Dynamic effects in pulsed NMR in easy plane antiferromagnets with large dynamic frequency shifts

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Pulsed NMR is studied in the easy-plane antiferromagnets $MnCO_3$ and $CsMnF_3$, which have large dynamic frequency shifts. The results of measurements of the amplitude characteristics show that the signals of both one- and two-pulse echos are formed by a frequency mechanism. The free-induction signal following a short radio-frequency pulse is investigated. The results agree satisfactorily with the theoretical concepts regarding the dynamics of nuclear spin motion in such systems. The previously observed "capture echo" is used to investigate the mechanism of capture of the spin system by a short radio-frequency pulse. A nonmonotonic dependence of the stimulated echo signal on the spacing between the second and third exciting pulses is detected. The longitudinal and transverse relaxation times are measured.

1. INTRODUCTION

Nuclear spins in magnetically-ordered substances are coupled at sufficiently low temperatures by the Suhl-Nakamura interaction[1,2]. This brings about an interesting situation wherein, on the one hand, the average values of the magnetic moments are still far from their nominal values, and on the other hand the spin system is collectivized to such a degree that it can be described in terms of the spin waves[3]. The clearest manifestation of the Suhl-Nakamura interaction is the so-called dynamic frequency shift, i.e., the deviation of the frequency ν_{NMR} of the homogeneous precession of the nuclear spins from the value $\gamma_n H_n$, where $H_n = AM$ is the effective field of the hyperfine interaction, γ_n is the nuclear gyromagnetic ratio, and M is the sublattice magnetization.

Many investigations of magnets with Suhl-Nakamura interaction were carried out by stationary methods[4-7]. The main result is the possibility of describing the dynamic shift in the form

$$\nu_{NMR}=\gamma_n H_n-\nu_p(H, T_s) \quad \text{at} \quad \nu_p \ll \gamma_n H_n, \tag{1}$$

where H is the external magnetic field and T_S is the spin temperature, which can differ, when an RF field is applied, from the lattice temperature and from the temperature of the electron spin system. These experiments, however, did not make it possible to study the dynamics of the motion of the nuclear spins when an RF field is applied. Such investigations would be extremely interesting, since, as shown already theoretically by de Gennes et al.[3], the frequency of the homogeneous precession of the nuclear spins should depend also on the deviation angle θ of the nuclear spins from the equilibrium position, i.e., the formula that should be satisfied in place of (1) is

$$\nu_{NMR}=\nu_{n0}-\nu_p(H, T_s)\cos\theta, \tag{2}$$

where $\nu_{n0} = \gamma_n H_n$ is the unshifted hyperfine frequency. A theoretical analysis of this question has demonstrated, in particular, the possibility of aperiodic motion of nuclear spins following application of an RF field[8].

The dynamics of the motion of the nuclear spins can be investigated experimentally with the aid of pulsed NMR, particularly spin echo. This raises a number of additional interesting problems. For example, as shown by Gould[9], a possibility exists of a frequency mechanism (different from that considered by Hahn[10]) of spin-echo formation. The gist of this mechanism is that the compensation of the "fan" of transverse spin components, a compensation needed to produce the echo signal, can be the result of a regular shift of the spin precession frequency under the influence of RF pulses. It is indicated by Petrov et al.[11] that spin echo in nuclear spin systems with large dynamic frequency shift can be due precisely to the frequency mechanism, and calculations were made for this case. At present there are no other known systems in which the frequency mechanism can be realized. In addition, spin echo makes it possible to measure directly the transverse-relaxation time T_2 needed for the study of the Suhl-Nakamura interaction.

It is no accident that a number of papers have been recently published on spin echo in systems of magnetic nuclei with large differential frequency shifts ($RbMnF_3$[11], MnO[12], $MnCO_3$, and $CsMnF_3$[13]). Unfortunately, owing to the complexity of the interpretation, the available experimental data are insufficient for the solution of the problems raised above. Recently, however, in pulsed investigations of NMR and $MnCO_3$, there were observed interesting effects of "capture echo"[14] and one-pulse echo[15], with the aid of which we hope to come closer to an understanding of the occurring phenomena.

In this paper we present the results of an investigation of pulsed NMR in the easy-plane antiferromagnets $MnCO_3$ and $CsMnF_3$. The magnetic properties of these substances have been quite thoroughly investigated[16]. Stationary NMR was investigated in[4] ($MnCO_3$) and[5] ($CsMnF_3$). The frequency of the homogeneous spin precession of the nuclei is described satisfactorily by the formula

$$\nu_{NMR}=\nu_{n0}(1-\gamma_e^2 H_E A\langle m\rangle_z/\nu_e^2), \tag{3}$$

where γ_e is the electron gyromagnetic ratio, H_E is the effective exchange field, A is the hyperfine interaction constant, $\langle m \rangle_z$ is the average projection of the magnetic moment of the nuclei on the direction of the electron sublattice, and ν_e is the AFMR frequency, with $\nu_e = \gamma_e H$ for $CsMnF_3$ and $\nu_e = \gamma_e\sqrt{H(H + H_D)}$ for $MnCO_3$, where H_d is the Dzyaloshinskiĭ field. Nuclear spin waves were detected in these substances in[17] by observing "parallel pumping". All the phenomena described below were observed in both substances, but the main investigations were made on $MnCO_3$. The results presented below pertain to this substance in all cases, unless otherwise stipulated.

