Mechanism of formation of single-pulse echo in Hahn spin systems

V. P. Chekmarev, M. I. Kurkin, and S. I. Goloshchapov

A. F. Ioffe Physicotechnical Institute, USSR Academy of Sciences
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Results are presented of experimental and theoretical investigations of the mechanism of formation of a single-pulse echo (echo following one exciting pulse) in spin systems described by the Bloch classical equations. It is shown that a single-pulse echo can be observed only from spins whose resonant frequency differs from the frequency of the exciting pulse. The cause of the appearance of the single-pulse echo is the ellipsoidal shape of the projection of the trajectories of the vector of the nuclear magnetization in a rotating coordinate system on the *xy* plane during the time of the action of the exciting pulse, caused by the inclination of the precession axis to the *z* axis. The time of appearance, the shape, and the parameters of the single-pulse echo depend substantially on the concrete conditions of the observation (power and duration of the pulse, width, and waveform of the exciting part of the resonant line, bandwidths of the receiving channel of the spectrometer, the method of excitation, etc.). The mechanism of formation of stimulated echo after two exciting pulses is considered. The efficiencies of the considered mechanism of single-pulse echo formation and of the frequency-modulation mechanism are compared.

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The spin echo phenomenon, discovered by Hahn in 1950,[1] consists in the fact that action of two (or more) radiofrequency pulses on a system results, after a time equal to the interval between these pulses, in a response of the spin system in the form of an electromagnetic pulse that contains information on the properties of this spin system and the parameters of the exciting pulses. At the present time the Hahn spin echo is one of the most widely used methods of nuclear magnetic resonance (NMR) and electron resonance, which are widely used to study the properties of all kinds of substances—liquids, gases, solids, complex chemical compounds, and so forth.

Further investigations have shown that in a number of cases, even after one exciting pulse, a pulse response of the spin system, reminiscent of spin echo, is observed besides the free-induction signal (which characterizes the decay of the transverse magnetization component). Single-pulse echo is a pulsed resonant response of a spin system to the action of a single exciting radiofrequency (rf) pulse, occurring at an instant of time approximately equal to the duration of the pulse τ after it is turned off.

The first to point to the possibility of observing a single-pulse echo in a spin system was Bloom.[2] The single-pulse echo signal from protons in water, observed by Bloom, consisted of two maxima separated by a sharp minimum at $t=\tau$ (Fig. 1a). In these experiments the proton NMR line width, equal to the receiver bandwidth ($\Delta F = 200$ kHz) was much larger than the maximum amplitude of the exciting pulse ($\omega_1 = \gamma_n H_1 = 20$ kHz, where γ_n is the gyromagnetic ratio for protons). Bloom has established that the main contribution to the single-pulse echo is made by isochromates,[1)] whose resonant frequency $\omega_{\text{NMR}j}$ differs from the frequency of the exciting pulse ($|\omega_{\text{NMR}j} - \omega_{\text{rf}}| \gg \omega_1$), and indicated that the expression for the motion of the nuclear-magnetization vector after the action of the pulse contains a term $\exp[-i\Delta\omega_j(t-\tau)]$ responsible for the "double-hump" shape of the single-pulse echo. Here $\Delta\omega_j = \omega_{\text{NMR}j} - \omega_{\text{rf}}$.

Signals of similar shape, of single-pulse echo from Co^{59} nuclei located in domains and in domain walls in metallic cobalt, were observed in Ref. 3. It is interesting that the numerical integration of Bloom's equations of motion, performed in Ref. 3 for a wide range of detunings ($|\Delta\omega_{j\max}| \approx 100\omega_1$), did not reveal the single-pulse echo effect.

The question of the mechanism whereby the single-pulse echo is produced in Hahn spin systems,[2)] of the dependence of its shape and of its properties on the experimental conditions, thus remained open prior to our present investigation.

