Pseudoecho in the nuclear magnetic resonance of a solid

N. A. Sergeev, A. V. Sapiga, and D. S. Ryabushkin
M. V. Frunze State University, Simferopol'

(Submitted 25 December 1988)
Pis'ma Zh. Eksp. Teor. Fiz. **49**, No. 6, 323–326 (25 March 1989)

An in-phase echo in the NMR of ^{19}F nuclei in CaF_2 has been detected. The behavior of this echo differs from the familiar solid-echo signal. A theory which explains the particular features of the in-phase echo that have been observed is developed.

Homogeneous interactions in a nuclear spin system (dipole-dipole interactions, exchange interactions, Suhl-Nakamura interactions, etc.) can, as we know, lead to the formation of a two-pulse spin echo.[1] The echo which was studied most thoroughly is the so-called solid echo which occurs at the time $t = \tau$ as a result of application of two pulses, $90^\circ_y - \tau - \beta^\circ_x - t$, to the spin system. The first pulse, a 90° pulse, is directed along the y axis in a rotating coordinate system, and the second pulse, 90° out of phase, causes the nuclear spins to rotate through an angle β around the x axis in the rotating coordinate system.[2–5] We have detected an echo signal in CaF_2 [a nuclear magnetic resonance (NMR) of ^{19}F nuclei] when an in-phase, two-pulse sequence of pulses was applied to a system of nuclear spins, $90^\circ_y - \tau - \beta^\circ_y$ (Fig. 1). Analysis of the behavior of this echo as a function of the parameters of the pulse train, τ and β, showed that the behavior of the in-phase echo is dramatically different from that of the solid echo. First, at $\tau \lesssim 55$ μs the position of the maximum of the in-phase echo does not depend

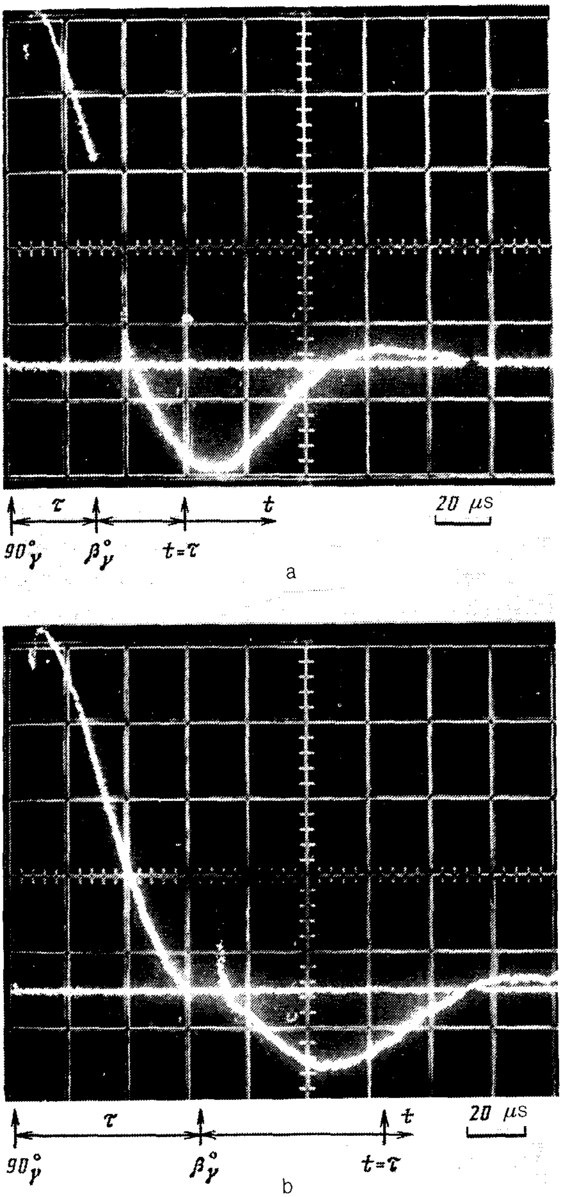

FIG. 1. The in-phase echo in CaF_2. The external magnetic field $\mathbf{B}_0 \| [111]$, $\beta \approx 55°$. (a) $\tau = 30\ \mu s$, (b) $\tau = 60\ \mu s$. The $t = \tau$ position is indicated by a strobing pulse.