2. SAMPLES AND MEASUREMENT PROCEDURE

All the measurements were made on synthetic single crystals. The $MnCO_3$ crystals were grown by Ikornikova, by the hydrothermal synthesis method, at the Crystallography Institute of the USSR Academy of Sciences[18]. The samples were plates of irregular shape, whose plane coincided with the basal plane of the crystal. For the investigations, the samples were finished in the form of disks. The $CsMnF_3$ crystals were grown by the Bridgman method at our Institute by Petrov[19] 1). The samples had an irregular shape.

The measurements were peformed with a pulsed NMR spectrometer in the frequency range 360—500 MHz. A block diagram of the spectrometer is shown in Fig. 1. We used both incoherent and incoherent series of RF pulses. The minimal pulse duration was $t_\nu \approx 0.7\ \mu$sec. The power of the RF pulses fed to the sample was varied with a precision attenuator. The amplitude of the echo signal was measured both with the precision attenuator and by direct reading against the oscilloscope scale. The sensitivity of the superheterodyne receiver was of the order of 10^{-13} W. We had to measure directly the echo-signal frequency. These measurements were performed by fine-tuning the superheterodyne receiver; this called for preliminary calibration against the signal of an external oscillator. To obtain RF pulses of varying amplitude we used two signal generators, one for each pulse.

The sample was placed in a helical resonator, in the antinode of the magnetic field (for a half-wave helix, the antinode is at the center of the resonator). The resonator figure of merit was $Q \approx 300$. The resonator was excited by inductive coupling by a ring coaxial with the resonator. The coupling was chosen close to critical. The magnetic component of the RF field was polarized along the resonator axis, and its amplitude is described satisfactorily by the formula

$$h^2 \approx 8\pi QP/\nu V, \tag{4}$$

where P is the incoming RF power, ν the resonator working frequency, and V the resonator volume. The maximum RF-field amplitude in our experiment was $h \approx 3$ Oe. In all the experiments, the RF and the constant magnetic fields were mutually perpendicular and in the basal plane of the sample. The constant magnetic field was produced with a laboratory electromagnet. The field inhomogeneity over the sample dimensions was 0.5 Oe, which is much less than the line width and does not affect the measurement results.

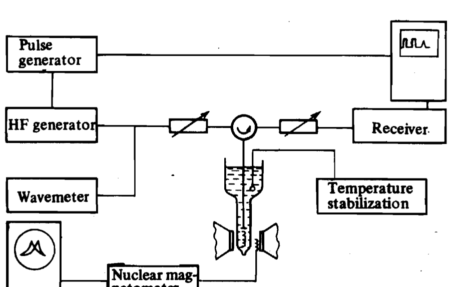

FIG. 1. Block diagram of spectrometer.

All the measurements were made in the temperature range 4.2 – 1.4°K. To prevent overheating, the samples were placed directly in the liquid-helium bath. Temperature stabilization and measurement were made with a germanium thermometer accurate to 0.03°K.

3. EXPERIMENTAL RESULTS

1) Free Precession

Free precession is defined as RF emission by the excited spin system immediately after the exciting RF pulse is turned off. Investigation of free precession permits a direct study of the dynamics of the motion of the nuclear spins under the influence of the RF fields, since the signal amplitude ss proportional to the transverse magnetization of the nuclei. Unfortunately, the free-precession signal has an irregular chopped-up form, which makes the measurements quite difficult[2]). We investigated the amplitude of the free-precession signal immediately after a short RF pulse. When the power or duration of the pulse is varied, the precession amplitude goes through a maximum. The power at which the signal maximum is reached, as a function of pulse duration, is shown in Fig. 2. We see that this dependence is described satisfactorily by the formula

$$P_{max} \sim t_\nu^{-3}. \tag{5}$$

From the theory of the dynamics of spin motion, developed by Turov et al.[8], it follows that with increasing power the free-precession signal amplitude should go through a series of successive maxima, the first maximum occurring when the following condition is satisfied

$$\nu_1^2 = 1/3^{1/2}\nu_p t_\nu^3, \tag{6}$$

where $\nu_1 = \gamma_n \eta h$ is the amplitude of the RF field in frequency units, and η is the gain. This formula can also be obtained from simple considerations. It is clear that the singularity in the precession signal should appear at the instant when the spin-precession frequency shift becomes equal to the frequency width of the exciting pulse. This leads to the condition

$$\nu_p \theta^2/2 \approx 1/t_\nu,$$

and if we substitute here $\theta = \nu_1 t_\nu$, then we obtain formula (6), apart from a numerical factor.

