Experimental separation of frequency spin echo signal

Yu. M. Bun'kov and V. V. Dmitriev

Institute of Physics Problems, USSR Academy of Scienes
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It is shown that the theory of the mechanism of formation of a frequency-modulated (FM) echo does not describe completely the properties of the echo signals in system with dynamic frequency shift (DFS). A strong spin-echo signal was observed, caused apparently by other nonlinear properties of systems with coupled electron-nuclear precession. A spin echo signal whose properties correspond to the concepts of the frequency mechanism of echo formation has been separated in experiment. Possible alternate mechanisms of echo-signal formation in system with coupled electron-nuclear precession are discussed.

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1. INTRODUCTION

Among the most interesting objects recently investigated by magnetic-resonance methods are systems with coupled electron-nuclear precession. The latter arises in magnetically ordered systems under conditions of large nuclear magnetization and relatively low FMR (AFMR) frequencies. The largest coupling of the nuclear and electron precessions is observed in antiferromagnets containing Mn. It has also been observed on Mn-containing ferrites and Fe containing antiferromagnets,[1] as well as in thin ferromagnetic films containing Co.[2]

The interest is systems with coupled electron-nuclear precession is due to the strong nonlinear properties of these systems. They manifest themselves in the fact that the frequencies of the joint oscillations (ω_{ne} and ω_{en}) differ from the frequencies due to the local fields at the nuclei and at the electrons (ω_{n0} and ω_{e0}), i.e., a dynamic frequency shift (DFS) takes place. The size of this shift of NMR can be comparable with the unshifted NMR frequency and depends on the relative orientation and magnitudes of the magnetizations of the nuclear and electron spin systems. Under pulsed excitation of the coupled electron-nuclear precession, this type of nonlinearity should lead to formation of an echo signal due to the redistribution of natural frequencies of the oscillators—to a frequency-modulation mechanism (FM echo). Another type of nonlinearity of the considered systems is noncircular precession of the combined electron-nuclear magnetization due to the anisotropic properties of the magnets. This type of nonlinearity makes possible parametric excitation of a coupled electron-nuclear precession, and is used to obtain parametric-echo signals.[3] A survey of the experimental research and the ideas concerning the mechanisms of echo-signal formation in systems with coupled nuclear-spin precession is given in Ref. 1.

In addition to nonlinear resonant properties, systems with coupled electron-nuclear precession have unusual ordered properties. When solving the problem of coupled electron-nuclear oscillations, it becomes necessary to consider the motion of an electron magnetic system in the average field exerted by the precessing nuclei, and simultaneously the action of the hyperfine field on the nuclei. The distinguishing feature of this problem is that the electron spin system is ordered, whereas the nuclear system is paramagnetic. In this case, when considering oscillations close to the unshifted NMR frequency (ω_{n0}), it becomes possible to separate two principally different regions. In real crystals there is straggling of the hyperfine field at closely located nuclei (microinhomogeneous broadening $\delta\omega$). If the calculated DFS ($\omega_p = \omega_{n0} - \omega_{ne}$) is such that $\omega_p \ll \delta\omega$, then the microinhomogeneous broadening suppresses the DFS. In this case, when the nuclear system is excited it becomes rapidly dephased and one can speak of ordinary NMR. The presence of an ordered electron spin system leads only to the well known enhancement effect and to indirect interaction of the Suhl-Nakamura type between the nuclear spins. On the other hand if $\omega_p \gg \delta\omega$, then suppression of the microinhomogeneous broadening takes place. This means that the nuclear spins precess coherently under the influence of the precession of the ordered electron spin system. The coherence radius is of the order of 10^2–10^4 interatomic distances. Coherent spin precession at such distances causes the electron magnetization likewise to precess at quasi-NMR frequency. The result is a self-consistent motion of the nuclear and electron subsystem—coupled electron-nuclear precession. Owing to coherence of the nuclear precession, the nuclear spin system can be described in the language of sublattices with a magnetization determined by the Curie law, while magnets with coupled electron-nuclear precession can be separated into a separate class of magnets with nuclear sublattices.

