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Single-pulse and secondary echoes in systems with a large inhomogeneous broadening of NMR lines

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In the framework of the Mims transformation matrix method the equations for the nuclear magnetizations are obtained which describe the dynamics of nuclear spin-systems with strong Larmor and Rabi inhomogeneous broadenings of the NMR line in conditions of their nonequilibrium which were earlier obtained by the statistical tensors method. As an example, the properties of the proton single-pulse echo and its secondary signals in a test material (silicone oil) coated on the surface of high-T_c superconducting-oxide powders and in metallic hydride are presented.

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The single-pulse echo (SPE) is a resonance response of the inhomogeneously broadened nuclear spin system to the application of a solitary radiofrequency (rf) pulse arising at a time approximately equal to the pulse duration τ after its termination. Though SPE was discovered by Bloom in 1955 for protons in water placed in an inhomogeneous magnetic field, the mechanism of SPE formation is not yet so clear-cut as for the classical Hahn two-pulse echo (TPE) and it continues to attract researcher's attention [1].

The point is that the theoretical models based exclusively on strong Larmor inhomogeneous broadening (LIB) do not agree with the experimentally observed signals but instead result in the formation of oscillatory free-induction decays (OFIDs) [1].

SPE formation mechanisms could be conditionally subdivided into two classes: the first one is so called edge-type mechanisms where rf pulse edges act like rf pulses in the TPE method, such as the distortion mechanism [1] and the mechanism connected with the consideration of spectral densities of sufficiently steep rf pulse edges [2], and the second class includes mechanisms of an internal nature due to particular nonlinearities in the dynamics of spin systems, for example, connected with a strong dynamic frequency shift of the NMR frequency or with a nonlinear dynamics of nuclear spins due to the simulteneous presence of large Larmor and Rabi inhomogeneous broadenings of the NMR line [1].

In this work we consider in more detail the so-called multipulse mechanism of SPE formation, presented in Ref. 1, for systems with both types of frequency inhomogeneities of NMR lines. An important example of such a system is that of nuclei arranged in the domain walls (DW) of multidomain magnets, both in the normal metals, due to the metallic skin effect, and in the normal cores of Abrikosov vortices in type-II superconductors. Earlier in [3] we have investigated the properties of the SPE formation in lithium ferrite. It was established that its properties differ sharply from the SPE properties in hexagonal cobalt, where it is formed by the distortion mechanism. Therefore the conclusion was made on the possible effectiveness of the SPE internal mechanism of formation in lithium ferrite. But its concrete mechanism was not finally established.

Later on, the effectiveness of the multipulse mechanism of SPE formation was experimentally established in this magnet [4]. Moreover, the secondary echo signals of SPE and the two-pulse echo were also formed by this mechanism.

It was shown in [1] that the multipulse mechanism of SPE formation was effective in some multidomain ferromagnets like Fe and FeV. From this point of view further theoretical and experimental investigations of SPE multipulse mechanism formation in systems with large Larmor and Rabi inhomogeneous broadenings of NMR lines are of practical interest.

In Ref. 1, using the formalism of statistical tensors, a theoretical investigation of the SPE and its secondary echo-signal formation mechanism was carried out, allowing for both large Larmor and Rabi inhomogeneous broadenings of the NMR line when the repetition period of the rf pulses T obeys the inequality $T_3 << T_2 < T < T_1$, where T_1 is the spin–lattice relaxation time, T_2 is the transverse irreversible relaxation time, and T_3 characterizes the transverse reversible relaxation time ($T_3 \sim 1/\Delta$, were Δ is the half-width at half-maximum of the inhomogeneously broadened line), therefore a spin system was in a nonequilibrium state before the application of the exciting rf pulse, and only a longitudinal component of the nuclear magnetization was important before the rf pulse. It was shown that a dephasing of the nuclear spin system was accumulated during n-time pulse excitations and restored within a time interval elapsing from the trailing edge of the last «counting» [$(n+1)$th] pulse in the multipulse train. This resulted in the SPE formation and also its secondary signals at times which were multiples of the rf pulse duration after termination of the «counting» rf pulse.

Let us show further a simple classical derivation of the equations describing the nuclear spin-system dynamics in the investigated case, in the framework of the usual classical approach by solving Bloch equations or by the equivalent Mim's transformation matrix method [5]. We will use the last one as the most visual from the experimental point of view.