Investigations of the nature of the phenomenon of single-pulse echo began to attract particular attention after 1974, when this phenomenon was observed in crystals with large dynamic frequency shifts (DFS) of the NMR, namely $MnCO_3$ and $CsMnF_3$ (Refs. 4 and 5, Fig. 1b). It

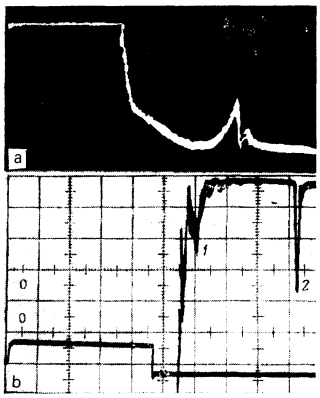

FIG. 1. Shape of single-pulse echo: (a)—from protons in water (frequency 30 MHz, Ref. 2), and (b)—from Mn^{55} nuclei in $MnCO_3$: 1—free induction signal, 2—echo signal. On the lower trace is shown a wave-meter signal that shows the position of the exciting pulse. Pulse and echo frequencies 616 and 612 MHz, respectively.[5]

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turned out that the frequency-modulation mechanism that produces the two-pulse echo signal in these crystals forms also a single-pulse echo signal of high intensity, whose frequency and width are determined by the inherent characteristics of the spin system. In this case, secondary single-pulse echo signals were also observed at instants of times that were multiples of the pulse duration ($t = n\tau$, where $n = 2, 3, \ldots$).

We present here the results of an experimental and theoretical investigation of single-pulse echo in Hahn nuclear spin system. The formation mechanisms and intensities of the echo are compared in Hahn spin systems and in spin systems with DFS.[7] A brief report of the results was published in Ref. 8.

1. EXPERIMENTAL RESULTS

The single-pulse nuclear-echo signal was observed in experiment from Mn^{55} nuclei in spinel $MnFe_2O_4$ at $T = 77$ and 4.2 K in the frequency bands 580–582 and 575–591 MHz respectively, and also in the garnet $Eu_3Fe_5O_{12}$ from the nuclei Eu^{151} and Eu^{153} at $T = 4.2$ K in the frequency band 550–700 MHz. The maximum intensity of the single-pulse echo was 5–15% of the maximum intensity of the usual two-pulse echo.[3)] This ratio for $MnFeO_4$ was approximately the same at 77 and 4.2 K. The pulses used in the experiments were 8–30 μsec in duration and up to 8 W in power. The experimental results for both crystals are similar, but it is more convenient to distinguish between two different observations.

1. *Nonresonant excitation*, i.e., the frequency of the exciting pulse differs from the nuclear-spin NMR frequencies that fall in the amplification band of the receiver. In this case the duration and intensity of the free-induction signal is smaller than in the case of resonant excitation, so that observation of the single-pulse echo is easier. A distinct single-pulse echo was observed in these crystals, with a single maximum at $t \approx \tau$ (Fig. 2). The width of the echo at half-height coincides with the width of the two-pulse echo and amounts to ~1.5 μsec. We note that this value did not depend on the pulse duration. The intensity of the single-pulse echo increases with increasing pulse power (Fig. 3). The time of appearance of the single pulse echo is equal to $\sim\tau$ and depends little on the pulse power, but when the pulse frequency approaches the frequency to which the reciever is tuned (when the detuning is decreased) the time of appearance of the single-pulse echo decreases monotonically to values $t = \tau - 2$ to $\tau - 3$ μsec.

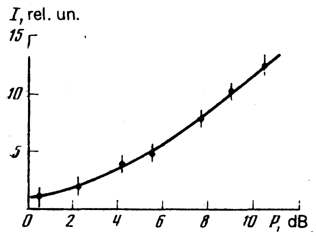

FIG. 3. Intensity I of single-pulse echo of Mn^{55} nuclei in $MnFe_2O_4$ vs. the pulse power P; $T = 4.2$ K, $f_{rf} = 579.5$ MHz, $f_{NMR} = 581.5$ MHz, $\tau = 15$ μsec, pulse power at zero DB is $P_0 = 0.06$ W.

2. *Resonant excitation*, i.e., the receiver is tuned to the frequency of the exciting pulses. Let us examine the singularities of the observation of single-pulse echo when the power P of the exciting pulse is increased. In this case, at a certain value of P, the free-induction signal damping becomes nonmonotonic. With increasing P, the duration of the induction decreases and a broad (~4 μsec) single-pulse echo appears against the background of the induction at an instant $t = \tau - 4$ to 5 μsec. With further increase of P, the times of appearance of the single-pulse echo and of the induction signal become entirely different, the echo appearance time increases to $t = \tau$, its width decreases monotonically to 1.5 μsec, and the echo intensity drops to zero with increasing pulse power. The maximum intensity of the single-pulse echo under these conditions is smaller by a factor 4–5 than in the case of nonresonant excitation (Fig. 4).