Knowing the RF power, we can calculate from (4) the amplitude of the RF field in the resonator. Further, from the slope of the lines in Fig. 2 we can estimate the gain η. The values $\eta = 140$ and $\eta = 240$ obtained by us are in satisfactory agreement with the theoretical values determined from the formula $\eta = H_n/h$, namely $\eta = 160$ and $\eta = 280$. This confirms the validity of the statements by Turov et al.[8], and we obtain an independent method of establishing the scale of the RF field amplitude, a scale that we shall use subsequently.

We have succeeded in observing directly the shift produced in the natural frequency of the spins by the RF field (Fig. 3). The signal frequency was measured by tuning a narrow-band superheterodyne receiver. Curve 1 of Fig. 3 was obtained at low power of the exciting pulse, and curve 2 was obtained near the maximum of the precession amplitude. The magnitude of the frequency shift was of the order of the pulse width. It is interesting that the frequency shift is accompanied by line broadening. This broadening should manifest itself in a decrease of the time constant T^* of the precession-

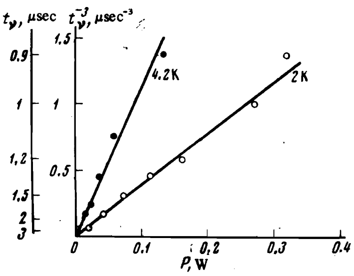

FIG. 2

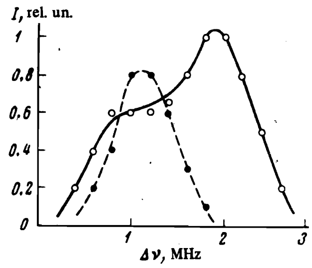

FIG. 3

FIG. 2. Dependence of the duration of the RF pulses at which the free-precession signal takes place on the pulse power; ν_{NMR} = 610 MHz.

FIG. 3. Free-precession signal intensity vs. the frequency to which the superheterodyne receiver is tuned: ●—low RF pulse power; ○—near the maximum of the precession-signal amplitude.

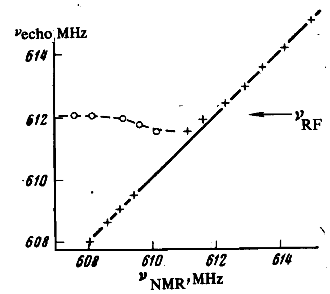

FIG. 4

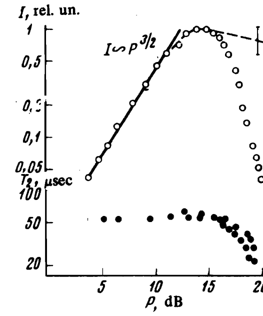

FIG. 5

FIG. 4. Echo-signal frequency vs. NMR frequency: +—ordinary echo, ○—capture echo; T ~ 2°K.

FIG. 5. Signal amplitude (a) and two-pulse signal fall-off time constant (b) as functions of the power of the exciting RF pulses. Dashed—relative signal amplitude after subtracting the relaxation change, ν_{NMR} = 610 MHz, T ~ 2°K.

signal fall-off, which is inversely proportional to the line width $\Delta\nu$. Unfortunately, because of the very chopped-up precession signal, we were unable to measure T^* directly. It was possible, however, to observe the free-precession signal duration, i.e., the time reckoned from the end of the pulse to the instant when the precession signal becomes comparable with the receiver noise. We observed the maximum duration of the free precession at a pulse RF power 8—10 dB lower than necessary to attain the maximum of the precession amplitude. This means that the broadening of the NMR line begins to manifest itself at RF field powers such that the shift of the natural free precession becomes of the order of the MNR line width.

2) Two-Pulse Echo

We continued the study of a two-pulse echo in $MnCO_3$ and $CsMnF_3$. All the investigations, unless otherwise stipulated, were carried out at equal amplitudes and durations of the exciting RF pulses. We investigated the spectrum of the echo signal as a function of the magnetic field in the field range 0.5—5 kOe. The spectrum at low RF-pulse powers was found to agree well with the data on stationary NMR[4]. At the same time, at high exciting-pulse powers, the echo was observed in a wide range of differences between ν_{RF} and ν_{NMR}. We have investigated the signal-echo frequencies as a function of the external magnetic field at a constant RF pulse frequency (Fig. 4). The echo-signal frequency always coincides with ν_{NMR}, with the exception of the special case of "capture echo," which will be considered later on.

The echo behaves quite differently at small $|\delta\nu| \lesssim \Delta\nu$ and large $|\delta\nu| \gg \Delta\nu$ frequency deviations ($\delta\nu = \nu_{RF} - \nu_{NMR}$, $\Delta\nu$ is the unperturbed NMR line width). We shall find it convenient to consider these cases separately.