Let us consider the case when a local static field H_n is directed along Z axis, and a rf field is along the X axis of the rotating coordinate system (RCS) [5,6]. The modulus of $\mathbf{H}_{\text{eff}}$ in the RCS could be expressed by:

$$H_{\text{eff}} = \frac{1}{\gamma_n}\sqrt{\Delta\omega_j^2 + \omega_1^2} = \frac{\overline{\omega_1}}{\gamma_n}\sqrt{a^2 + x^2}\,. \qquad (1)$$

Here $x = \Delta\omega_j/\overline{\omega_1}$, where $\Delta\omega_j = \omega_j - \omega_0$ isochromate frequency $a = \eta/\overline{\eta}$ (or $a = \omega_1/\overline{\omega_1}$), where η is the rf field gain factor and $\overline{\eta}$ its mean value; $\overline{\omega_1} = \overline{\eta}\omega_1^{APPL}$ is a mean value of rf amplitude in frequency units; $\omega_1 = \eta\omega_1^{APPL}$ is Rabi frequency of applied rf field and γ_n is the nuclear gyromagnetic ratio. In addition, let us introduce the following designations [1] for the mean value of the pulse area $y = \overline{\omega_1}\Delta t$, where Δt is the rf pulse duration, $b = \overline{\omega_1}\tau$ is a characteristic of the time interval following a pulsed excitation and is measured from the trailing edge of the rf pulse; ω_0 designates the center of the resonance line, and ω_j is the frequency of jth isochromate. The transformation matrix describing the rotation of the magnetization vector around $\mathbf{H}_{\text{eff}}$ is [6]: $\overline{m} = (\overline{m}_x; \overline{m}_y; \overline{m}_z)$

$$(R) = \begin{bmatrix} S_\psi^2 + C_\psi^2 C_\theta & -C_\psi S_\theta & S_\psi C_\psi(1 - C_\theta) \\ C_\psi S_\theta & C_\theta & -S_\psi S_\theta \\ S_\psi C_\psi(1 - C_\theta) & S_\psi S_\theta & C_\psi^2 + S_\psi^2 C_\theta \end{bmatrix}, \qquad (2)$$

C_ψ, S_ψ, C_θ, and S_θ stand for $\cos\psi, \sin\psi, \cos\theta$, and $\sin\theta$, and $\Psi = \text{tg}^{-1}(\omega_1/\Delta\omega_j)$ is the angle between the effective field $\mathbf{H}_{\text{eff}}$ and Z axis; θ is the angle by which the magnetization turns about the effective field $\mathbf{H}_{\text{eff}}$ during the pulse time Δt: $\theta = \gamma_n H_{\text{eff}} t$, where $\mathbf{H}_{\text{eff}}$ is given by (1).

Let us consider first the case of single-pulse excitation. Let

$$X_j = m_{xj}/m;\; Y_j = m_{yj}/m;\; Z_j = m_{zj}/m,$$
$$\text{and } \overline{\mu} = (X_j; Y_j; Z_j),$$

where m is the equilibrium nuclear magnetization and at the equilibrium $\overline{\mu}_{\text{eq}} = (0;0;1)$.

It before the excitation by rf pulse a nuclear spin system was at equilibrium conditions, and therefore $\overline{\mu}_{\text{eq}} = (0;0;1)$, then the result of rf pulse action is presented by $\overline{\mu} = (R)\overline{\mu}_{\text{eq}}$.

At the termination of rf pulse isochromates precess freely around the Z axis; this is described by the matrix:

$$R_\varphi = \begin{pmatrix} C_\varphi & -S_\varphi & 0 \\ S_\varphi & C_\varphi & 0 \\ 0 & 0 & 1 \end{pmatrix},$$

where $\varphi = \Delta\omega_j\tau$ is the angle of rotation of the isochromate around the Z axis, and τ is the time elapsing from the trailing edge of a pulse. Therefore, we have finally:

$$\overline{\mu}_1 = (R_\varphi)(R)\overline{\mu}_{\text{eq}} = \begin{pmatrix} C_\varphi S_\psi C_\psi(1 - C_\theta) + S_\varphi S_\psi S_\theta \\ S_\varphi S_\psi C_\psi(1 - C_\theta) - C_\varphi S_\psi S_\theta \\ C_\psi^2 + S_\psi^2 C_\theta \end{pmatrix}, \qquad (3)$$

or in the adopted designations:

