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NMR MAGIC ECHO IN NATROLITE

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The features of Fenzke magic echo in the simplest case of three pulses are investigated – shape of the signal, the time of the echo maximum formation, dependence of the response amplitude on time, the temperature dependence of the echo. It is shown good qualitative and quantitative agreement of theoretical and experimental results for hydrogen-containing systems with dipole-dipole interaction and internal molecular mobility.
Keywords: nuclear magnetic resonance, magic echo, natrolite.

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INTRODUCTION

In theory and practice of nuclear magnetic resonance (NMR) the magic echo is called a pulse response that forms in times much more than the time of spin-spin relaxation. Obviously, this phenomenon can't be explained within the framework of classical approach (for example, with the help of Bloch equations) and need using of quantum theory.

There are some pulse series producing formation of magic echo [1–3]. Practically in all works on the subject the main attention was attended to the time dependence of the echo amplitude. The reason is that evaluation of response shape is possible but a big quantity of used pulses makes mathematical calculation too complicated. As a consequence, final results look non-demonstrative and this devalues such a type of evaluations.

In given paper Fenzke magic series was investigated and there were two reasons of that. At first, just Fenzke series gives possibility to use only three pulses. So, result of theoretical calculations is a quite compact formula, convenient for theoretical analysis. At second, the authors of the paper have such a NMR equipment that allows to use three pulses to the limit. At the same time, as is demonstrated below, results of the investigation keep all the typical features of the magic echo.

1. THEORY

In general case Fenzke series consists of $2n$ (n = 1,2, …) pulses $90°_x$ applied along x axis of the rotating system of axes (time intervals between the pulses are 2τ) and the final pulse $90°_y$ that locates for τ from the last $90°_x$ pulse. The simpliest variant of the series containing only two $90°_x$ pulses is represented at Fig. 1.

For evaluation the magic echo shape the standard theoretical method based on formalism of density matrix was used.

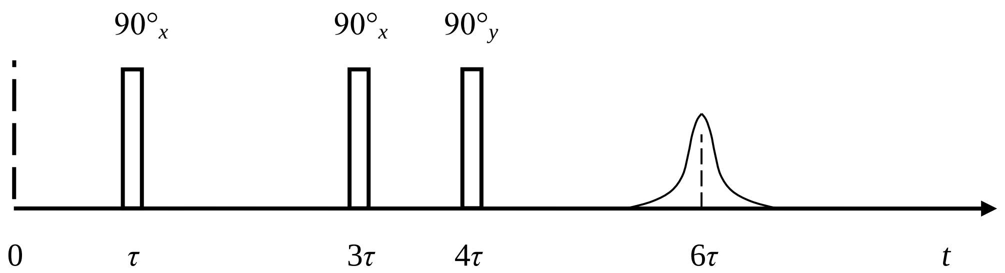


Fig. 1. Formation of Fenzke magic echo in the simpliest version.

In accordance with that the signal of the echo may be written as

$$V(t) = \frac{Tr(\rho(t)\cdot I_x)}{Tr(I_x^{\,2})}, \qquad (1)$$

where $\rho(t)$ is the operator of density matrix at the moment t, I_x is the operator of x-component of the sample's spin in rotating system of axes.

The action of $90°_x$ pulse has the result of exchange the components of total spin accordingly the rule: $I_x \to I_x$, $I_y \to -I_z$, $I_z \to I_y$. The similar rule for the $90°_y$ pulse has the form $I_x \to I_z$, $I_y \to I_y$, $I_z \to -I_x$. The operator of density matrix is evaluated from Liouville equation:

$$\frac{\partial\rho}{\partial t} = i[\rho, H], \qquad (2)$$

where $\hbar H$ is the Hamiltonian of dipole-dipole interaction that depends on time because of internal molecular mobility.

Solution of the equation (2) may be written with the help of T-exponents as

$$\rho(t) = \exp(-i\int_0^t H(t')dt')\rho(0)\exp(i\int_0^t H(t')dt'). \qquad (3)$$

Writing expressions type (3) for each time interval, free from the pulses, and calculating the trace in (1) with the help of full set of Hamiltonian eigenfunctions, have:

$$V(t) = \left\langle \exp(i\int_\tau^{3\tau}\omega(t')dt' - i\int_{4\tau}^{t}\omega(t'')dt'') \right\rangle, \qquad (4)$$

where angle brackets mean averaging connected with internal molecular mobility in the solid, ω is a frequency corresponding a transition between two possible energy states.