In all the earlier investigations of coupled electron-nuclear precession it was assumed that the effects due to the microinhomogeneous broadening can be neglected.[1)] In this case the two types of nonlinearity described above take place in the considered system. In particular, if the system is excited by two resonant pulses, a spin-echo should be produced on account of the dependence of the spin-precession frequency on the amplitude of their excitation (FM echo). This formation mechanism was proposed by Gold[5] for the description of the echo signal in a plasma. It has come to be treated as an FM echo after an echo signal having properties different from the usual Hahn echo[6] was observed in spin systems with DFS. Before describing briefly the main properties of the FM echo, we note that in the case of systems with coupled electron-nuclear precession (as well as for ordered electron systems), what oscillates coherently at the frequency of the homogeneous resonance is an entire region of the crystal (with characteristic dimensions 10^2-10^4 Å), rather than the magnetic moment of an individual nucleus as in ordinary NMR. The dephasing of the induction signal after the exciting pulse is due to the scatter of the local conditions (and hence frequencies), for the different regions of the crystal.

Thus, if dispersion effects are disregarded, the only oscillator in the case of systems with coupled electron-nuclear precession is a macroscopic assembly of nuclear and electron spins located close to each other, which we shall henceforth call a coherent spin group. We had to emphasize the peculiarity of collective effects in quasi-NMR in systems with coupled electron-nuclear precession, inasmuch as in the preceding papers dealing with echo-signal formation in such systems the analysis was carried out using independent nuclei, just at in ordinary NMR, while the role of the electron spin system was reduced to the effect of DFS and amplification. This has frequently misled the reader. Moreover, we propose that the main contribution to the echo signal comes precisely from the interaction of the nuclear and electron spins, and was therefore automatically left out of the earlier description.

The frequency of the homogeneous precession of the nuclear and electron magnetizations ($\mathbf{M}_n$ and $\mathbf{M}_e$) of the quasinuclear mode of coupled electron-nuclear oscillations is defined by the equation

$$\omega_{ne}(\theta)=\omega_{n0}-\omega_p\cos\theta, \tag{1}$$

where θ is the angle of deflection of $\mathbf{M}_n$ from the equilibrium direction. It follows from the experiments that the scatter of ω_{ne} in different regions of the crystal is determined by the scatter of ω_p and is due to the scatter of the AFMR frequencies.

Let a short resonant pulse deflect the nuclear magnetization by an angle α. After a certain time, the electron-nuclear precession in the different regions of the crystal becomes dephased because of the macroscopic inhomogeneous broadening.

In each crystal region with characteriztic size 10^2-10^4 Å the nuclear and electron magnetizations will continue to precess coherently. If at a certain instant τ we apply a second resonant pulse of the same intensity, then its action on the different coherent spin groups will be determined by the relation between the phases of the electron-nuclear precession and the resonant radiofrequency (RF) pulse. Thus, if $\Delta\varphi=\omega_{ne}\tau-\varphi_{\mathrm{RF}}=2k\pi$, then the amplitude of the excitation of the electron-nuclear precession is increased and the angle of inclination of the nuclear magnetization becomes 2α. On the contrary, if $\Delta\varphi=(2k+1)\pi$, then their deflection angle will be zero. Recognizing that the precession frequency depends on the angle of deflection of the nuclear magnetization, the distribution of the oscillator density in frequency turns out to be modulated with a period $2\pi/\tau$. It is this modulation which leads to a partial phasing of the precession of the electron-nuclear magnetization at the instants of time n i.e., to the appearance of the spin-echo signals. Details of the theory of the mechanism whereby the FM echo signal is produced in systems with DFS can be found in Refs. 7–9. A number of experimental properties of the echo signals in systems with coupled electron-nuclear precession agree well with the FM-echo theory.[1] However, the substantial discrepancy between theory and experiment concerning the dependence of the echo-signal intensity on the delay between the RF pulses remained unclear. The point is that according to the theory the intensity of the FM-echo signal at an instant τ after the second pulse should be described by the formula

$$I=\mathrm{const}\cdot\eta^2(\alpha^2J_2^2(p)e^{-4\tau/T_2}+\beta^2J_1^2(p)\cdot e^{-2\tau/T_2}), \tag{2}$$

where I is the intensity of the echo signal in units of power, $p=\alpha\beta\tau\omega_p\exp(-\tau/\tau_2)$, α and β are the nuclear-magnetization deflection angles due respectively to the first and second RF pulses, T_2 is the spin-spin relaxation time, $J_1(p)$ and $J_2(p)$ are Bessel functions of first and second order, and η is the RF field amplification coefficient.