It is interesting that the transverse relaxation time T_2 measured by the single- and two-pulse procedures is somewhat different. For example, in $MnFe_2O_4$ at $T = 4.2$ K and $f_{rec} = f_{rf} = 584.3$ MHz, the time T_2 measured by the two-pulse procedure is 10 μsec, as against 7 μsec by the single-pulse procedure. The corresponding values for $T = 77$ K at $f_{rf} = 582.1$ MHz and $t_{rec} = 583.6$ MHz are 8.5 and 7 μsec.

2. MECHANISM OF FORMATION OF SINGLE-PULSE ECHO

What is the nature of the single-pulse echo phenomenon in a Hahn spin system?

Assume that an exciting pulse of duration τ, amplitude H_1, and frequency ω_{rf} is applied to a system of nuclear spins in an equilibrium position. The motion of the nuclear-magnetization vector $\mathbf{m}_j$ of the jth isochromate,

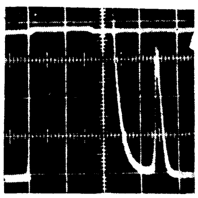

FIG. 2. Shape of single-pulse echo of Mn^{55} nuclei in $MnFe_2O_4$ under nonresonant excitation. Upper trace-signal from wavemeter, showing the pulse duration. Temperature $T = 4.2$ K, $f_{rf} = 579.5$ MHz, $f_{NMR} = 581.5$ MHz, $\tau = 15$ μsec, $P = 1$ W, receiver bandwidth 1 MHz.

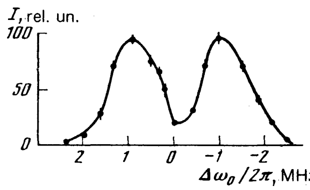

FIG. 4. Dependence of single-pulse echo intensity of Eu^{151} nuclei in $Eu_3Fe_5O_{12}$ on the detuning $\Delta\omega_0$ of the pulse frequency ω_{rf} from the receiver frequency ω_{NMR} $\Delta\omega_0 = \omega_{NMR} - \omega_{rf}$; $T = 4.2$ K, $f_{NMR} = 644.0$ MHz, $\tau = 10$ μsec, $P = 8.0$ W.

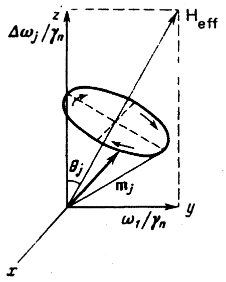

FIG. 5. Precession of nuclear magnetization vector $\mathbf{m}_j$ of j-th isochromate around the effective field $\mathbf{H}_{eff}$ (1) in a rotating coordinate frame, $\Delta\omega_j > 0$.

in a coordinate frame that rotates at a frequency ω_{rf}, constitutes then precession about an effective field (Ref. 2)[4)] (see Fig. 5)

$$\mathbf{H}_{eff} = \frac{1}{\gamma_n}(\Delta\omega_j\mathbf{z}+\omega_1\mathbf{y}), \tag{1}$$

described by a system of equations

$$\dot{x}_j=\Delta\omega_j y_j-\omega_1 z_j,\ \dot{y}_j=-\Delta\omega_j x_j,\quad \dot{z}_j=\omega_1 x_j, \tag{2}$$

where γ_n is the nuclear gyromagnetic ratio, z and y are unit vectors of the rotating coordinate system (Fig. 5), $\omega_1=\gamma_n\eta H_1$ is the pulse amplitude in frequency units, and η is the gain of the rf field, which reaches 10^3-10^4 in magnets[9] (for paramagnets and diamagnets we have $\eta=1$)

$$x_j=m_{xj}/m,\quad y_j=m_{yj}/m,\quad z_j=m_{zj}/m,\quad \Delta\omega_j=\omega_{NMR}-\omega_{rf} \tag{3}$$

is the detuning for the jth isochromate, and m is the equilibrium value of the nuclear magnetization.

The solution of the system (2) under initial conditions $x_j(0)=y_j(0)=0$, $z_j(0)=1$ is

$$\begin{aligned} x_j&=-\sin\theta_j\sin\Delta\omega_j't,\\ y_j&=-\sin\theta_j\cos\theta_j\cos\Delta\omega_j't+\sin\theta_j\cos\theta_j,\\ z_j&=\sin^2\theta_j\cos\Delta\omega_j't+\cos^2\theta_j, \end{aligned} \tag{4}$$

where θ_j is the angle between $\mathbf{H}_{eff}(1)$ and the z axis (Fig. 5),

$$\sin\theta_j=\omega_1/\Delta\omega_j',\quad \cos\theta_j=\Delta\omega_j/\Delta\omega_j',\quad \Delta\omega_j'=(\Delta\omega_j^2+\omega_1^2)^{1/2} \tag{5}$$

is the angular velocity of the precession of the jth isochromate around $\mathbf{H}_{eff}$.