Use the known formula for evaluating the means

$$\langle\exp(iA)\rangle = \exp(-\frac{1}{2}\langle A^2\rangle), \qquad (5)$$

as well and choose Gaussian distribution for description the random fields on resonating nuclei and Markov's model of mobility. In such case

$$\left\langle \omega(t')\omega(t'')\right\rangle = \overline{M}_2 + \Delta M_2 \cdot \exp(-\frac{|t'-t''|}{\tau_c}). \qquad (6)$$

Here $\overline{M}_2$ is the second moment of a NMR line narrowed by mobility, ΔM_2 is the difference of the second moments of absorption lines in rigid and fast-moving systems, τ_c is the time of correlation (average time of standing in given lattice configuration).

Finally:

$$V(t) = \exp\left\{ -\frac{1}{2}\overline{M}_2 (t-6\tau)^2 - \Delta M_2 \tau_c^2 \left[\frac{t-2\tau}{\tau_c} + F_1(t) + F_2(\tau) - 2 \right] \right\}, \qquad (7)$$

where
$$F_1(t) = \exp(-\frac{t}{\tau_c})\left[\exp(\frac{4\tau}{\tau_c}) + \exp(\frac{3\tau}{\tau_c}) - \exp(\frac{\tau}{\tau_c}) \right],$$

$$F_2(\tau) = \exp(-\frac{\tau}{\tau_c})\left[\exp(-\frac{2\tau}{\tau_c}) + \exp(-\frac{\tau}{\tau_c}) - 1) \right].$$

2. EXPERIMENT

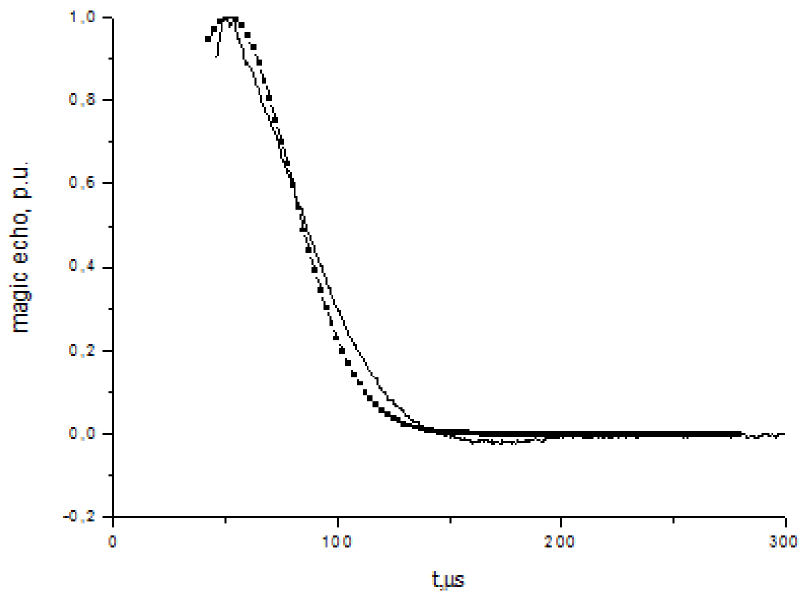
Choice of a sample for experiments was predetermined by chosen function of Gaussian distribution of the random fields on nuclei. Obviously, it is necessary to study systems with great quantity of hydrogen nuclei and without any separated groups. Following this principle, the experiments were carried out in a crystal of natrolite $Na_2Al_2Si_3O_{10}\cdot 2(H_2O)$.

The next characteristics of Fenzke magic echo were analysed: a) general shape of the signal, b) the moment of echo maximum formation, c) dependence of the response amplitude on time, d) temperature dependence of the echo.

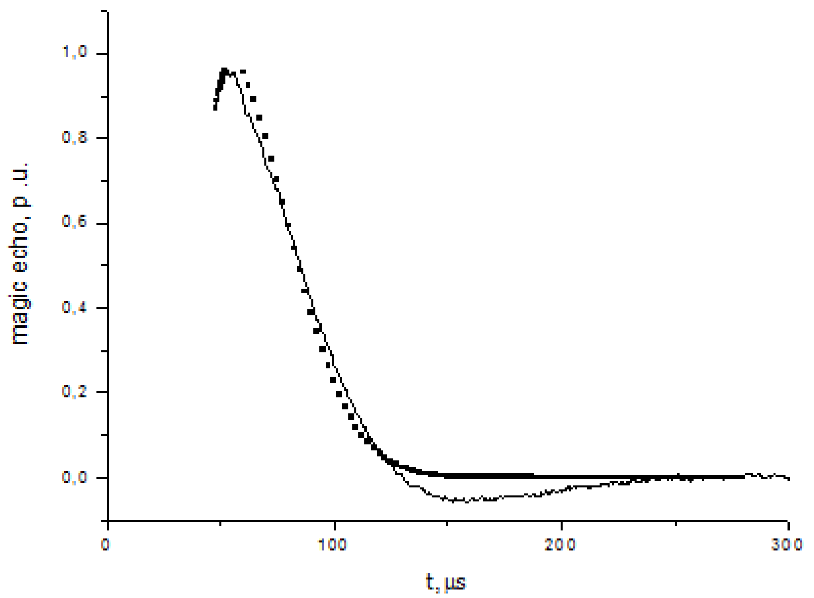
Signals of the echo are shown on the Fig. 2. Theoretical lines are represented by points. Here two orientations of the external magnetic field are represented: along the axis [100] of the crystal (a) and along the axis [010] (b). Accuracy of measuring here and on was in limit of 5% as maximum. There were taken $M_2 = 1.9\cdot 10^{-8}\ T^2$, $T = 300\ K$, potential barrier $U = 42\ kJ/mol$, ante-exponential factor in the expression for τ_c was $1.2\cdot 10^{-11}$ s.