$$\frac{m_x}{m} = \cos bx\,\frac{ax}{a^2 + x^2}\left(1 - \cos y\sqrt{a^2 + x^2}\right) + \sin bx\,\frac{a}{\sqrt{a^2 + x^2}}\sin y\sqrt{a^2 + x^2}\,,$$
$$\frac{m_y}{m} = \sin bx\,\frac{ax}{a^2 + x^2}\left(1 - \cos y\sqrt{a^2 + x^2}\right) - \cos bx\,\frac{a}{\sqrt{a^2 + x^2}}\sin y\sqrt{a^2 + x^2}\,, \qquad (4)$$
$$\frac{m_z}{m} = 1 - \frac{a^2}{a^2 + x^2}\left(1 - \cos y\sqrt{a^2 + x^2}\right).$$

Expressions (4) coincide with the corresponding ones obtained in [1] for the case of single-pulse excitation, and similar expressions [7] obtained by solving the system of Bloch equations for inhomogeneously broadened Hahn systems.

Let us find now the effect of n-time rf excitation in the framework of model [1], when before the next rf pulse of a train only the longitudinal component of nuclear magnetization remains. It is not difficult to prove by successive matrix multiplication that expression for nuclear magnetization before the final «counting» $(n+1)$th pulse is:

$$\bar{\mu}_n = (C_\psi^2 + S_\psi^2 C_\theta)^n \bar{\mu}_{\rm eq} ,$$

where $\bar{\mu}_{\rm eq} = (0;0;1)$.

Then the result of excitation by the «counting» pulse and following free precession of magnetization is described by the expressions

$$\bar{\mu}_{n+1} = (R_\varphi)(R)\bar{\mu}_n =$$
$$= (C_\psi^2 + S_\psi^2 C_\theta)^n \begin{pmatrix} C_\varphi S_\psi C_\psi (1 - C_\theta) + S_\varphi S_\psi S_\theta \\ S_\varphi S_\psi C_\psi (1 - C_\theta) - C_\varphi S_\psi S_\theta \\ C_\psi^2 + S_\psi^2 C_\theta \end{pmatrix}, \qquad (5)$$

which is similar to the one for single-pulse excitation but allowing for a new initial condition.

It follows from previous expressions (5) in accepted designations:

$$\frac{m_x}{m} = \left(1 - \frac{a^2}{a^2 + x^2}\left[1 - \cos y\sqrt{a^2 + x^2}\right]\right)^n \times$$
$$\times \left[\cos bx \frac{ax}{a^2 + x^2}\left(1 - \cos y\sqrt{a^2 + x^2}\right) + \right.$$
$$\left. + \sin bx \frac{a}{\sqrt{a^2 + x^2}} \sin y\sqrt{a^2 + x^2}\right], \qquad (6)$$

$$\frac{m_y}{m} = \left(1 - \frac{a^2}{a^2 + x^2}\left[1 - \cos y\sqrt{a^2 + x^2}\right]\right)^n \times$$
$$\times \left[\sin bx \frac{ax}{a^2 + x^2}\left(1 - \cos y\sqrt{a^2 + x^2}\right) + \right.$$
$$\left. + \cos bx \frac{a}{\sqrt{a^2 + x^2}} \sin y\sqrt{a^2 + x^2}\right].$$

These expressions coincide with the ones obtained in [1] using the formalism of statistical tensors. The nth degree multiplier has a simple physical meaning of a longitudinal nuclear magnetization created by n preliminary pulses of a multipulse train reflecting the spin system's memory of the excitation. The expressions for the SPE and its secondary echo signal amplitudes using similar expressions for nuclear magnetization vectors were already obtained in [1]. It is easy to prove that above considered approach could be immediately applied to the case of periodic two-pulse excitation, which is of interest for description of secondary echo signals in the investigated systems.

Let us know also [1] that the effect of SPE and its secondary echo signals formation is present for a large LIB in isolation but is stronger in the simultaneous presence of both frequency inhomogeneities, as in the case of multidomain ferromagnets and type II superconductors.

Let us illustrate some of the above-mentioned dependences on concrete examples of practical interest.

Experimental results were obtained on a Bruker «Minispec p20» NMR spectrometer provided with a «Kawasaki Electronica» digital signal averager at room and liquid nitrogen temperatures.