To describe the single-pulse echo it suffices to know only the transverse components $m_{\perp j}=m(x_j+iy_j)$, which can be conveniently written in the form of a sum of three terms:

$$m_{\perp j}(t)=m_{\perp j}^{(1)}+m_{\perp j}^{(2)}(t)+m_{\perp j}^{(3)}(t), \tag{6}$$

where

$$m_{\perp j}^{(1)}=im\sin\theta_j\cos\theta_j \tag{6a}$$

is the component of $m_{\perp j}$ independent of t and connected with the projection of $\mathbf{m}$ on the field $\mathbf{H}_{eff}(1)$ (Fig. 5),

$$m_{\perp j}^{(2)}(t)=-im\sin\theta_j\cos^2(\theta_j/2)\exp\{-i\Delta\omega_j't\}, \tag{6b}$$

$$m_{\perp j}^{(3)}(t)=im\sin\theta_j\sin^2(\theta_j/2)\exp\{i\Delta\omega_j't\} \tag{6c}$$

are circular components rotating around the z axis with frequencies $\pm\Delta\omega_j'(5)$. The cause of these components is easily understood by recognizing that their sum $(m_{\perp j}^{(2)}+m_{\perp j}^{(3)})$ describes the motion of $m_{\perp j}$ along an ellipse, with semiaxes $m|\sin\theta_j|$ and $m|\sin\theta_j\cos\theta_j|$, which is the projection of the base of the precession cone (Fig. 5) on the xy plane.

After the pulse is turned off, the motion of $\mathbf{m}_j$ is described by the system (2) with $\omega_1=0$ and constitutes precession about the $\mathbf{z}$ axis with frequency $\Delta\omega_j(3)$. Thus, the induction signal following the pulse is given by

$$I(t+\tau)=cm_\perp(t+\tau)=\sum_j cm_{\perp j}(\tau+t)=\sum_j cm_{\perp j}(\tau)\exp\{-i\Delta\omega_j t\}, \tag{7}$$

where c is a coefficient that takes into account the geometry of the experiment (the filling factor, the matching of the channels, etc.), summation over j means summation over the isochromates whose frequencies lie in the receiver bandwidth, and the time t is reckoned from the instant τ when the pulse is turned off.

If we neglect the frequency between the frequencies $\Delta\omega_j(3)$ and $\Delta\omega_j'(5)$, then Eq. (7) coincides with the expression for m after two short pulses separated by an interval τ.[2] The term

$$m_\perp^{(1)}(\tau+t)=\sum_j im\sin\theta_j\cos\theta_j\exp\{-i\Delta\omega_j t\} \tag{7a}$$

would then describe the decay of the induction signal produced by the second term, the term

$$m_\perp^{(2)}(\tau+t)=-\sum_j im\sin\theta_j\cos^2\frac{\theta_j}{2}\exp\{-i(\Delta\omega_j t+\Delta\omega_j't)\} \tag{7b}$$

would describe the decay of the induction signal due to the first pulse, and the term

$$m_\perp^{(3)}(\tau+t)=\sum_j im\sin\theta_j\sin^2\frac{\theta_j}{2}\exp\{-i(\Delta\omega_j t-\Delta\omega_j't)\} \tag{7c}$$

would correspond to the two-pulse echo signal produced at $t=\tau$, when the phase $(\Delta\omega_j t-\Delta\omega_j\tau)=0$, i.e., is the same for all the isochromates. In the case of a single pulse, owing to $\Delta\omega_j\neq\Delta\omega_j'$, this requirement is not satisfied strictly for any t, and therefore the signals of the single-pulse echos can occur only under certain conditions, when the indicated requirement is satisfied with sufficient accuracy. To determine these conditions, it is convenient to rewrite Eq. (3) for $\Delta\omega_j$ in the form

$$\Delta\omega_j=\Delta\omega_0+\Omega_j, \tag{8}$$

where $\Delta\omega_0$ is the detuning from the center of the investigated section of the NMR line width $\Omega_{j\,max}$ (Fig. 6). We consider the case $|\Delta\omega_0|\gg\Omega_{j\,max}$. The expression (5) for $\Delta\omega_j'$ can then be written in series form:

