SHAPE OF TWO-PULSE NMR ECHOES IN SOLIDS

N.A. SERGEEV, A.V. SAPIGA and D.S. RYABUSHKIN
Simferopol State University, Simferopol 333036, USSR

Received 30 January 1989; accepted for publication 14 March 1989
Communicated by D. Bloch

A new approach to calculate the echo shape in solids is developed. The obtained experimental data agree well with the derived theoretical expressions describing the shape of the two-pulse echoes in CaF_2.

Up to the present time, the evaluations of the two-pulse NMR echo shapes in solids are provided using a power-series expansion in times τ and t (τ is the pulse separation and t is the time after the second pulse) [1-5]. These evaluations of the echo shape in terms of the "moment" expansion permit one only to describe the short-time behavior of the spin-echo amplitude. The problem of two-pulse echo shape has been solved exactly only for simple two- and three-spin systems [4,6,7]. In this Letter we present a new approach to calculate the echo shape in solids, which allows one to obtain a general analytical expression for the shape of the two-pulse NMR echoes in solids.

The transient response of the spins, in the rotating frame, to a resonant $90°$–τ–R–t sequence is [1]

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

where R is the operator describing the second rf-pulse excitation and

$$\langle A | B \rangle = \mathrm{Tr}(A^+ B),$$

$$| I_x(t) \rangle = \exp(\mathrm{i}tL) | I_x \rangle,$$

$L = [\mathscr{H},\ ]$ is a Liouville superoperator [8], and $\mathscr{H}$ is the interaction Hamiltonian of the spin system.

Let us introduce the orthogonal basis set of vectors $|k\rangle$ [8],

$$|k\rangle = \left(1 - \sum_{m=0}^{k-1} \frac{|m\rangle\langle m|}{\langle m|m\rangle}\right) L^k | I_x \rangle,$$

$$|0\rangle = I_x, \tag{2}$$

and represent the vector of the spin-system state $|I_x(t)\rangle$ in the form

$$|I_x(t)\rangle = \sum_{k=0}^{\infty} G_k(t) |k\rangle, \tag{3}$$

where $G_0(t) = \langle 0 | I_x(t) \rangle / \langle 0 | 0 \rangle$ is the free induction decay (FID).

The functions $G_k(t)$ are described by the following set of equations [8],

$$-\mathrm{i}\frac{\mathrm{d}G_0}{\mathrm{d}t} = \nu_0^2 G_1,$$

$$-\mathrm{i}\frac{\mathrm{d}G_k}{\mathrm{d}t} = G_{k-1} + \nu_k^2 G_{k+1} \quad k = 1, 2, \ldots, \tag{4}$$

where $\nu_k^2 = \langle k+1 | k+1 \rangle / \langle k | k \rangle$ ($k = 0, 1, 2, \ldots$). The first coefficients ν_k^2 are [8]

$$\nu_0^2 = M_2, \quad \nu_1^2 = (M_4 - M_2^2)/M_2,$$

where M_2 and M_4 are the second and the fourth moments of the NMR line shape. From (4) it is easy to see that the functions $G_k(t)$ ($k>0$) are determined only by the function $G_0(t)$ (FID) and the coefficients ν_k^2.

Using (3) we obtain from (1) the following general expression for the shape of the two-pulse transient response of the spins,

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

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

We now consider the echo responses to resonant

$90°$–τ–$90°_{90°}$–t (XY) and $90°$–τ–$\beta°_{0°}$ (XX) pulse sequences.

(1) For the XY sequence we have $R=\exp(-\mathrm{i}\pi I_x/2)$. Evaluation of $\langle k|\tilde{l}\rangle/\langle 0|0\rangle$ with dipolar Hamiltonian gives

$$V(\tau,t)=G_0(\tau)G_0(t)+\frac{1}{M_2}\frac{\mathrm{d}G_0(\tau)}{\mathrm{d}\tau}\frac{\mathrm{d}G_0(t)}{\mathrm{d}t}+\dots\,. \tag{6}$$

The short-time behavior of the functions $G_k(t)$ is t^k and therefore we may describe the shape of the transient response of spins by the few first terms in (5). For crystal CaF_2, as was shown in ref. [9], the theoretical expression for FID,

$$G_0(t)=J_1(2\sqrt{M_2}\,t)/\sqrt{M_2}\,t\,, \tag{7}$$

agrees well with the experimental data. In (7) $J_1(x)$ is the Bessel function of the first kind. Using (7) and restricting only to two terms in (6) we constructed the dependence of the echo amplitude and its time position on τ (fig. 1). From fig. 1 it is clear that the obtained experimental data agree well with theoretical predictions. It is interesting that the maximum of the XY-echo is observed at time position $t<\tau$, when τ is increased.