A. Small deviations. Depending on the RF pulse power, the echo-signal intensity goes through a maximum (Fig. 5a). The spin rotation angle is in this case $\theta_{max} \approx 2-5°$. No other maxima were observed with further increase of power, up to powers exceeding P_{max} by 20 dB. At low powers, the signal intensity is $I \propto P^{1/2}$. The maximum of the echo amplitude is observed at pulse powers 8—10 dB lower than needed to attain the free-precession signal maximum. Depending on the pulse duration, the position of the maximum shift, and the condition $P_{max} \propto t_\nu^{-2}$ is satisfied. Consequently, the echo maximum occurs at constant angles of spin rotation from the equilibrium conditions, and accordingly, at a constant value of the spin-precession frequency. The value of this shift $\nu_p\theta_{max}^2/2$ is close to the unperturbed NMR line width. The maximum of the echo signal occurs simultaneously with the maximum duration of the free-precession frequency. It can therefore be concluded that with further increase of the amplitude of the RF pulses a broadening takes place in the NMR line.

We have investigated the dependence of the shape of the envelope of the echo fall-off on the RF field power. This envelope has everywhere the shape of an exponential whose time constant does not depend on the power at $P < P_{max}$ and decrease with further increase of the power (Fig. 5b).3) This behavior allows us to conclude that at low RF-power levels we measure the true time T_2 of the transverse relaxation. For a delay between pulses reduced to zero, at powers higher than P_{max}, we obtain a plateau on the plot of the echo-signal amplitude against the RF power (dashed curve on Fig. 5a).

At small frequency deviations, the maximum echo signal decreases with increasing detuning (Fig. 6).

B. Large frequency deviations. The dependence of the echo signal intensity on the power in this detuning region is shown in Fig. 7. At low powers, the law $I \propto p^{3/2}$ is also satisfied and then, starting with a certain power $P_{plateau}$, the echo signal ceases to increase. The intensity of the signal depends little on the duration of the RF pulses when the condition $t_\nu < 1/\Delta\nu$ is satisfied. The envelope of the echo fall-off signal is exponential and has a time constant of the same value as T_2 measured at low frequency differences. The relaxation, just as in the case of small frequency differences, decreases with increasing RF power, but this decrease begins at RF pulse amplitudes 5—7 dB higher than $P_{plateau}$.

We have investigated the dependence of the RF power at which the plateau appears in the echo intensity on the frequency difference. In this experiment, the RF field frequency was constant and the frequency difference was produced by varying the external magnetic field. It turned out that the relation $P_{plateau} \propto \delta\nu^2$ was well satisfied.

Figure 6 shows the maximum value of the two-pulse echo signal as a function of the frequency deviation. The

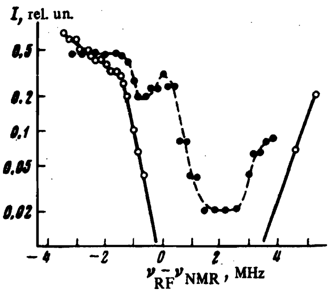

FIG. 6

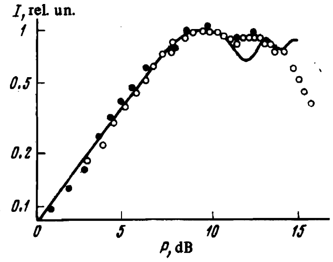

FIG. 7

FIG. 6. Maximum intensity of one-pulse (○) and two-pulse (●) echo vs. the frequency deviation. ν_{NMR} = 590 MHz, T = 2°K.

FIG. 7. Amplitude of one-pulse (○) and two-pulse (●) echo signal vs. the RF field power; ν_{NMR} = 590 MHz, $\delta\nu \approx 3$ MHz. Solid line—theoretical dependence.

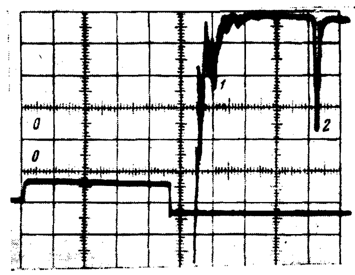

FIG. 8. Oscillogram of one-pulse echo signal: 1—free induction signal, 2—echo signal. The lower trace is the signal from a wavemeter, showing the position of the exciting pulse.

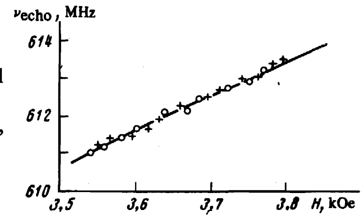

FIG. 9. One-pulse echo signal frequency vs. the external magnetic field: ○—ν_{RF} = 610.4 MHz, +—ν_{RF} = 616 MHz. Solid line—NMR spectrum (T = 2°K).

measurements were performed in the following manner. The external magnetic field, and hence the NMR frequency, were constant. The deviation was produced by varying the carrier frequency of the radio pulses. At each value of the frequency deviation $\delta\nu$ we measured the dependence of the echo-signal amplitude on the RF power and determined the largest amplitude. We see that at large frequency deviations the maximum echo-signal amplitude does not depend on the magnitude of the deviation. All the results obtained above on two-pulse echo at large frequency deviations pertain precisely to this region, and at small deviations they pertain to exact equality of ν_{RF} and ν_{NMR}. The ratio of the amplitudes of the echo signal at the center of the NMR line decreases with increasing dynamic frequency shift also at large detunings.