on τ and the echo occurs at $t \approx 42\ \mu s$, which does not coincide with the time $t = \tau$ (Fig. 2a). Second, the τ dependence of the amplitude of the in-phase echo is not a monotonically decreasing function but one which has a maximum at $\tau \approx 40\ \mu s$ (Fig. 2b). Finally, the β dependence of the in-phase echo amplitude is described by $\cos \beta \sin^2 \beta$, whereas in the case of a solid-echo signal it is described by $\sim \sin^2 \beta$.[5] Some of the

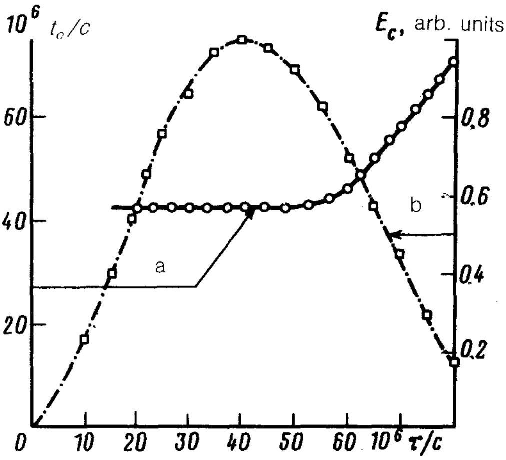

FIG. 2. Time evolution of t_c (a) and of the amplitude E_{c0} (b) of the in-phase echo in CaF_2 versus τ; $\beta \approx 55°$, $\mathbf{B}_0 \| [111]$.

peculiar features of the formation of an in-phase echo which were mentioned above were observed previously in solids with clearly defined spin groupings (CH_3, NH_3).[6–8] These features were attributed to the introduction of fictitious quadrupole Hamiltonians, reducing the solution of the problem to the known results on the in-phase echo in the NMR of quadrupole nuclei.[9–11] Since a CaF_2 single crystal has no clearly defined spin groupings, the detected in-phase echo signal suggests that this echo can occur in any spin systems with a homogeneous interaction.

To explain the observed characteristic features of the formation of an echo, let us consider the expression for an in-phase, two-pulse response signal. This expression can be written in the form[1]

$$E(\tau, t) = \langle I_x(t) \,|\, R I_x(\tau) R^{-1} \rangle / \langle I_x \,|\, I_x \rangle , \tag{1}$$

where $R = \exp(i\beta I_y)$ is an operator which describes the action of the second rf pulse, and $|I_x(t)\rangle = \exp(itL)|I_x\rangle$ is the density matrix of the nuclear spin system. Here $L = [\mathscr{H},...]$ is a Liouville superconductor, and $\mathscr{H}$ is the interaction Hamiltonian of the spin system. If an orthogonal set of vectors $|k\rangle$ is introduced in the Hilbert space of the spin operators ($|0\rangle = |I_x\rangle$), the state vector $|I_x(t)\rangle$ can be written in the form[12]

$$|I_x(t)\rangle = \sum_{k=0}^{\infty} G_k(t) \,|\, k\rangle , \tag{2}$$

where

$$G_k(t) = \langle k \,|\, I_x(t) \rangle / \langle k \,|\, k \rangle . \tag{3}$$

The functions $G_k(t)$ can be uniquely expressed in terms of $G_0(t)$ which describes the free-precession decay and also the moments M_n of the NMR spectrum[12]

$$-i \frac{dG_0}{dt} = \nu_0^2 G_1 ,$$

$$-i\frac{dG_1}{dt} = G_0 + \nu_1^2 G_2 , \tag{4}$$

. . . .

$$-i\frac{dG_k}{dt} = G_{k-1} + \nu_k^2 G_k .$$

Here $\nu_k^2 = \langle k+1|k+1\rangle/\langle k|k\rangle$ and, in particular, $\nu_0^2 = M_2$ and $\nu_1^2 = (M_4 - M_2^2)/M_2$ (Ref. 12). Substituting (2) in (1), we find

$$E(\tau, t) = \sum_{k,\,l=0}^{\infty} \frac{\langle k|\widetilde{l}\rangle}{\langle 0|0\rangle} G_k(\tau) G_l(t), \tag{5}$$

where $|\tilde{l}\rangle = R\,|l\rangle R^{-1}$.