(2) For the XX-sequence we have $R=\exp(-\mathrm{i}\beta I_y)$ (β is the rotation angle of the second pulse). Evaluation of the first coefficients $\langle k|\tilde{l}\rangle/\langle 0|0\rangle$ with the dipolar Hamiltonian gives

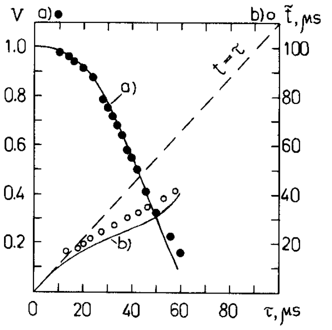

Fig. 1. (a) Dependence of the $90°$–τ–$90°_{90°}$ maximum echo amplitude $V(\tau,t)$ on the pulse spacing τ for ^{19}F in CaF_2 at room temperature ($H_0\|[111]$, $M_2=1.48\times10^9\ s^{-1}$). (b) Dependence of the time $\tilde{t}$, corresponding to the $90°$–τ–$90°_{90°}$ maximum echo amplitude, on the pulse spacing τ.

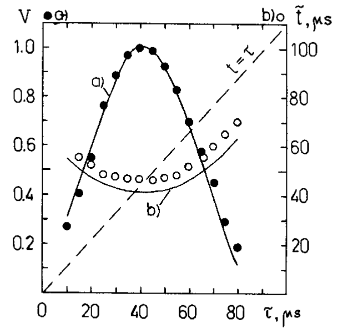

Fig. 2. (a) Dependence of the $90°$–τ–$55°$ maximum echo amplitude $V(\tau,t)$ on the pulse spacing τ for ^{19}F in CaF_2 at room temperature ($H_0\|[111]$, $M_4=2M_2^2$, $M_{4x}=-M_2^2/2$). (b) Dependence of the time $\tilde{t}$, corresponding to the $90°$–τ–$55°$ maximum echo amplitude, on the pulse spacing τ.

$$V(\tau,t)=\cos\beta\,G_0(t+\tau)$$
$$+\cos\beta\sin^2\beta\,M_{4\epsilon}G_2(\tau)\,G_2(t)+\dots\,, \tag{8}$$

where $M_{4\epsilon}=M_{4x}-M_4+M_2^2$ and M_{4x} is a correction term.

The first term in (8) corresponds to the FID, which is registered after the second pulse. The second term in (8) describes the form of the transient response of the spins. From (8) we may conclude that at constant τ the maximum of $V(\tau,t)$, i.e. the echo, is determined by the form of the function $G_2(t)$. Using (7) and restricting only to two terms in (8) we constructed the dependence of the echo amplitude and its time position on τ (fig. 2). Good agreement between theory and experiment is obtained. From fig. 2 we may conclude that the behavior of the XX-echo is quite different from the XY-echo.

Thus, the proposed new approach to calculate the echo shape allows one to describe all observed peculiarities of the two-pulse echoes in solids. Finally, it should be remarked that the method demonstrated here can be easily generalized to treat the echo shape in solids with molecular motions.

References

[1] N.A. Sergeev, A.V. Sapiga and D.S. Ryabushkin, Fiz. Tverd. Tela 31 (1989) 294.

[2] J.G. Powles and J.H. Strange, Proc. Phys. Soc. 82 (1963) 6.

[3] P. Mansfield, Phys. Rev. 137 (1965) 961.
[4] Yu.N. Moskvich, N.A. Sergeev and G.I. Dotsenko, Phys. Stat. Sol. (a) 30 (1975) 409.
[5] D.S. Ryabushkin and N.A. Sergeev, Izv. Vyssh. Uchebn. Zaved. Fiz. 12 (1984) 3.
[6] J.G. Powles and P. Mansfield, Phys. Lett. 2 (1962) 58.
[7] Yu.N. Moskvich, N.A. Sergeev and G.I. Dotsenko, Sov. Phys. Solid State 15 (1974) 1912.
[8] F. Lado, J.D. Memory and J. Parker, Phys. Rev. B 4 (1971) 1406.
[9] M. Engelsberg and I.J. Lowe, Phys. Rev. 12 (1975) 3547.