Figure 1 shows the averager record of SPE and its secondary signals from protons in a liquid solution of $MnCl_2$ (water was doped by Mn^{++} paramagnetic impurities by adding a paramagnetic solution of $MnCl_2$ in order to obtain a suitable length of the spin—lattice relaxation time T_1 for the data collection) under periodic excitation by a pulse train with a period $T = 4$ ms. The longitudinal and transverse relaxation times are, respectively, $T_1 = 86$ ms and $T_2 = 72$ ms at room temperature ($T = 300$ K). The standard inversion—recovery and spin-echo train pulse sequences were employed in this work for the T_1 and T_2 determinations, respectively.

In Fig. 2 the dependence of the peak intensities (curve *2*) of the SPE (curve *1*) and its secondary echo signal on the rf pulse repetition period T at room temperatures a liquid solution of $MnCl_2$ are presented.

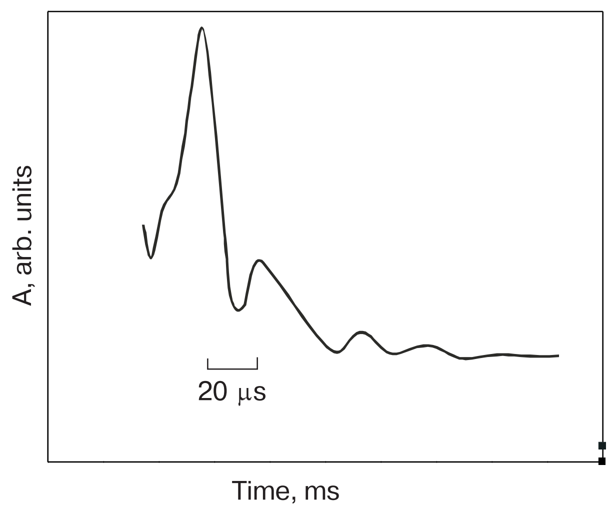

Fig. 1. Single-pulse echo and its secondary signals in a liquid solution of $MnCl_2$ at room temperature. $\tau = 20$ μs, $T = 4$ ms, $T_1 = 86$ ms, $T_2 = 72$ ms.

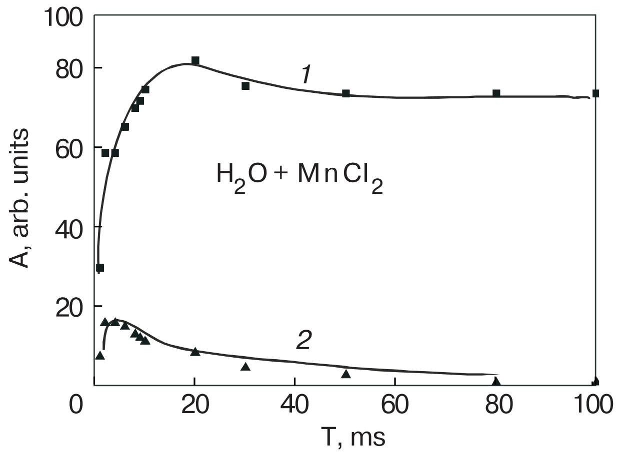

Fig. 2. Dependence of the SPE (*1*) and its secondary echo signal's peak intensities (*2*) on the rf pulse repetition period T at room temperatures in a liquid solution of $MnCl_2$.

The optimal inhomogeneous width of the NMR line for the observation of echo signals was achieved by using an additional iron plate placed in the magnet's clearance as in Ref. 8.

Let us consider in more detail the SPE signal formation for the example of protons in a test material (silicone oil (SO), Silicon KF96) coated on the surface of a powdered sample of the high-T_c superconductor (HTSC) YBCO-(SO + YBCO), which is an object similar the one used in Ref. 8 to study the effect of inhomogeneous broadening of NMR lines due to the formation of an Abrikosov vortex lattice in a HTSC.

Figure 3 shows the SPE record of investigated sample (SO + YBCO) at room temperature, and in Fig. 4 its peak intensity dependence on the rf pulse period T at room temperature (*a*), and at liquid nitrogen temperature (T = 77 K) (*b*).

