those given in[3], we obtain from (7) in the high-temperature approximation the following equations for the inverse temperatures (in the absence of spin-lattice relaxation):

$$d\beta_z/dt=-W_p(\beta_z-\beta_d),\quad d\beta_d/dt=f_pW_p(\beta_z-\beta_d),\tag{8}$$

where

$$W_p=\sqrt{\frac{\pi}{2}}\frac{[p\Omega\,\mathrm{tg}\,\theta J_p(a)]^2}{|k|\,\omega_L}\exp\left(-\frac{f_p}{2}\right),\quad f_p=\frac{(\omega_e-p\Omega)^2}{k^2\omega_L^2}$$

and ω_L is the frequency of precession of the spins in the local field.

The equations given enable us to find the rate $1/T_m$ of equalization of the temperatures of the Zeeman and dipole reservoirs:

$$1/T_m=W_p(1+f_p)$$
$$=\sqrt{\frac{\pi}{2}}\frac{[p\Omega\,\mathrm{tg}\,\theta J_p(a)]^2}{|k|\omega_L}\exp\left[-\frac{(\omega_e-p\Omega)^2}{2k^2\omega_L^2}\right]\left\{1+\frac{(\omega_e-p\Omega)^2}{k^2\omega_L^2}\right\}.\tag{9}$$

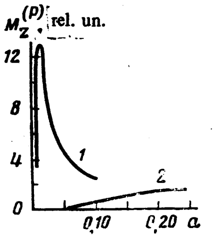

FIG. 2.

It can be seen from this that the rate of equalization of the temperatures is a resonance function of the frequencies, with resonances occurring when the conditions $\omega_e = p\Omega$ are fulfilled. On the other hand, the value of $1/T_m$ can be varied within wide limits by varying the parameters of the field $\mathbf{H}_1(t)$ and $\mathbf{H}_2(t)$, and can even be made to vanish when a takes a value coinciding with a zero of the Bessel function.

When the spin-lattice relaxation is taken into account the inverse temperatures of the subsystems are found from the equations

$$\frac{d\beta_z}{dt} = -W_p(\beta_z-\beta_d) - \frac{1}{T_{zp}}(\beta_z-\beta_z^0),$$
$$\frac{d\beta_d}{dt} = f_pW_p(\beta_z-\beta_d) - \frac{1}{T_{dp}}(\beta_d-\beta_d^0); \quad (10)$$
$$\beta_d^0 = \frac{\beta_L}{|k|}, \quad \beta_z^0 = \frac{\omega_0\cos\theta}{\omega_e - p\Omega}\beta_L,$$

where β_L is the inverse temperature of the lattice and T_{zp} and T_{dp} are the spin-lattice relaxation times of the Zeeman and dipole reservoirs in the RCF.

The stationary solution of Eqs. (10) has the form

$$\frac{\beta_z}{\beta_z^0} = \frac{1+f_pW_pT_{dp}}{1+W_p(T_{zp}+f_pT_{dp})}, \quad (11)$$
$$\frac{\beta_d}{\beta_z^0} = \frac{f_pW_pT_{dp}}{1+W_p(T_{zp}+f_pT_{dp})}. \quad (12)$$

Using these relations we can find the average values of the components of the magnetization of the spin system in the LCF. We cite as an example the expression for the z-component of the magnetization:

$$M_z^{(r)} = \chi_0H_0\frac{p\Omega\sin^2\theta}{1+W_p(T_{zp}+f_pT_{dp})}\sum_{q=-\infty}^{\infty}J_{q-p}(a)J_{-p}(a)$$
$$\times\{g'(\omega_e-p\Omega)\cos q\Omega t + g(\omega_e-p\Omega)\sin q\Omega t\}$$
$$-\chi_0H_0\cos^2\theta\frac{1+f_pW_pT_{dp}}{1+W_p(T_{zp}+f_pT_{dp})}, \quad (13)$$

where

$$g(x) = \int_0^\infty dt\exp\left\{-\frac{k^2}{2}\omega_L^2t^2\right\}\cos xt,$$
$$g'(x) = \int_0^\infty dt\exp\left\{-\frac{k^2}{2}\omega_L^2t^2\right\}\sin xt.$$

Thus, the magnetization of the spin system in the direction of the z axis contains an infinite set of harmonics with frequencies that are multiples of Ω and amplitudes that have a resonance dependence on the frequency and take their maximum values when the conditions

$$\omega_e - p\Omega = 0, \quad p = 1, 2, 3, \ldots, \quad (14)$$

are fulfilled, corresponding to observation of the p-th resonance in the effective field.