3) One-Pulse Echo

A one-pulse echo is a resonant response of the spin system to the action of a single exciting RF pulse, produced at time instances that are multiples of the pulse duration, and having a frequency and width determined by the characteristics of the spin system proper, and not by the exciting pulse. Data on our experimental observations of this effect and preliminary results of its investigation are given in[15].

Figure 8 shows an oscillogram of the signal of the one-pulse echo. This signal was observed only when the NMR frequency does not coincide with the frequency of the RF field. The minimum detuning at which it was possible to observe the signal, was 0.5 MHz (the NMR line width at this frequency is 0.3 MHz). The echo-signal frequency, however, coincides with the NMR frequency (Fig. 9). In this experiment the frequency of the RF pulse was constant at 610.4 or 616 MHz, and what was varied was the external magnetic field, and hence the NMR frequency. These investigations were carried out in a wide range of RF field frequencies, from 500 to 630 MHz, and good agreement between the echo-signal frequency and the NMR frequency was observed throughout.

We were able to observe in the experiment three signal echoes at t_ν, $2t_\nu$, $3t_\nu$ after the RF pulse. The first echo signal was observed at a pulse duration from 30 to 150 μsec. The secondary signals turned out to be weaker by one order of magnitude, and could be resolved only at $t_\nu \approx 20$ μsec. The amplitude of echo signal depends strongly on the rise and fall rates of the exciting pulse. When the front duration was increased from 0.3 to 0.8 μsec, the echo amplitude decreased by one order of magnitude.

With increasing pulse duration, the echo signal decreases exponentially with a time constant close to the time of the transverse relaxation T_2, measured with the aid of the two-pulse echo.

The one-pulse echo behaves in many respects quite similarly to the two-pulse echo at large frequency deviations. Figure 7 shows a plot of the one-pulse echo signal amplitude against the applied RF power. This plot was obtained with the same parameters as the analogous curve for the two-pulse echo. Good agreement of the results is observed. With increasing difference $\delta\nu$ between the NMR and RF frequencies, the power at which the plateau sits in also increases like $P_{plateau} \propto \delta\nu^2$.

Figure 6 shows the maximum amplitude of a one-pulse signal as a function of the frequency deviation. This dependence was measured at a constant NMR frequency, and the necessary detunings were produced by varying the radiofrequency. It is easy to see that the region of existence of the one-pulse echo signal coincides with the region of the existence of a two-pulse signal at large frequency deviations. A growth of the one-pulse echo signal intensity is observed when the frequency deviation increases above the inflection point on Fig. 6; this is most readily due to the steepening of the pulse fronts when the pulse frequency moves away from the resonator frequency. At any rate, when working with resonators having a lower Q, the maximum echo signal increases more strongly with increasing frequency deviation, whereas the inflection point remains in place. With increasing value of the dynamic frequency shift, the minimum frequency deviations needed to observe the one-pulse echo signal increase in magnitude.

We have attempted to observe a one-pulse echo in the ferrite $MnFe_2O_4$, which is a nuclear spin system with a dynamic frequency shift. At 4°K we observed a weak one-pulse echo, weaker by three orders of magnitude than the two-pulse signal. It was impossible to observe one-pulse echo in this substance at 77°K. It can therefore be concluded that the one-pulse echo is observed only in nuclear spin systems with large dynamic frequency shifts or in similar systems.

4) Echo-Signal Forming Mechanism

In the region when one-pulse and two-pulse echo exist, at large frequency deviations, the following condition is satisfied with sufficient accuracy:

$$|\delta\nu| = |\nu_{RF} - \nu_{NMR}| \gg \nu_p^{1/3} \nu_1^{2/3}. \quad (7)$$

Therefore, as follows from[8], the motion of the nuclear spins in first-order approximation can be regarded classically. But in the case of a "Hahn" phase mechanism of echo formation, the two-pulse echo signal has a noticeable amplitude only if the condition $|\delta\nu| \lesssim \nu_1$ is satisfied[21]. In our case $|\delta\nu| \approx 5$ MHz and $\nu_1 \approx 0.5$ MHz. It is also known that the phase mechanism of echo formation does not produce a noticeable one-pulse echo signal, at any rate at pulse durations $t_\nu \gtrsim T_2$.[22] Consequently, neither one-pulse nor two-pulse echo can in principle be described at large frequency deviations within the framework of the phase mechanism of echo formation.

