MAGIC ECHO AND SLOW MOTIONS IN SOLIDS

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Received 5 February 1985; accepted for publication 18 April 1985

Expressions describing the dependence of the "magic" echo amplitude on temperature and parameters of the Fenzke pulse sequence in the case of slow molecular motions have been obtained. Comparison of the derived expressions with the experimental data measured in polycrystalline stilbite and cyclohexane demonstrates a good agreement and shows possibilities of measuring motion parameters using the "magic" echoes.

It was shown first in ref. [1] that an unusual spin echo in solids can be produced by a pulse sequence of the special type at times t longer than the spin–spin relaxation time T_2. This echo was called the "magic" echo [2–7]. All theoretical considerations of the "magic" echo were made only for the case of a rigid lattice i.e. without taking into consideration the internal molecular and atomic motions usually observed in solids [8]. It is obvious that the presence of the thermal motions of the resonant nuclei in the studied sample can considerably change the conditions of the "magic" echo formation so far as the chaotic change of local magnetic fields in time induced by the internal motions will result in the loss of coherency of the nuclear spin motion produced by the applied pulse sequence. The aim of this paper is to study the possibilities of the generating "magic" echoes in solids with molecular motions.

We shall consider the "magic" echo produced by a very experimentally convenient pulse sequence proposed by Fenzke [4,5]

$$(\tau\text{–}P_X\text{–}2\tau\text{–}P_X\text{–}\tau)^n\text{–}P_Y\text{–}6n\tau\,.$$

Here P_X and P_Y are the 90° rf pulses applied respectively along the X and Y axes of the rotating frame, n is the number of pulse cycles in the used pulse sequence.

The interaction hamiltonian has the form [8]

$$\mathcal{H}(t) = \tfrac{1}{2}\gamma^2\hbar\sum_{i>j} R_{ij}^{-3}(t)[(1 - 3\cos^2\vartheta_{ij}(t) \times (3I_{iz}I_{jz} - I_i\cdot I_j)\,, \tag{1}$$

where γ is the gyromagnetic ratio of the resonant nuclei, $\hbar$ is the Plank constant, I_i is the vector operator of the ith spin, ϑ_{ij} is the angle between the R_{ij} vector connecting the nuclei i and j and the external magnetic field B_0.

Assuming that the stochastic process describing the molecular motion is gauss-markovian and using the known expansion of Magnus [9] we obtain the following expression for the amplitude of the NMR signal at time moment $6n\tau$

$$V(6n\tau) = \exp\left[-\frac{1}{2}\left(\int_0^{4n\tau} dt' \int_0^{4n\tau} dt''\, h(t'-t'')g(t')g(t'') - 2\int_0^{4n\tau} dt' \int_{4n\tau}^{6n\tau} dt''\, h(t'-t'')g(t') + \int_{4n\tau}^{6n\tau} dt' \int_{4n\tau}^{6n\tau} dt''\, h(t'-t'')\right)\right], \tag{2}$$

where

$$h(t'-t'') = \mathrm{Sp}\{\overline{[\mathcal{H}(t'),[\mathcal{H}(t''),I_x]]}I_x\}/\mathrm{Sp}(I_x^2). \quad (3)$$

The upper bar denotes the average on the stochastic motion of nuclei, $g(t)$ is the periodic function with period $t_c = 4\tau$

$$g(t) = 1, \quad \text{if} \quad (4n-3)\tau \leqslant t \leqslant (4n-1)\tau,$$

$$= 0, \quad \text{if} \quad (4n-1)\tau < t < 4n\tau.$$

For the sake of simplicity we choose the correlation function $h(t'-t'')$ in the form

$$h(|t'-t''|) = \bar{M}_2 + \Delta M_2 \exp(-|t'-t''|/\tau_c), \quad (4)$$

where $\Delta M_2 = M_2 - \bar{M}_2$, M_2 and $\bar{M}_2$ are the second moments of the NMR spectra correspondingly at temperatures of rigid lattice and fast motions ($\tau_c^{-1} \gg M_2^{1/2}$), τ_c is the correlation time describing the studied molecular motion.