Thus, on the basis of the analysis given, we can convince ourselves that a resonance and modulation dependence is intrinsic to the z-component of the magnetization in the LCF on excitation of magnetic transitions at the frequency ω_e, not only in gases, liquids and solids whose behavior is described satisfactorily by the Bloch equations but also in systems for which the Bloch equations are certainly incorrect. It is interesting to elucidate the role of $H_{2\perp}$ and $H_{2\parallel}$ in the formation of the resonance signal. This is done most simply by turning to the expression for the transition probability W_p (8). Using the series expansion of the Bessel function, we find the asymptotic values of W_p for $p=1$ and $p=2$ when $\omega_2/\Omega \ll 1$ ($a \ll 1$):

$$W_1 \approx \frac{1}{4}\left(\frac{\pi}{2}\right)^{1/2}\frac{\gamma^2}{|k|\omega_L}(H_{2\perp})^2e^{-f_1/2}[1+O(a^2)],$$
$$W_2 \approx \frac{1}{16}\left(\frac{\pi}{2}\right)^{1/2}\frac{\gamma^4}{|k|\omega_L\Omega^2}(H_{2\perp})^2(H_{2\parallel})^2e^{-f_2/2}[1+O(a^2)].$$

It follows from this that for the fundamental resonance ($\Omega = \omega_e$), for any value of the angle θ, the greatest contribution to the transition probability is given by the component of the field $\mathbf{H}_2$ perpendicular to $\mathbf{H}_e$. The characteristic feature in the excitation of the resonance at the frequency $\Omega = \omega_e/2$ ($p=2$) is the fact that the transition probability (W_2) is determined by the joint action of $H_{2\perp}$ and $H_{2\parallel}$, their relative contribution depending on the value of the angle θ. An analogous situation obtains in the excitation of the resonances at the frequencies ω_e/p for $p>2$.

Since, as follows from the relation (13), $M_z^{(r)}=0$ when $\theta=0$, $\pi/2$, observation of the resonance from the z-component is possible only when $0<\theta<\pi/2$. This means that both components of the field $\mathbf{H}_2$ take part in shaping the resonance signal. Even some features of the behavior of the fundamental signal ($p=1$) cannot be fully explained by taking into account only the effect of the transverse component $H_{2\perp}$, as was done in Ref. 1.

The analysis of the dependence of $M_z^{(r)}$ on θ and H_2 is carried out more conveniently using the examples of $M_z^{(1)}$ and $M_z^{(2)}$, which at exact resonance ($\omega_e=\Omega$, $\omega_e=2\Omega$) have the form

$$M_z^{(1)} \sim \frac{\sin^2\theta J_0(a)J_1(a)}{1+(\pi/2)^{1/2}T_{zp}(\Omega\,\mathrm{tg}\,\theta J_1(a))^2/(|k|\omega_L)},$$
$$M_z^{(2)} \sim \frac{\sin^2\theta J_1(a)J_2(a)}{1+4(\pi/2)^{1/2}T_{zp}(\Omega\,\mathrm{tg}\,\theta J_2(a))^2/(|k|\omega_L)}. \quad (15)$$

Figure 2 shows the dependences of $M_z^{(1)}$ and $M_z^{(2)}$ on the quantity a at $\theta=45°$. In the first case (for $M_z^{(1)}$) saturation of the resonance signal sets in at $a<0.01$ (curve 1). In the second case (curve 2) the resonance signal has no appreciable tendence to become saturated, even at $a\approx0.25$, i.e., at amplitudes of the field $\mathbf{H}_2$ that exceed the value of the saturating field for the first case by a factor of 25. This behavior of the resonance signals at frequencies $\omega_e=\Omega$ and $\omega_e=2\Omega$ becomes understandable if we take into account that, according to (6), the energy of the interaction of the spins with the rf field is proportional to $J_p(a)$ and falls sharply with increase of p.