An alternative in this case is the frequency mechanism of echo formation. Indeed, the regular shift of the natural frequencies of the spins, which occurs under the influence of the RF pulse, can in principle compensate for the irregular spreading of their phases, due to the inhomogeneous broadening. The mechanism of formation of one-pulse echo was described in detail in[20]. The echo-signal intensity is determined by the following formula:

$$I \propto \frac{\nu_1}{\delta\nu}\left[J_1^2(y) + \exp\left\{-\frac{2t_\nu}{T_2}\right\} J_2^2(y)\right]^{1/2} \exp\left\{-\frac{t_\nu}{T_2}\right\}, \quad (8)$$

where J_1 and J_2 are Bessel functions with argument

$$y = \nu_p \frac{\nu_1^2}{\delta\nu^2} t_\nu \exp\left\{-\frac{t_\nu}{T_2}\right\}.$$

It follows from this formula that at a sufficiently low RF pulse intensity, such that the condition for the smallness of the arguments of the Bessel functions is satisfied, the echo signal intensity is

$$I \propto \nu_p \frac{\nu_1^3}{\delta\nu^3} t_\nu \exp\left\{-\frac{2t_\nu}{T_2}\right\}, \quad (9)$$

i.e., $I \propto P^{3/2}$, and at $t_\nu \gtrsim T_2$ the signal decreases exponentially with increasing pulse duration, with a time constant on the order of T_2. With further increase of the RF power and of the signal intensity, a plateau with weak oscillations is observed (solid curve in Fig. 7). This plateau sets in when the first maximum of the function J_1 is reached, i.e., $P_{plateau} \propto \delta\nu^2$, in agreement with our results.

Two-pulse echo in nuclear spin systems with large dynamic frequency shift was investigated theoretically by M. P. Petrov, G. A. Smolenskiĭ, A. A. Petrov, and S. I. Stepanov[11]. The results of this work are not directly applicable to our case, since no account was taken in[11] of the frequency deviation. However, an analysis carried out by us jointly with M. I. Kurkin shows that the main results of[11] remain in force also in the presence of detunings, if the spin-rotation angles are taken to mean their maximum values $\theta = 2\nu_1/\delta\nu$. Then in the case of equal RF pulses the intensity of the two-pulse echo signal is also described by formula (8), where the pulse duration t_ν is now replaced by the distance τ between pulses.

Two effects are observed in the dependence of the signal on the duration of the RF pulses. First, the signal can occur at instants of time that differ from the delay between the pulses by an amount on the order of t_ν. Second, modulation of the echo-signal intensity should be observed, as a function of the frequency deviation, with a frequency on the order of $1/t_\nu$. These effects were observed by us in the experiments.

Unfortunately, owing to the large value of the free-precession signal, we were unable to investigate the echo at small delays between the pulses, $\tau < T_2$, i.e., in the region where, according to formula (8), an increase of the echo signal should be observed with increasing distance between the pulses.

Inasmuch as the nonlinearity of spin motion was not taken into account in[11], the results there do not apply directly to the case of two-pulse echo at the center of the NMR line. The analysis here is very complicated, and we are able to consider only limiting cases. At spin rotation angles much smaller than the maximum possible, the results of[11] remain in force. The amplitudes and durations of the pulses should in this case satisfy the condition

$$\nu_p \nu_1^2 t_\nu^3 \ll 1.$$

At spin-rotation angles close to the maximum ($\nu_p \nu_t^2 t^3 \sim 1$) there is no echo signal (private communication from M. I. Kurkin). The criterion for the onset of a signal maximum obtained in[11], namely $\nu_p \theta^2 \tau e^{-\tau/T_2} \approx 2$, and the relations that follow from this criterion between the power and duration of the RF pulses, are approximately satisfied under our conditions. The form of the dependence of the echo-signal intensity on the RF power (Fig. 5a, dashed), agree qualitatively with the results of[11]. The fact that the two-pulse echo signal at the center of the NMR line is due to the frequency formation mechanism is evidenced also by the near-equality of the echo signal amplitudes at the center and at the wings of the line. The phase mechanism should, at the same spin-rotation angle, yield an echo signal smaller by a factor $\nu_p \tau e^{-\tau/T_2} \approx 10^2$. Thus, we can state that both one-pulse and two-pulse echo are produced via the frequency mechanism.

Of great interest is an investigation of the limits of the region of existence of one-pulse echo (Fig. 6). We assume that the reason for the absence of a signal at the center of the NMR line is that in this region the motion of the spins is essentially nonlinear. Then the region where there is no one-pulse echo signal should be approximately symmetrical about a certain frequency deviation $\delta\nu_a$, at which the spins move along an aperiodic trajectory. At the same deviation, a minimum two-pulse echo signal should be observed.

The sought detuning should satisfy two equations:

$$\nu_p \frac{\nu_1^2}{\delta\nu_a^2} \tau e^{-\tau/T_2} \approx 2 \quad (10)$$

which is the condition for the maximum of the echo, and

$$\delta\nu_a = 3 \cdot 2^{-4/3} \nu_p^{1/3} \nu_1^{2/3} \quad (11)$$

which is the equation of the aperiodic trajectory from[8]. From this we obtain for $\delta\nu_a$

$$\delta\nu_a \approx 20/\tau e^{-\tau/T_2}. \quad (12)$$

In our case we have $\delta\nu_a \approx 1.5$ MHz, in satisfactory agreement with the center of the curves on Fig. 6.