$$\Delta\omega_j'=\Delta\omega_0'+\Omega_j\Delta\omega_0/\Delta\omega_0'+{}^1/_2\Omega_j^2\omega_1^2/\Delta\omega_0'^3+\ldots, \tag{9}$$

where the frequency is $\Delta\omega_0'=(\Delta\omega_0^2+\omega_1^2)^{1/2}$, and its sign is the same as that of $\Delta\omega_0$. If the terms quadratic in Ω_j can be neglected in (9), then it follows from (8) and (9) that at

$$t=t_e=\tau\frac{\Delta\omega_0}{(\Delta\omega_0^2+\omega_1^2)^{1/2}} \tag{10}$$

the phase shift

$$\varphi_j=\Delta\omega_j t-\Delta\omega_j'\tau=-\omega_1\tau\frac{\omega_1}{(\Delta\omega_0^2+\omega_1^2)^{1/2}} \tag{11}$$

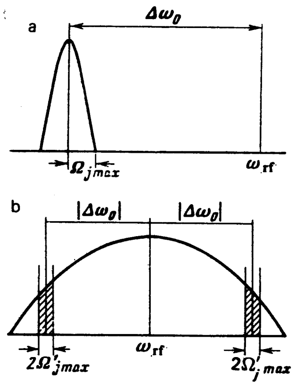

FIG. 6. Different cases of excitation of single-pulse echo a—$|\Delta\omega_0| \gg |\Omega_j|$—nonresonant excitation, b—symmetrical resonant excitation. The symmetrical sections that satisfy the condition of nonresonant excitation are shaded.

does not depend on j, i.e., it is the same for all the isochromates. Thus, the time $t=t_e$ (10) corresponds to the instant of appearance of the single-pulse echo. In contrast to the two-pulse echo, when $t=\tau$, the time of appearance of the single-pulse echo is $t_e<\tau$. The reason is that according to (9) the width of the investigated section of the NMR line narrows down during the time of action of the pulse $[\Omega_{max}(\Delta\omega_0/\Delta\omega_0')<\Omega_{max})$, so that the rate of dephasing of the isochromates is shorter than the rate of their phasing after the pulse.

The width of the single-pulse echo signal, just as that of the two-pulse signal, is determined by the decay time of the induction signal of the investigated section of the NMR line after the pulse: $T_2^*=2\pi/\Omega_{max}$.

The expression for the amplitude of the single-pulse echo will be written out for the condition of nonresonant excitation $|\Delta\omega_0|\gg|\Omega_j|$ and $|\Delta\omega_0|\gg\omega_1$, when the relaxation processes in Eqs. (2) can be taken into account in Eqs. (2) in a sufficiently simple manner:

$$I(\tau+t_e)={}^1/_2 cm\eta\,|\omega_1/\Delta\omega_0|^3\exp\{-(\tau+t_e)/T_2\}, \qquad (12)$$

where T_2 is the transverse relaxation time. Thus, the amplitude of the single-pulse echo is proportional to the square root of the pulse power $P\propto\omega_1^2$, just as in the case of a two-pulse echo at small deviation angles. The dependence of $I(\tau+t_e)$ on τ, however, is determined on the relaxation time T_2 only if we can neglect in (9) the terms quadratic in Ω_j, i.e., the corresponding phase shift is

$$|\Delta\varphi_j|=|{}^1/_2\Omega_j^2\tau\omega_1^2/(\Delta\omega_0^2+\omega_1^2)^{3/2}|\ll 2\pi$$

for all the isochromates. When $\Delta\varphi_j$ is taken into account, the phase shifts $\varphi_j=\Delta\omega_j t-\Delta\omega_j'\tau$ turn out to be different for the different isochromates at all values of t, and therefore at $|\Delta\varphi_j|\gg 2\pi$ the amplitude of the single-pulse echo should vanish. Since the $|\Delta\varphi_j|$ increase with increasing τ, the influence of the terms quadratic in Ω_j and the higher terms in (9) can be regarded as an additional relaxation process due to the mechanism of formation of the single-pulse echo. Thus, the relaxation time T_2 measured with the aid of the single-pulse echo may turn out to be smaller than that measured with a two-pulse echo.