Easy to see that in position [010] a part of the signal forms below zero level though theoretical signal is totally over it. It means that in some orientations of the crystal necessary to use more complicated model in comparison with Gaussian distribution of random fields.

Fig. 3 demonstrates dependence of the moment that peak of the echo forms on time τ. Obviously, the echo forms at the time 6τ, in full accordance with (7).



a)



b)

Fig. 2. Shape of the magic echo in natrolite.

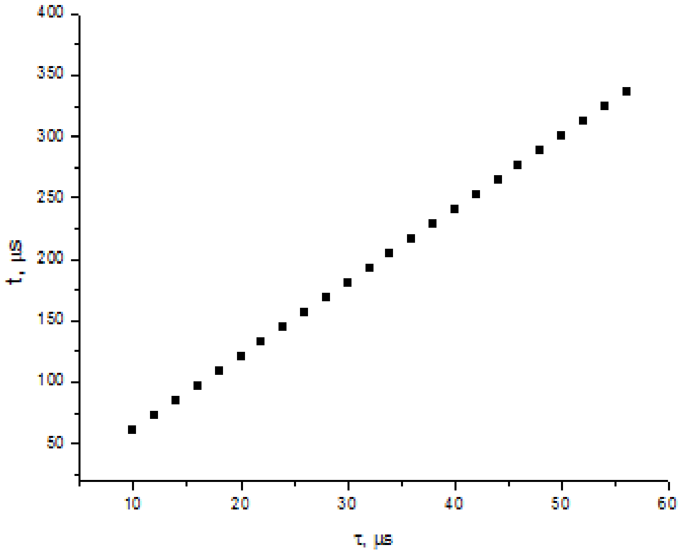


Fig. 3. Dependence of the echo peak on time (points mean experiment).

Dependence of the echo amplitude on the time τ is represented at the Fig. 4. In given case one can say only about general agreement because question about presence or absence of singularities on the experimental curve is a special task demanding separate investigation. In any case the model of Gaussian distribution of the random fields on the nuclei excludes any singularity.

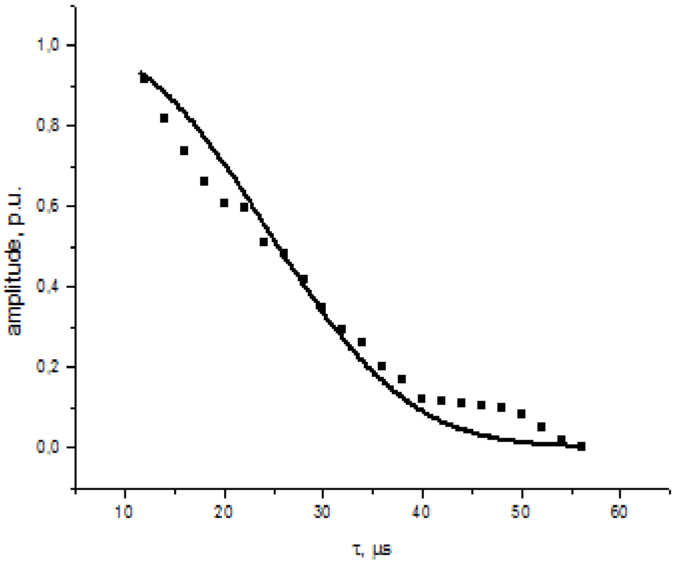


Fig. 4. Dependence of the echo amplitude on time.

Temperature dependences of any pulse responses (solid-echo, in-phase echo, etc.) usually have singularities that can't be explained by descriptive classic models. As analysis of the formula (7) shows, Fenzke magic echo has such a singularity, too. At the Fig. 5 it is demonstrated dependence of the echo amplitude on parameter $\alpha = \tau/\tau_c$.