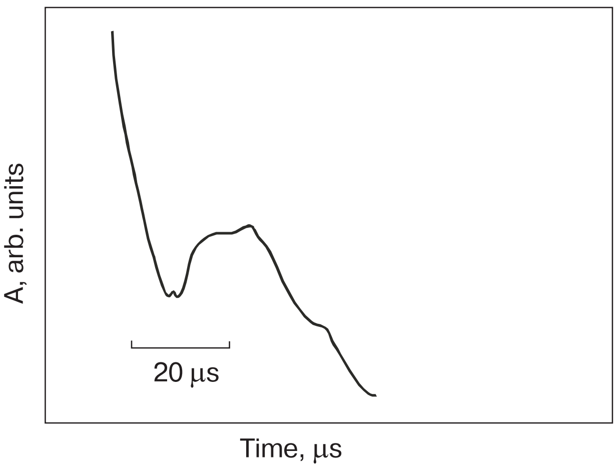

Fig. 3. SPE in silicone oil (SO) mixed with YBCO powder (SO + YBCO) at room temperature. T = 500 ms, T_2 = = 150 ms, T_1 = 350 ms.

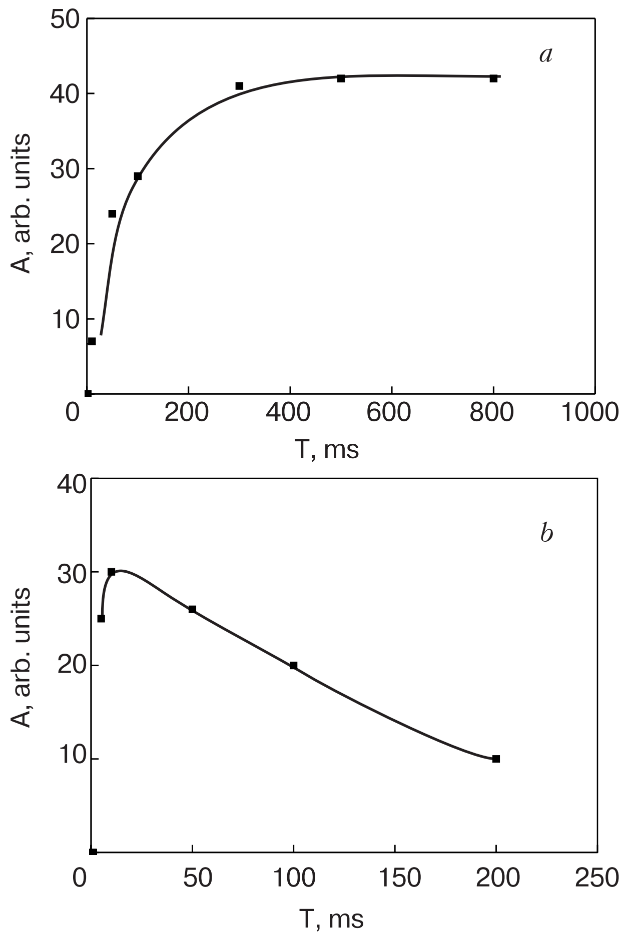

Fig. 4. Dependence of SPE peak intensities on the period T of the single-pulse train at room temperature (*a*) and at liquid nitrogen temperature (*b*) in SO + YBCO.

We note that at the given maximal rf pulse length of the spectrometer (20 μs) for the observation of the SPE signal one should introduce an artificial external magnetic field inhomogeneity (with the help of an additional iron plate [8]) to allow for condition (1)). At the same time at T = 77 K (*b*), the SPE signal is observed in an homogeneous magnetic field, but the inhomogeneity of the NMR line is caused by the effect of the Abrikosov vortex lattice (AVL) formation.

The character of the dependence on the repetition period T points on a comparatively large role of the multipulse mechanism in the SPE formation at low temperatures.

The SO concentration in the sample under investigation was chosen as small as possible for enhancement of the vortex lattice effect [9].

For comparision, in Fig. 5,*a* a record of the TPE and its secondary echo signals is presented for an SO + YBCO sample with a larger concentration of coating material to obtain more intense signals, while Fig. 4,*b* shows the peak intensity dependences of the TPE (curve *1*) and its secondary signal (curve *2*) on