It must be noted that the mechanism of formation of the single-pulse echo (just as the Hahn mechanism of the two-pulse echo formation in the case of a non-180° second pulse) makes it possible to observe stimulated echo when an additional exciting pulse is applied. In the case of the Hahn echo the possibility of observing the stimulated echo is brought about by the fact that the z component of the ith isochromate, after the second exciting pulse, depends on the phase of its transverse component at the start of the first pulse, $\varphi_j=\Delta\omega_j\tau_{12}$. In our case of single-pulse echo, the inclination of the isochromate precession axis relative to the **z** axis during the time of action of the pulse [that causes the trajectory in the xy plane to be ellipsoidal in the xy plane and produces the single-pulse echo (4), Fig. 5] makes the z-component of the isochromate dependent on the phase of its transverse component at the instant of termination of the pulse $\varphi=\Delta\omega_j'\tau$ (4). Thus, inclination of $\mathbf{H}_{eff}$ (1) to the **z** axis during the time of action of the pulse gives rise both to a single-pulse echo and to a possibility of observing stimulated echo.

Under nonresonant excitation (Fig. 6a) the time of appearance of the stimulated echo, due to the single-pulse mechanism, coincides with the time (10) of appearance of the single-pulse echo, if t is reckoned from the end of the auxiliary pulse. Its intensity is

$$I_{st}\approx{}^1/_2 cm\eta\sin\alpha\,|\omega_1/\Delta\omega_0|^2\exp\{-2\tau/T_2\}\exp\{-\tau_{12}/T_1\}, \qquad (13)$$

where α is the angle of rotation of the isochromates by the auxiliary pulse, and τ_{12} is the interval between the exciting and auxiliary pulses.[5)]

In the case of resonant excitation, no analytic expression can be obtained for the intensity of the single-pulse echo, but some qualitative estimates can be made and enable us to describe the behavior of the single-pulse echo.

Consider the case of symmetrical resonant excitation, when the pulse frequency is equal to the frequency of the center of the symmetrical NMR line, i.e., $\Delta\omega_0=0$ (Fig. 6b). In this case the NMR line can be represented as a set of symmetrical sections satisfying the considered case of nonresonant excitation. We consider a pair of such symmetrical sections, Fig. 6b. It is easily shown that the motion of any pair of symmetrical isochromates (with equal absolute values of the detuning $|\Delta\omega_j|$) is described by two cones (4) that are symmetrical about the xz plane and have opposite directions of rotation (Fig. 7). It is seen from this figure, as well as from (4)–(6), that the sum of the y components for the two symmetrical isochromates is equal to zero at any instant of time. Thus, the amplitude of the single-pulse echo in the case of symmetrical excitation can be obtained by integrating the real part of expression (7). We recall that the single-pulse echo from one section was formed in a direction making an angle $\varphi_\perp$ (11) with the **y** axis. Taking into account the opposite signs of the rates of rotation of the symmetric isochromates, and the symmetry of the trajectories relative to the xz plane, we find that if $|\Delta\omega_0|\gg\omega_1$ and $\omega_1\tau\leqslant 1$ no single-pulse echo will be observed at the instant $t_0\approx\tau$, because the signals from the symmetrical sections cancel each other. A net

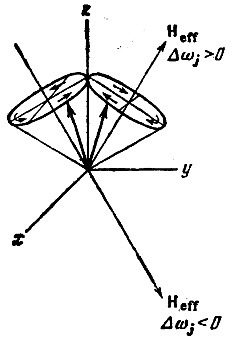

FIG. 7. Precession of nuclear magnetizations of two symmetrical (relative to ω_{rf}) isochromates around the corresponding $\mathbf{H}_{eff}$ (1). The trajectories are symmetrical relative to the xz plane.

transverse magnetization, however, will exist at $t<t_0$ and $t>t_0$, owing to the presence of x components in the partially phased signals of the single-pulse echo from the symmetrical sections. This form of the signal of the single-pulse echo with two maxima was observed experimentally in Refs. 2 and 3 (Fig. 1a).

At $\varphi_\perp = \pi/2 + k\pi$ (11), however, the single-pulse echo signals are phased along the **x** axis. The shape of the net signal will have in this case one maximum, in analogy with the shape of the two-pulse echo. Our qualitative analysis shows that the shape and the time of appearance of the single-pulse echo under resonant excitation depend strongly on the concrete experimental conditions (power and duration of the pulse, width and shape of the excited part of the NMR line, bandwidth of the receiving channel, method of excitation, etc.). Under resonant excitation, a single-pulse echo has a more complicated shape and a longer duration than under nonresonant excitation. Rigorous relations for the parameters of a single-pulse echo in the case of resonant excitation can be obtained by numerically integrating the expressions in (7).