For small p we obtain

$$I=\mathrm{const}\cdot\eta^2\alpha^2\beta^4\omega_p^2\tau^2e^{-4\tau/T_2}. \tag{3}$$

This means that the plot of the intensity of the FM-echo signal against τ should go through a maximum at $\tau=\frac{1}{2}T_2$. The increase of the echo-signal intensity with increasing τ at small delays τ is clear distinguishing feature of an FM echo. In fact, the second RF pulse effects the frequency modulation of the NMR line. For a spin-echo signal to the produced, a certain time must elapse, during which the frequency modulation leads to a redistribution of the precession phases. This redistribution is larger the longer τ. However, notwithstanding the fact that the two-pulse echo in systems with DFS were ascribed to the frequency mechanism, what was observed in practice was only a monotonic decrease of the intensity of the two-pulse echo with increasing delay.[7–9] In our experiments we have attempted to determine the cause of this discrepancy between the experimental data and the theory.

2. MEASUREMENT PROCEDURE

All the measurements were made on an antiferromagnetic easy-plane $CsMnF_3$ single crystal grown at our Institute.[2)] The crystal was a parallelepiped with characteristic dimensions ~3 mm. The crystal was x-ray oriented. The measurements were made at helium tem-

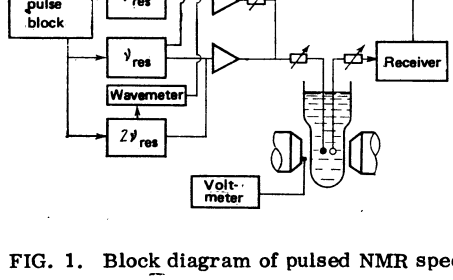

FIG. 1. Block diagram of pulsed NMR spectrometer.

peratures in the frequency band 500–700 MHz. To obtain the echo signal we used a pulsed NMR spectrometer (Fig. 1) with generators of both the resonant and the doubled frequency (for the investigation by the parametric-echo method). The RF pulses were fed from the generators to a single-turn coil in which the sample was placed. The echo signal was received by a second coil and fed to a superheterodyne receiver. The signal from the receiver was fed to an oscilloscope, on the screen of which its time scan was observed. The second oscilloscope beam received signals from wavemeters used to measure the frequency. The delay τ between the RF pulses was measured with a Ch3-19 frequency meter, and the echo-signal amplitude was measured on the oscilloscope screen. The constant magnetic field was produced with a laboratory electromagnet and measured with a Hall pickup. The RF and constant fields were in the easy plane of the crystal magnetization.

3. FREQUENCY ECHO

The parametric-echo method makes a possible reliable measurement of the spin-spin relaxation times in systems with DFS.[3] Using this method, we chose a $CsMnF_3$ crystal with anomalously long spin-spin relaxation times (T_2 reached 140 μsec under the experimental conditions). It did not differ from the other crystal in all other properties. It can only be noted that the NMR line width at small DFS was much smaller for this crystal than for all others. A detailed analysis, both theoretical and experimental, of the real relaxation mechanisms in systems with DSF remains a most complicated matter and is not considered in this paper.

The chosen crystal was used by us to investigate the echo-signal formation mechanism in systems with DSF, which were excited by a pair of resonant pulses. It turned out that the dependence of the echo-signal intensity on the delay has clearly distinguished regions (Fig. 2): a region of short delays, in which a monotonically decreasing signal is observed, and a region of long delays, in which the dependence takes the form characteristic of the theory of the FM echo. The experiment described in Fig. 2 was performed at a DFS value $\omega_p/2\pi = 27$ MHz, at which the spin-spin relaxation time

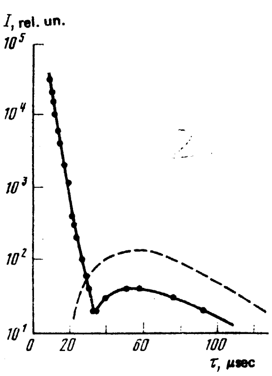

FIG. 2. Dependences of the intensity of a two-pulse echo in $CsMnF_3$ on the delay between the RF pulses at a temperature 2.0 K, a spin-spin relaxation time 118 μsec, and $\nu = 639$ MHz.