For simplicity the item with $\overline{M}_2$ is ignored. Parameter $M_2\tau^2$ was chosen 0.136, 0.5 and 0.9. The first one corresponds natrolite if τ = 10 μs, the second and third ones are illustrative. So, this dependence has a minimum at $\tau/\tau_c = 0.725$ and this fact allows to find important parameters of molecular mobility in given system.

If to consider the time of correlation depends on potential barrier U accordingly Arrhenius law, i.e.

$$\tau_c = \tau_0 \cdot \exp(\frac{U}{RT}),$$

then necessary to find two experimental dependences on temperature for different τ. These dependences will give temperatures in minimums. After that theoretical lines (like demonstrated at Fig. 5) will define α. Solution of the system of two equations allows to calculate U:

$$U = \frac{R}{1/T_2 - 1/T_1} \cdot \ln\frac{\tau_2}{\tau_1}.$$

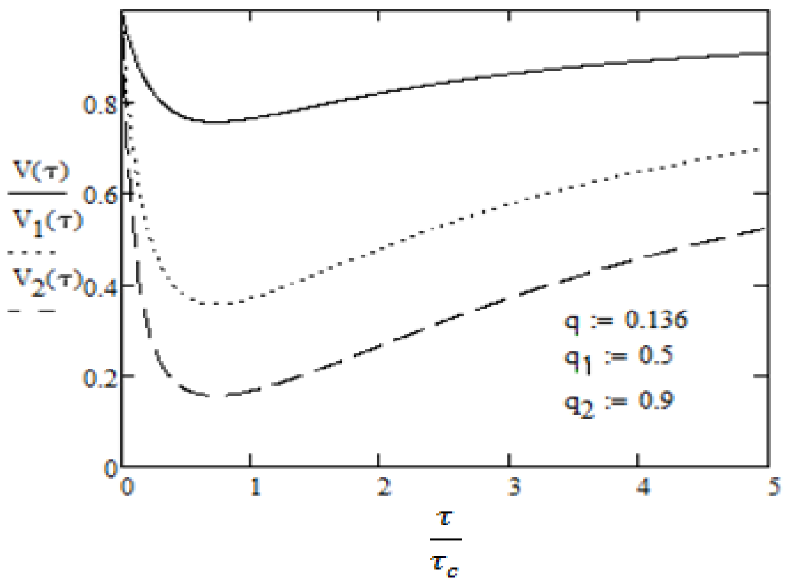


Fig. 5. Temperature dependence of the magic echo amplitude. Symbol q means $M_2\tau^2$. The first curve (q = 0.136) describes the natrolite sample, other curves have illustrative character.

CONCLUSIONS

The formula (7) for Fenzke magic echo satisfactorily describes responses of many particle systems with Gaussian distribution of the random fields on nuclei and Markov's process of mobility. Good quantitative accordance of theory and experiment is marked for time dependence of the echo amplitude. Maximum of the response forms at the time 6τ. The temperature dependence of the echo contains minimum that allows to find potential barrier and ante-exponential factor in law of Arrhenius for correlation time.

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Рябушкін Д. С. Магічне відлуння ЯМР у натроліті / Д. С. Рябушкін, А. В. Сапіга, Е. С. Редька // Вчені записки Таврійського національного університету імені В. И. Вернадського. Серія : Фізико-математичні науки. – 2013. – Т. 26 (65), № 2. – С. 125-131.
Досліджено особливості магічного відлуння Фенцке в простому випадку трьох імпульсів – форма сигналу, залежність амплітуди відгуку від часу, момент формування максимуму луни, температурна залежність луни. Показано добре якісна і кількісна згода теоретичних і експериментальних результатів для водневомісних систем з диполь-дипольною взаємодією і внутрішньої молекулярної рухливістю.
Ключові слова: ядерний магнітний резонанс, магічне відлуння, натроліт.

Рябушкин Д. С. Магическое эхо ЯМР в натролите / Д. С. Рябушкин, А. В. Сапига, Е. С. Редька // Ученые записки Таврического национального университета имени В. И. Вернадского. Серия : Физико-математические науки. – 2013. – Т. 26 (65), № 2. – С. 125-131.
Исследованы особенности магического эха Фенцке в простейшем случае трех импульсов – форма сигнала, зависимость амплитуды отклика от времени, момент формирования максимума эха, температурная зависимость эха. Показано хорошее качественное и количественное согласие теоретических и экспериментальных результатов для водородосодержащих систем с диполь-дипольным взаимодействием и внутренней молекулярной подвижностью.
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