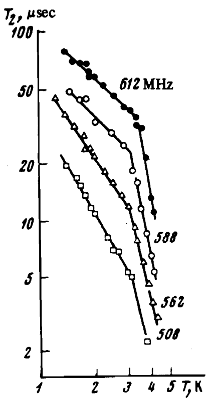

FIG. 10

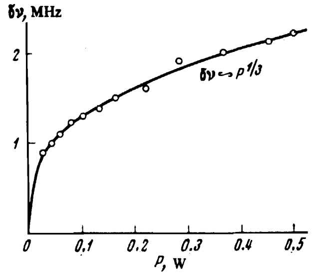

FIG. 11

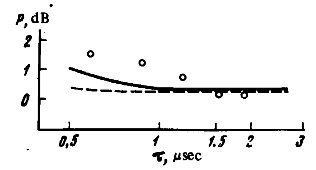

FIG. 12

FIG. 10. Transverse relaxation time T_2 as a function of the temperature (the numbers on the curves are the values of ν_{NMR}).

FIG. 11. Capture-echo spectrum vs. the power of the exciting pulses; ν_{NMR} = 610 MHz, T = 2°K.

FIG. 12. Dependence of the RF power at which capture echo is observed at a given frequency deviation $\delta\nu$ = 3 MHz on the pulse duration. Dashed curve—calculation in the case of an ideal rectangular pulse, solid curve—calculation with allowance for the real pulse waveform.

Our experiments have shown that T_2 decreases with increasing ν_p (Fig. 10). Consequently, the minimum values of the frequency deviations at which one-pulse echo is observed and the dip and the two-pulse echo is observed should increase. This is indeed observed in experiment. Thus, the investigated dependence of the maximum echo signal on the difference between ν_{RF} and ν_{NMR} should yield indirect information on the dynamics of the spin motion.

5) Capture Echo

The capture of a nuclear spin system by a high-frequency field is a process wherein a sufficiently strong field causes to precession frequency of the nuclear spins to change and take on the value ν_{RF}. This effect was investigated in $MnCO_3$ for sufficiently long ($t_\nu \gg T_2$) RF pulses and was described within the framework of the variation of the spin temperature[4]. We have observed an analogous phenomenon following the action of two short RF pulses on a spin system--"capture echo"[14].

The gist of the phenomenon is the following: Two high-power ($h \approx$ 1—10 Oe) RF pulses, of frequency ν_{RF} higher than the resonant frequency ν_{NMR}, are applied to a nuclear spin system. An echo signal at the frequency ν_{RF} is then observed in a definite range of frequency differences $\delta\nu = \nu_{RF} - \nu_{NMR}$. The signal frequency, just as in the preceding experiments, was measured by tuning a superheterodyne receiver. The capture-echo signal frequency as a function of the external magnetic field is shown by circles on Fig. 4. The RF power needed to observe the capture echo is higher, and the signal amplitude is lower, than in the case of ordinary echo at the same detuning $\delta\nu$. To exclude the influence of the resonator, we determined the frequencies of the capture echoes at various positions of ν_{RF} and ν_{NMR} relative to the resonator frequency. The echo signal was always observed at the frequency ν_{RF}. The signal width was ~1 MHz at $H \approx$ 4 kOe, this being three or four times larger than the NMR width. The echo signal decreased exponentially with increasing distance between pulses, with a time constant $T' \approx 0.2\ T_2$.[4)]

At a given exciting-pulse power, the echo is observed in a narrow frequency-deviation range. The position and amplitude of the signal are then practically independent of the shapes of the samples.[5)] Consequently the capture echo is not connected with excitation of oscillations in the long-wave region of the nuclear spin-wave spectrum. The echo spectrum is satisfactorily described by the formula

$$\delta\nu = k(\gamma_n \eta h)^{2/3} \nu_p^{1/3} = k \nu_1^{2/3} \nu_p^{1/3}, \qquad (13)$$

where k = 1.6 ± 0.4 for pulses of 1 μsec duration (Fig. 11). The value of ν_1 was determined by us independently by measuring the singularities of the free-precession signal. The dependence of the power needed to observe the signal at a given deviation on the pulse frequency is shown in Fig. 12. We investigated the behavior of the capture echo under separate variation of the powers of the first and second pulses. The echo spectrum is determined by the first pulse and does not depend on the second. The signal amplitude is maximal when the condition $P_1/P_2 \approx 3$ is satisfied.

It can therefore be assumed that the nuclear spin system is entirely captured by the first pulse, while the second serves only to form the echo signal. Consequently we can investigate the capture mechanisms by determining the spectral dependences of the capture echo.