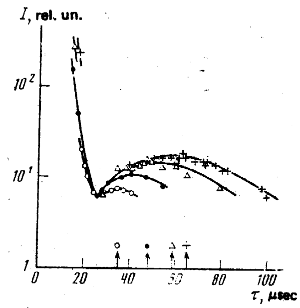

FIG. 3. Dependence of the intensity of a two-pulse echo in $CsMnF_3$, divided by η^2, on the delay between the RF pulses for different temperatures. The arrows mark the values of $\tau = \frac{1}{2}T_2$ at the corresponding temperatures. NMR frequency 639 MHz: ○) $T = 3.0$ K, ●) $T = 2.46$ K, △) $T = 2.0$ K, +) $T = 1.7$ K.

is close to its maximum at the given temperature. At other values of the DFS the time decreases, the "hump-shaped" dependence shifts to the left and is masked by a strong echo signal at short delays. It must be noted that the form of the echo signal is different in these regions. At short delays the echo signal is broader than in the region of long delays. To verify the dependence of the time of maximum-echo formation on T_2, we have plotted the echo-signal intensity against the delay at various temperatures and at identical echo-signal formation conditions (constant values of the DFS and of the angles of the deflection of the nuclear magnetization by RF pulses). The results of the experiment are shown in Fig. 3. The parametric-echo method was simultaneously used to measure the times T_2 at the same temperatures (the values of $\tau = \frac{1}{2}T_2$ at the corresponding temperatures are shown by the arrows in Fig. 3). Not only the positions, but also the relative intensities of the maxima of the echo signal agree well with the FM-echo theory [formula (3)]. Moreover, the dependence of the echo-signal intensity on the delay time agrees also with the curve corresponding to the FM-echo theory and shown dashed in Fig. 2. It follows from these data the the echo signal formed at large delays is frequency dependent and is well described by the FM-echo theory.

Using the methods described in Ref. 3, we succeeded in measuring the deflection of the spins by the RF pulses and to calibrate the nuclear-induction signal. A long (5 μsec) resonant RF pulse, which excited only part of the spins, was applied at a frequency close to double the resonant frequency, and the parametric echo signal from the spins excited by the resonant pulse was observed. From Eq. (1) we find that the change of the spin precession frequency at a small angle of deflection from the equilibrium direction, compared with the precession frequency of a spin wave with extremely small excitation, is determined by the formula

$$\delta\omega_{nc} = \omega_p\theta^2/2. \tag{4}$$

By varying the power of the first resonant RF pulse by tuning the frequency of the parametric pulse to the maximum of the parametric-echo signal (meaning equality of the parametric-pulse frequency to double the precession frequency of the spins excited by the resonant RF pulse) we were able, by measuring the parametric-pulse frequency, to establish the spin deflection angles. For the experiment whose results are shown in Fig. 2, these angles amount to 0.005 rad. If the parametric-echo intensity is extrapolated to zero delay between the resonant and parametric pulses, the obtained intensity will be smaller by a factor ε^2 ($\varepsilon = \gamma_n \eta_\parallel h_\parallel \tau_n$, $\eta_\parallel$ is the coefficient of amplification of the longitudinal RF field $h_\parallel$, and τ_n is the duration of the parametric pulse) than the nuclear-induction signal.[3] To estimate ε we used the parametric-buildup method.[3] At the instant of formation of the parametric echo signal by the long parametric pulse, one more parametric pulse is applied to the sample. During the time of action of the second parametric pulse the spin system oscillations is built up parametrically, and the amplitude of the echo signal therefore decreases at a rate $I_0 \gamma_n \eta_\parallel h_\parallel$ (I_0 is the amplitude of the parametric echo signal). Thus, knowing the angles of deflection of the spins by the RF pulses and the magnitude of the induction signal, we can estimate theoretically the expected intensity of the FM-echo signal (see the dashed curve in Fig. 2). At short delays, the echo-signal intensity greatly exceeds the intensity expected from the FM-echo theory. We have therefore dubbed the echo signal in the short-delay region "giant" echo.