Thus, the theory given has confirmed the idea we put forward earlier about using the resonance and modulation dependence of the z-component of the magnetization in the LCF to investigate the magnetic resonance phenomena in the RCF in gases, liquids and solids. The idea has been experimentally confirmed for gases in Refs. 2, and for liquids and solids in the work of Mefed and Atsarkin,[4] who proposed an induction method for the observation of M_z.

3. MAGNETIC RESONANCE IN THE ROTATING FRAME IN THE CASE OF A STRONG RF FIELD

We shall consider now the experimental situation in which the second term in (6) is greater than the spin-spin interaction energy. In this case we cannot distinguish spins of a Zeeman and a dipole subsystem in the system, and in the doubly rotating coordinate frome a spin temperature T_s is established,[5] to which corresponds the magnetization

$$M_p^{(r)'}=M_p^0\frac{(\omega_e-p\Omega)^2}{(\omega_e-p\Omega)^2+(p\Omega\,\mathrm{tg}\,\theta J_p(a))^2+k^2\omega_L^2}, \tag{16}$$

where M_p^0 is the initial magnetization in the direction of the effective field.

Transforming to the LCF, we obtain the following expression for the component M_z of the magnetization:

$$M_z^{(r)}=M_0\cos\theta\frac{(\omega_e-p\Omega)^2}{(\omega_e-p\Omega)^2+(p\Omega\,\mathrm{tg}\,\theta J_p(a))^2+k^2\omega_L^2}$$

$$\times\left\{\cos\theta-\frac{p\Omega\sin\theta\,\mathrm{tg}\,\theta}{\omega_e-p\Omega}\sum_{q=-\infty}J_{q-p}(a)J_{-p}(a)\cos q\Omega t\right\}, \tag{17}$$

where for the initial value M_p^0 we have taken the quantity $M_0\cos\theta$ (M_0 is the magnetization of the spins in the field H_0).

In the magnetization (17) there are both constant terms and terms modulated at frequencies $q\Omega$, the latter terms being of special interest from the point of view of the detection of the resonance. The amplitudes of all the harmonics contain a resonance dependence on the frequencies of the applied fields and take their maximum value when the condition $\omega_e-p\Omega=0$ is fulfilled. The term with the denominator $(p\Omega J_p(a)\tan\theta)^2$ describes the rf broadening of the resonance, due to real transitions induced by the component $H_{2\perp}$ of the field $\mathbf{H}_2(t)$. This broadening becomes negligibly small at small angles θ, since in this case $H_{2\perp}$ becomes a small quantity and $H_{2\parallel}$ plays the main role.

Also characteristic is the fact that in the resonance denominator of (17) there appears the term $k^2\omega_L^2$, where $k=1/2(3\cos^2\theta-1)$, which is responsible for the dipolar broadening of the resonance line in the effective field. When the angle $\theta=\arccos(1/\sqrt{3})$ we have $k=0$, which leads to the effect, well known in magnetic resonance, of narrowing of the resonance line.

The authors express their deep gratitude to A. Mefed and V. Atsarkin for discussions on the results of the work.

[1]A. G. Redfield, Phys. Rev. 98, 1787 (1955).
[2]L. N. Novikov and V. G. Pokazan'ev, Pis'ma Zh. Eksp. Teor. Fiz. 4, 393 (1966) [JETP Lett. 4, 266 (1966)]; V. G. Pokazan'ev and L. I. Yakub, Zh. Eksp. Teor. Fiz. 53, 1287 (1967) [Sov. Phys. JETP 26, 752 (1968)]; Izv. Vyssh. Uchebn. Zaved. Radiofiz. 11, 714 (1968).
[3]D. N. Zubarev, Neravnovesnaya statisticheskaya termodinamika (Nonequilibrium Statistical Thermodynamics), Nauka, M., 1971 (English translation published by Consultants Bureau, N. Y., 1974).
[4]A. E. Mefed and V. A. Atsarkin, Pis'ma Zh. Eksp. Teor. Fiz. 25, 233 (1977) [JETP Lett. 25, 215 (1977)].
[5]M. Goldman, Spin Temperature and Nuclear Magnetic Resonance in Solids, Oxford University Press, 1970. (Russ. transl. Mir., M., 1972).

Translated by P. J. Shepherd.