3. EFFECTIVENESS OF FORMATION MECHANISMS

We see thus that single-pulse echo can be observed not only in nuclear spin system with DFS of the NMR,[4,5] but also in ordinary spin systems.[2,3,8] In crystals with DFS, the single-pulse echo is formed by a frequency-modulation mechanism. The cause of the echo is the dependence of isochromate precession frequency on the phase of its transverse component. This dependence is governed by the correlation between the z-component of the isochromate and the phase of its transverse component (4) and is due to the inclination of the isochromate-precession axis during the time of action of the pulse (1) relative to the **z** axis.

The cause of single-pulse echo in Hahn nuclear spin systems (without DFS) is the ellipsoidal shape of the projection of the trajectory of the nuclear magnetization vector on the xy plane during the time of the exciting pulse; this is also due to the inclination of the precession axis during the time of the pulse.

Thus, a common feature of single-pulse echo in spin systems with DFS and in Hahn spin systems is that, in contrast to the two-pulse echo, the contribution to the intensity of the single-pulse echo is made only by those isochromates whose natural frequency does not coincide with the frequency of the exciting pulse, i.e., the nonresonantly excited part of the NMR line.

The ratio of the signal intensities of single-pulse echo in nuclear systems with DFS (I_{ω_p}) [see Eq. (9) of Ref. 5] and in Hahn spin systems [I, Eq. (12)], under identical observation condition, is

$$m = I_{\omega_p}/I = 2\omega_p\tau. \tag{14}$$

This explains the high intensity of the single-pulse echo in crystals with large DFS, for which the DFS is equal to $\omega_p/2\pi = 30-100$ MHz ($\tau = 10-50$ μsec). The mechanism of formation of a single-pulse echo, considered in the present paper, together with the frequency modulation mechanism, participates in the formation of the single-pulse echo in spin systems with DFS, but its contribution to the echo intensity under these conditions is $1/m$ (14). The corresponding terms were therefore discarded in the calculations of Refs. 5 and 10. Analysis shows that the main contribution to the single-pulse echo signal in systems with DFS is made precisely by those components of the transverse nuclear magnetization which do not take part in the formation of the single-pulse echo in the Hahn systems [first and second terms in (6)]. In crystals without DFS these components are observed only in the form of a free-induction signal. This reflects the main difference between the mechanisms of formation of single-pulse echo in the two considered cases. We note also that the mechanism whereby the single-pulse echo is formed in Hahn systems, in contrast to the frequency-modulation mechanism, does not presuppose the presence of secondary single-pulse echo signals.

The single-pulse echo method can yield practically the same information on a spin system as the two-pulse echo method. The properties of the single-pulse echo and the conditions for its observation must be taken into account in three-pulse information-reduction systems based on spin echo.[11] Moreover, at sufficient signal intensity it is possible to develop devices for the reduction of rf pulses on the basis of the single-pulse echo phenomenon. An advantage of such systems is that there is no need for reading pulses in the reduction and that the complications connected with the need of synchronizing the information and reading pulses are eliminated.

We note in conclusion that a single-pulse echo produced by the mechanism described can be observed not only in nuclear spin systems, but in other resonant systems described by the Bloch equations, particularly in an electron spin system and in experiments on photon echo.

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[1]We assume that the macroscopic magnetization can be broken up into a number of isochromatic components that have different precession frequencies. Each isochromate consists of a

sufficiently large number of nuclear spins, so that it can be treated macroscopically. On the other hand, the frequency interval Δf of the precession of the nuclear spins, which enter in an individual isochromate regardless of their location in the crystal, must be small enough to be able to neglect the inhomogeneity of the precession frequency within the limits of the isochromate.

2) We define as a Hahn system a system of spins whose precession frequencies do not depend on the amplitude of the excitation of the spin system. The two-pulse echo in such spin systems is formed by the Hahn mechanism.[1]

3) In the comparison of the intensities, the duration τ of the pulse that exites the single-pulse echo has been chosen equal to the delay τ_{12} between two pulses in the two-pulse measurement procedure, so as to exclude the influence of relaxation effects.

4) We assume that the vector $\mathbf{H}_1$ in a rotating coordinate system is directed along the **y** axis. The relaxation processes in (2) are disregarded for simplicity.