4. GIANT ECHO

The FM-echo theory [in particular, Eq. (3)] was developed for the case when one can neglect the change of the spin-precession frequency during the time of action of the RF pulses, i.e., under the condition

$$K = \omega_p \omega_\gamma \tau_{pul}^2 \ll 1. \quad (5)$$

Here $\omega_\gamma = \gamma_n \eta h$, h is the RF field amplitude, and τ_{pul} is the RF pulse duration.[11] If the condition (5) is satisfied the spin deflection angles are equal to $\omega_\gamma \tau_{pul}$ and the echo-signal intensity should not change when τ_{pul} and ω_γ change simultaneously in such a way that the product $\omega_\gamma \tau_{pul}$ remains constant. On the other hand if the condition (5) is not satisfied, then the echo-signal intensity should differ from that calculated by formula (3) and should depend on the value of K. In our experiments, K was of the order of 0.5. It could be assumed that a giant echo is formed nevertheless via the frequency mechanism, and the disparity with the theory at small τ is due to insufficient fulfillment of the condition (5). To check on this we plotted the FM-echo signal intensity against the delay for different values of τ_{pul} and correspondingly different K (under the condition $\omega_\gamma \tau_{pul}$ = const).

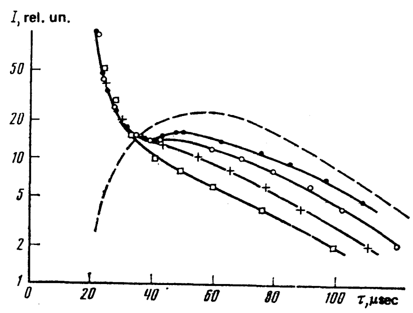

FIG. 4. Intensity of two-pulse echo in $CsMnF_3$ vs. the delay by RF pulses for different durations of the second pulse (under condition $\omega_\gamma \tau_{pul}$ = const). The dashed line is the theoretical dependence of the FM-echo intensity on τ: ●) $\tau_{pul\,2} = 0.6$ μsec ($K = 1.5$), ○) 0.8 μsec, +) 1.2 μsec, □) 1.8 μsec; $\nu = 639$ MHz, $T = 2.0$ K.

The obtained curves (Fig. 4) allow us to track the variation of the shapes of the $I(\tau)$ curves with decreasing K. It is seen that for large delays the shape of the experimental curves approaches the theoretical one with decreasing K. At the same time, if the delays are short the echo intensity is practically independent of K. This allows us to conclude that the giant echo is not formed by the mechanism considered above. The nature of the giant echo has not yet been explained within the framework of the prevailing notions concerning the dynamics of the nuclear magnetization in systems with DFS. An analysis of spin motion in systems with DFS makes it possible to point out one singularity with which the nature of the giant echo is possibly connected.

The point is that in the derivation of the equations of motion in Ref. 11 use was made of the sublattice model of the nuclear subsystem. It was assumed that the DFS had completely suppressed the microinhomogeneous broadening. A situation can arise, however, wherein the suppression of the microinhomogeneous DSF broadening is violated for certain groups of spins. Assume that the amplitude of the second RF pulse is comparable with the amplitude of the field produced by the coherent nuclei and acting on the electrons in a plane perpendicular to the direction of the external constant field. In this case there exist coherent spin groups that precess in antiphase with the RF fields. For these spins the nonperpendicular component of the hyperfine field, acting on the nuclei and leading to coherent nuclear precession, vanishes. The nuclear precession in these groups should become dephased within a time $\tau_0 \sim 1/\delta\omega$, which is comparable with the duration of the RF pulse. As a result, these spin groups lose their transverse magnetization and this leads to nonlinear amplitude modulation of the NMR line. Owing to the nonlinear amplitude modulation of the NMR, a spin-echo signal should be produced at instants of time $n\tau$ ($n = 1, 2, 3\ldots$) after the second RF pulse. The proposed relaxation mechanism of echo formation may in fact be the cause of the giant echo observed in the experiments.