Expanding the function $g(t)$ in a Fourier series and substituting eq. (4) into eq. (2) we obtain the expression for the dependence of the "magic" echo amplitude on the motion frequency $\nu_c = \tau_c^{-1}$, the interval between the pulses τ and number of pulse cycles n

$$V(6n\tau) = \exp(-6n\tau/T_{2e}), \quad (5)$$

where

$$T_{2e}^{-1} = \tfrac{2}{3}\Delta M_2\tau_c - \tfrac{1}{6}\Delta M_2\tau_c \mathrm{th}(\alpha)/\alpha$$

$$+ (\Delta M_2\tau_c/12n\alpha)(e^{-2n\alpha} - 1)$$

$$\times [2 + (e^{-2n\alpha} + 1)(1 - e^{-2n\alpha} + 1/2\,\mathrm{ch}\,\alpha)/\mathrm{ch}\,\alpha],$$

$$\alpha = \tau/\tau_c. \quad (6)$$

The dependence of $T_{2e}\Delta M_2\tau$ on $\alpha = \tau/\tau_c$ is shown for some values of n in fig. 1. From fig. 1 it can be seen that the $T_{2e}\Delta M_2\tau$ as a function of $\alpha^{-1} = \tau_c/\tau$ has for given n a definite minimum. So, for example, for $n = 2$, $T_{2e}\Delta M_2\tau$ has a minimum equal to

$$(T_{2e}\Delta M_2\tau)_{\min} = 1.77 \quad (7)$$

at $\alpha^{-1} = 3$.

The analysis of eq. (6) shows that in the limit of fast motion ($\tau/\tau_c \gg 1$) the time constant of the decrease of the "magic" echo amplitude T_{2e} can be expressed by the simple expression

$$T_{2e}^{-1} \approx \tfrac{2}{3}\Delta M_2\tau_c. \quad (8)$$

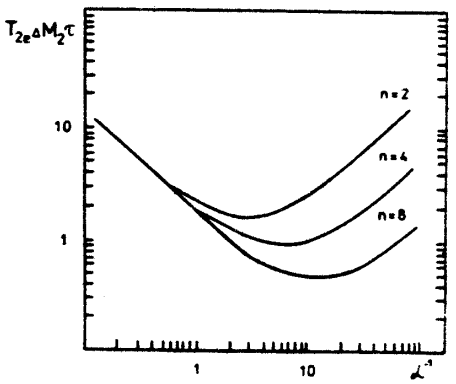

Fig. 1. The theoretical dependence of $T_{2e}\Delta M_2\tau$ on $\alpha^{-1} = \tau_c/\tau$ for some values of pulse cycles n in the Fenzke pulse sequence.

demonstrating that T_{2e}^{-1} in the high temperature limit is determined only by the temperature dependence of τ_c.

The theoretical results obtained were used for the analysis of temperature dependences of the "magic" echo amplitudes $V(6n\tau)$ in polycrystalline cyclohexane and stilbite. All measurements were performed with constant number of the pulse cycles $n = 2$. The dependence of the "magic" echo amplitude at $t = 6n\tau$ on τ was measured at each temperature. The measurements have shown that this dependence at all temperatures is exponential with time constant $\tau_c = T_{2e}/6n$. The

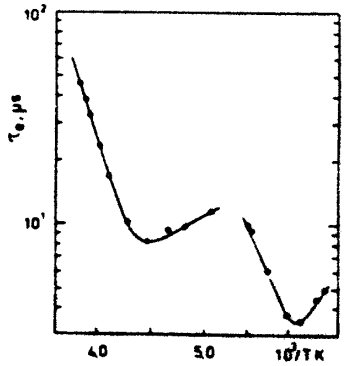

Fig. 2. The experimental temperature dependence of $\tau_c = T_{2e}/6n$ for the polycrystalline cyclohexane (●) and stilbite (○). All measurements of the "magic" echo amplitudes were made at 30 MHz, the 90° rf pulse width was equal to 2.1 μs, the "dead" time of the receiver was 4.5 μs.

measured temperature dependences of τ_c for the polycrystalline samples of stilbite ($NaCa_4Al_{10}Si_{26}O_{72} \cdot 28H_2O$) and cyclohexane ($C_6H_{12}$) are shown in fig. 2. Using eqs. (7) and (8) and the experimental values of ΔM_2 (25 G^2 for the case of stilbite [10] and 19 G^2 for cyclohexane [11]) the correlation times of cyclohexane and water molecule motions can be easily calculated from these τ_c values. The calculated τ_c values are fitted very well by the Arrhenius expression

$$\tau_c = \tau_0 \exp(E_{act}/RT),$$

with parameters $E_{act} = 7.3 \pm 0.3$ kcal/mole, $\tau_0 = (2 \pm 1.5) \times 10^{-13}$ s for water molecule diffusion in stilbite and $E_{act} = 5.1 \pm 0.3$ kcal/mole, $\tau_0 = (4.0 \pm 2.0) \times 10^{-13}$ s for the reorientation of the cyclohexane molecule around its threefold axis in the low-temperature monoclinic phase. These parameters agree well with the values of E_{act} and τ_0 measured recently in these solids by other NMR methods [12–14] demonstrating the correctness of the theoretical expressions derived and possibilities of the "magic" echo to study the slow molecular motions in solids.

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