Nuclear spin motion was investigated in[8] for systems with dynamic frequency shift at times $t \ll T_2$. It follows from that paper that there exists a set of possible spin-motion trajectories, on which the precession frequency of the nuclear angular momenta changes from ν_{NMR} to ν_{RF}. These are trajectories close to the aperiodic trajectory, which is realized in the presence of a frequency deviation (see formula (11)). This result is in satisfactory agreement with our data (formula (13)). The theory, however, does not contain a dependence of the frequency deviation on the pulse duration at $t_\nu \gtrsim 1.0$ μsec for the case of an ideal rectangular pulse. We have numerically integrated the equations of motion from[8] for a pulse with rise and fall times on the order of 0.5 μsec. This results in satisfactory agreement with experiment. The calculation data are shown by the solid line in Fig. 12.

We can thus state that at frequency deviations $\delta\nu \lesssim 5$ MHz, in the case of short pulses ($t_\nu \ll T_2$), the capture of a nuclear spin system by a microwave field can be satisfactorily described within the framework of the dynamics of nuclear-spin motion. At the same time, additional research is necessary to study the mechanism whereby the capture echo is formed.

6) Stimulated Echo

Stimulated echo was investigated in $MnCO_3$ by the standard three-pulse procedure. The signal was observed in the frequency range 615—630 MHz at temperatures 4.2—1.5°K. The maximum signal was observed at the same RF pulse parameters at which the two-pulse echo is maximal. The dependence of the signal on the distance between the second and third pulses had a nonmonotonic character (Fig. 13).

At low delays $\tau_2 \lesssim 200$ μsec, the signal decreases rapidly with a time constant ~50 μsec, and the signal amplitude increases with increasing difference between

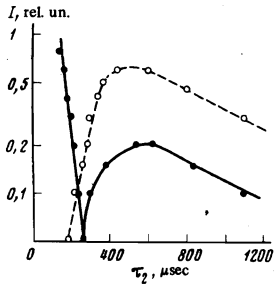

FIG. 13. Dependence of the stimulated-echo intensity on the distance τ_2 between the second and third pulses: ○—at $\nu_{RF} = \nu_{NMR}$, ●—at RF − NMR = 0.5 MHz; ν_{NMR} = 620 MHz, T = 4.2°K.

ν_{NMR} and ν_{RF}. At the NMR line center there is no signal. With further increase of τ_2, the signal goes through a maximum. The position of the maximum depends little on the detuning. The signal intensity reaches a maximum value at the center of the NMR line. This follows by an exponential decrease of the signal with a time constant close to the value of T_1 measured in[4]. The character of the dependence does not change qualitatively when the temperature is lowered, but the echo-signal intensity decreases in this case. An abrupt change in the time constant of the stimulated-echo signal envelope was observed in[23]. In addition, just as in our case, the authors of[23] were able to observe stimulated echo only in a narrow frequency band near the unshifter NMR frequency ν_{n0}. These factors indicate that the observed effects are close. Our values depend little on the magnetic field and on the temperature ($T_1 \approx$ 750 μsec at 4.2°K and $T_1 \approx$ 1100 μsec at T = 1.7°K), in accord with the results of[4].

4. CONCLUSION

We have succeeded in showing that spin echo in nuclear spin systems with large dynamic frequency shifts are produced by a frequency-dependent mechanism. Within the framework of this mechanism, we were able to predict and observe experimentally a number of interesting phenomena, and in particular one-pulse echo. At the same time, significant manifestations of this mechanism, namely nonmonotonicity of the echo signal as a function of the distance between exciting pulses and the "enhancement" of the echo when the RF signal is excited by pulses of different amplitude[11] could not be observed as yet. It was shown that the behavior of the free-precession signal amplitude is satisfactorily described within the framework of the dynamics, described in[8], of the motion of nuclear spins in systems with dynamic frequency shift. This dynamics also describes satisfactorily the capture of a spin system by a short RF pulse. However, the mechanism whereby the capture echo is formed is not yet clear. We propose that spin echo enables us, at sufficiently low RF power, to measure real transverse spin relaxation times T_2, although this question is subject to both experimental and theoretical difficulties[24,25].

It must be emphasized that all the described phenomena were investigated by us in the case when the NMR line is inhomogeneously broadened. As ν_{NMR} approaches ν_{n0}, the inhomogeneous and homogeneous line widths become comparable in magnitude. In this region, new interesting phenomena are observed, but still remain unexplained, we have in mind the behavior of the stimulated-echo signal and the strong difference between the position of the echo signal and the value of the doubled time delay between the RF pulses[26].

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[1)] The authors are deeply grateful to N. Yu. Ikornikova and S. V. Petrov for supplying the samples.
[2)] This irregularity may be due to the chopped-up shape of the AFMR line.
[3)] The possibility that the echo-signal fall-off envelope behaves in this manner is indicated in [12,20].
[4)] We assume that the decrease of the time constant is connected with the line broadening. The mechanism of a similar phenomenon was investigated in [12].
[5)] We have investigated both crystals of irregular shape and those finished in the form of disks.

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