CONCLUSION

As a result of our study we succeeded in resolving the contradiction between the theory of FM-echo formation and the experimental results of the last 9 years. It turned that the mechanism that produces the FM echo in magnets with coupled electron-nuclear precession is effective only at long delay times between the pulses. In the case of short delays, the FM echo is "jammed" by the giant-echo signal, whose character is not connected with the traditional FM echo. When the delay between pulses is increased, the decay rate constant of the giant-echo signal intensity depends little on the spin-lattice relaxation time.

The relaxation mechanism proposed in this article for the formation of the giant echo cannot claim to explain its properties fully. At present, however, it is the only possible feature of the dynamics of spins with DFS which can lead to so appreciable a deviation of the properties of the giant echo from the developed theory of FM echo in systems with DFS. A possible alternative of the relaxation mechanism is participation of other resonant systems in the formation of the giant echo.

It must be noted that systems with coupled electron-nuclear precession are analogous to a number of other systems in which an external action leads to the onset of coherent states. Examples are the coherent state of paramagnetic impurities under the action of an RF field[12] or the superradiant transitions in laser systems.[13] The echo-signal formation mechanism proposed in this article and connected with induced violation of coherence can also be effective in those systems.

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[1)]A recent paper by Tsifrinovich and Krasnov[4] reports an investigation of the influence of the DFS on the microinhomogeneous broadening for a line with a Lorentz shape. Their results, however, agree poorly with the experimental data, possibly as a result of the choice of the form of the broadening.

[2)]The authors thank S. V. Petrov for supplying the crystals.

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Exact solution of the one-ion problem for a magnet with one-ion anisotropy in a field of arbitrary direction

F. P. Onufrieva

Odessa State University
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An exact quantum-mechanical solution is obtained for the one-ion problem for a magnet with one-ion isotropy, located in a magnetic field of arbitrary direction, for a spin $S=1$. The solution is based on the formalism of the theory of unitary symmetry, in particular on the properties of $SU(3)$ Lie algebra, to which belong the operators that characterize the state of an individual ion. After a number of exact transformation, the one-ion Hamiltonian is reduced to a form for which the determination of the eigenvalues and eigenvectors, of the partition function, of the magnetic susceptibility, of the thermodynamic functions, and others is a trivial problem.

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INTRODUCTION

The simplest model of a system consisting of magnetic ions in lattice sites, in the presence of one-ion anisotropy (OA) and of a magnetic field of arbitrary direction, is described by the Hamiltonian

$$\mathcal{H}=\mathcal{H}_1+\mathcal{H}_{\text{вз}},\quad \mathcal{H}_1=\mathcal{H}^a+\mathcal{H}^h;$$
$$\mathcal{H}^a=d\sum_i (S_i^z)^2+\varepsilon\sum_i[(S_i^x)^2-(S_i^y)^2],$$
$$\mathcal{H}^h=-h_\parallel\sum_i S_i^z-h_\perp\sum_i S_i^x,\quad \mathcal{H}_{\text{вз}}=\sum_{\substack{ij\\ \alpha\beta=x,y,z}} J_{ij}^{\alpha\beta}S_i^\alpha S_j^\beta. \qquad (1)$$

$h_\parallel$ and $h_\perp$ in (1) are the magnetic-field components parallel and perpendicular to the z axis; for simplicity, the perpendicular component is assumed directed along the x axis. The one-ion anisotropy described by $\mathcal{H}^a$ takes into account the presence of a crystal field that distorts the states of the isolated ion, and the spin-orbit and spin-spin couplings of the electrons of the magnetic ion in the site i. In the case $S=1$, the Hamiltonian $\mathcal{H}^a$ written above has the most general form ($\mathcal{H}^a$ is constant at $S=\frac{1}{2}$). At $S>1$ operators of higher degrees