5) Expression (7) shows that in the case when the first exciting pulse satisfies the nonresonant excitation condition and the second pulse is resonant, then three additional echo signals at the instants of time τ_{12} and $\tau_{12}\pm\tau_{12}\Delta\omega_0/(\Delta\omega_0^2+\omega_1^2)^{1/2}$, phased by the Hahn mechanism, can appear following the action of the pulses, on top of the stimulated echo due to the single-pulse mechanism.

[1]E. L. Hahn, Phys. Rev. **76**, 145 (1949); **77**, 297 (1950); **80**, 580 (1950).

[2]A. L. Bloom, Phys. Rev. **98**, 1105 (1955).

[3]B. M. Stearns, AIP Conf. Proc. **10**, 1644 (1972).

[4]Yu. M. Bun'kov, B. S. Dumesh, and M. I. Kurkin, Pis'ma Zh. Eksp. Teor. Fiz. **19**, 216 (1974) [JETP Lett. **19**, 132 (1974)].

[5]Yu. M. Bun'kov and B. S. Dumesh, Zh. Eksp. Teor. Fiz. **68**, 1161 (1975) [Sov. Phys. JETP **41**, 576 (1975)].

[6]M. P. Petrov, G. A. Smolenskiĭ, A. A. Petrov, and S. I. Stepanov, Fiz. Tverd. Tela (Leningrad) **15**, 184 (1973) [Sov. Phys. Solid State **15**, 126 (1973)]; P. M. Richards, C. R. Christensen, B. D. Guenther, and A. C. Daniel, Phys. Rev. **134**, 2216 (1971).

[7]P. G. de Gennes, P. A. Pincus, F. Hartmann-Bourton, and J. M. Winter, Phys. Rev. **129**, 1105 (1963).

[8]V. P. Chekmarev, M. P. Petrov, and A. I. Maksikov, Abstracts of All-Union Conf. on the Physics of Magnetic Phenomena, IÉP Akad. Nauk Ukr. SSR, Donetsk, 1977, p. 17.

[9]E. A. Turov and M. P. Petrov, Yadernyĭ magnitnyĭ rezonans v ferro-i antiferromagnetikakh (Nuclear Magnetic Resonance in Ferro-and Antiferromagnets), Nauka, Moscow, 1969.

[10]V. P. Chekmarev and M. I. Kurkin, Fiz. Tverd. Tela (Leningrad) **18**, 1954 (1976) [Sov. Phys. Solid State **18**, 1137 (1976)].

[11]M. P. Petrov and S. I. Stepanov, Obzory po elektronnoĭ tekhnike Ser. 1, No. 10, 385 (1976).

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Electron emission from condensed noble gases

E. M. Gushchin, A. A. Kruglov, V. V. Litskevich, A. N. Lebedev, I. M. Obodovskiĭ, and S. V. Somov

Moscow Engineering-Physics Institute

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A pulsed ionization chamber was used to measure the dependences of the emission coefficient (departure probability) of conduction electrons from liquid Ar and from solid and liquid Xe in their own gas at equilibrium, as functions of the external electric field intensity. It is shown that the emission coefficient reaches unity in fields exceeding 1 kV/cm for Ar and exceeding 5 kV/cm for Xe. The emission curve calculated under the assumption of scattering by only acoustic phonons yields for solid Xe a mean free path and an average electron energy 10^{-5} cm and 0.5 eV respectively at $E = 2$ kV/cm.

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INTRODUCTION

At the present time, condensed noble gases are attracting increasing attention in research, first as simple objects for the study of electronic processes, and second as promising working media for elementary-particle detectors. Little attention has been paid so far, however, to one of the most interesting properties of condensed noble gases—the emission of conduction electrons from the condensed phase into gas or vacuum under the influence of an external electric field.[1,2] Yet studies of the dependence of the emission coefficient (of the electron escape probability) on the electric field intensity at various temperatures can yield important information on the electronic processes in condensed noble gases, and also make it possible to formulate the principles of construction of two-phase emission instruments. We have measured in this connection the coefficients of emission of electrons from liquid argon and from liquid and solid xenon. The results and their discussion are the subject of this article.

EXPERIMENTAL SETUP

To investigate the emission properties of condensed noble gases we used the setup described in detail in Ref. 3. The initial gas was cleaned for two hours to rid it of impurities, using a titanium getter heated to 1000 °C, and was condensed in the two-electrode ionization chamber shown in Fig. 1. Prior to admission of the gas, the chamber was kept in a vacuum cryostat and evacuated for 10 hours to a pressure ~10^{-5} Torr.

The source of the ionizing radiation was a pulsed

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