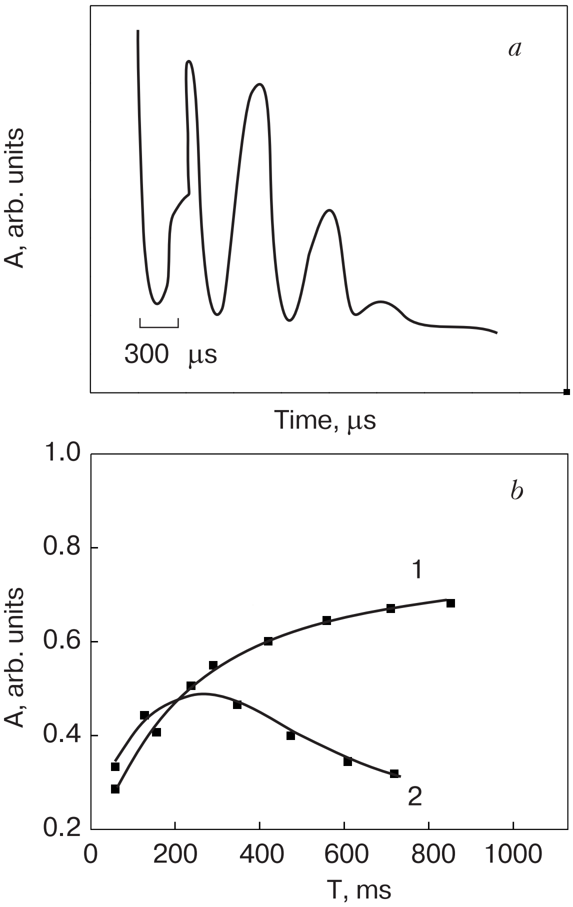

Fig. 5. Two-pulse echo (TPE) and its secondary signals in SO + YBCO (*a*). Dependences of TPE (*1*), and its secondary signal peak intensities (*2*) on the period T of the two-pulse train (*b*). The marks show the time position of the rf pulses for T = 300 K.

the period T of the two-pulse train at room temperature.

It is seen that dependences of the SPE and secondary TPE signals on T have a similar character, reflecting the significant contribution of the multipulse mechanism in the SPE intensity. It is known that secondary TPE signals are formed by the multipulse mechanism in proton-containing systems [10].

Vanadium hydride ($VH_{0.68}$) could be considered as one more example of a system possessing both types of inhomogeneities. In this case the inhomogeneities are the result of the metallic skin effect. Figure 6 shows the dependence of the SPE signal peak intensity on T at room temperature. In this case its intensity is practically unchanged with increase of T showing that the contribution of the distortion mechanism is significant in this material, as it is in some metallic ferromagnets [1].

Analysis of the results obtained shows that the SPE could be useful not only for a simple determination of the characteristic relaxation parameters of inhomogeneously broadened spin systems, but could provide an interesting approach to the study of AVL dynamics using the SPE signal due to the effect of magnetic field inhomogeneity caused by the AVL formation.

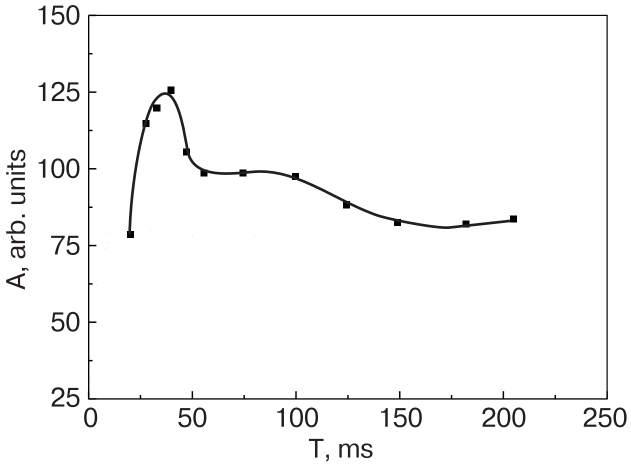

Fig. 6. The dependence of the SPE peak intensity on the period T of the single-pulse train in vanadium hydride $VH_{0.68}$. τ = 20 μs, T = 300 K.

This allows one to use the SPE effect for the study of AVL stimulated dynamics using pulsed and low frequency magnetic fields [11].

In conclusion, in the framework of a simple classical approach using Mim's transformation matrix method, the equations for the nuclear magnetizations are obtained which describe the dynamics of nuclear spin systems with strong Larmor and Rabi inhomogeneous broadenings of NMR lines in conditions of their unequilibrium.

Properties of the proton single-pulse echo and its secondary signals in a test material (silicone oil) coated on the surface of high-T_c superconducting-oxide powders and in metallic hydride are presented.

In addition, it is shown experimentally that the single-pulse echo effect gives an opportunity to obtain valuable information on the inhomogeneous NMR broadening, reflecting the character of the microscopic distribution of magnetic field in such systems as superconductors, hydrides of metals, and so on.

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