Evaluation of the initial coefficients $\langle k|\tilde{l}\rangle/\langle 0|0\rangle$ for the secular part of the Hamiltonian of the dipole-dipole interaction[13] leads to the following expression for the in-phase response signal:

$$E(\tau, t) = \cos\beta G_0(t+\tau) + \cos\beta\sin^2\beta M_{4\epsilon} G_2(\tau)G_2(t) + \ldots , \tag{6}$$

where $M_{4\epsilon} = M_{4x} - M_4 + M_2^2$, and M_{4x} is the correction term.[3]

For small values of t the functions $G_k(t)$ ($k \geqslant 0$) behave as t^k. We can therefore expect that at small values of τ and t the in-phase response can be described by considering only several terms of the series (6). In (6) the term next to $\cos\beta$ describes the free-precession decay which is detected after the end of the second pulse. The in-phase echo signal is described by the expression

$$E_c(\tau, t) = \cos\beta\sin^2\beta M_{4\epsilon} G_2(\tau)G_2(t). \tag{7}$$

For a constant value of τ the time-dependent position, t_e, of the in-phase echo peak is given by the function $G_2(t)$. As can be seen from (7), t_e does not depend on τ. The in-phase echo is therefore not an echo in the usual sense, in which an echo signal can be represented as a function of $(t-\tau)$ with a maximum at $T_e = \tau$. The particular features of this pseudoecho can be illustrated by assuming that $G_0(t)$ is a Gaussian curve

$$G_0(t) = \exp(-M_2 t^2/2). \tag{8}$$

Substituting (8) into (4) and taking into account that $\nu_1^2 = 2M_2$ for a Gaussian curve, we find

$$G_2(t) = -\frac{1}{2} t^2 G_0(t). \tag{9}$$

The function $G_2(t)$ has a maximum at $t_e = \sqrt{M_2}$ and, as can be seen from (9), does indeed resemble an echo signal.

Expression (7) accordingly describes all of the observable features of the in-phase pseudoecho: independence of its time-dependent position on τ, the mismatch between the echo peak and the time $t = \tau$, the dependence of the echo amplitude on τ, and the dependence of the in-phase echo amplitude on the angle of rotation of the second rf pulse, β.

We note in conclusion that the form of the in-phase echo is determined by the function $G_2(t)$, as follows from (7). This function in turn contains the term $\sim \langle [\mathscr{H},[\mathscr{H},I_x]] | I_x(t) \rangle$, as can be seen from (3). In contrast with the free-precession signal, given by $\sim \langle I_x | I_x(t) \rangle$, the in-phase echo signal thus makes it possible to observe the time evolution of the double commutator $[\mathscr{H},[\mathscr{H},I_x]]$, broadening the experimental capabilities of the NMR method in the study of the dynamics of uniformly broadened spin systems.

[1]Mansfield, in: Progress NMR Spectroscopy **8**, 41 (1971).
[2]J. G. Powles and P. Mansfield, Phys. Lett. **2**, 58 (1962).
[3]J. G. Powles and J. H. Strange, Proc. Phys. Soc. **82**, 6 (1963).
[4]P. Mansfield, Phys. Rev. **137**, 961 (1965).
[5]R. Hausser and G. Siegle, Phys. Lett. **19**, 356 (1965).
[6]P. S. Allen, W. Harding, and P. Mansfield, J. Phys. **C5**, L89 (1972).
[7]Yu. N. Moskvich, N. A. Sergeev, and G. I. Dotsenko, Fiz. Tverd. Tela **15**, 2854 (1973) [Sov. Phys. Solid State **15**, 1912 (1973)].
[8]Yu. N. Moskvich, N. A. Sergeev, and G. I. Dotsenko, Phys. Stat. Sol. (a) **30**, 409 (1975).
[9]I. Solomon, Phys. Rev. **110**, 61 (1958).
[10]G. Bonera and M. Galimberti, Solid State Commun. **4**, 589 (1966).
[11]P. Mansfield, D. E. Mac Laughlin, and J. Butterworth, J. Phys. **C3**, 107 (1970).
[12]F. Lado, J. D. Memory, and G. Parker, Phys. Rev. **B4**, 1406 (1971).
[13]A. Abragam, *The Principles of Nuclear Magnetism*, Clarendon Press, Oxford, 1961.

Translated by S. J. Amoretty