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NR 232 ACTA PHYSICA NR 9 ROK 1998

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MAGIC ECHOES IN NMR OF SOLIDS WITH THERMAL MOTION

1. INTRODUCTION

Among the most extraordinary phenomena in NMR of solids is the magic spin echo [2, 3, 7, 9, 10, 12, 13, 14]. This phenomenon occurs in a many-body spin system with „homogeneously" spin-spin couplings and can be thought of as arising from a reversal of the sign of the interaction Hamiltonian describing the spin-spin couplings. Such reversal of the sign of the interaction Hamiltonian, induced by coherent averaging under sequences of radio-frequency pulses, has made possible a negative time development of the spin system and this time-reversal phenomenon is observed as magic echo at the time t_e longer than the spin-spin relaxation time T_2.

The influence of a thermal motions of a nuclei in solids on the Fenzke et al [3, 13] magic pulse sequence was considered in ref. [8, 11]. In this report we analyse the effects of a thermal motions on the modified pulse sequence WHH-4, which also allows obtain the magic echoes [4].

2. MAGIC ECHOES

Since the magic-echo phenomena have been previously described in great detail [4, 5], only a brief sketch of the theoretical foundations will be given.

Consider a system of dipole-dipole coupled spin I = 1/2 nuclei with the secular dipolar interaction Hamiltonian H_z [1,5]. If the density operator of a spin system is $\sigma(0)$ and at the time t = 0 a δ-pulse cyclic and periodic sequence is applied, the density operator at the time $t = Nt_c$ (t_c is a period of n-pulse sequence) has the form [4, 5]

$$\sigma(Nt_c) = [U(t_c)]^N \sigma(0)[U^{-1}(t_c)]^N. \tag{1}$$

The propagator $U(t_c)$ describes the evolution of a spin system in the period from t = 0 to t_c and may be written, in the first order of coherent averaging theory [4, 5], as

$$U(t_c) = \exp\left[-it_c H_{av}^{(1)}\right], \tag{2}$$

where

$$H_{av}^{(1)} = \sum_{0 \le i \le n} H_i(t_i/t_c) \tag{3}$$

and

$$H_i = R_i H_z R_i^{-1}. \tag{4}$$

In eq. (3) t_i is the time interval between i-pulse and (i – 1) pulse. The rotation operators R_i in eq.(4) are related to the rotation operators P_i, which describe the effects of the rf pulses, according to [4, 5]

$$R_i = P_1 P_2 \cdots P_{i-1} P_i \tag{5}$$

with the supplementary condition of a cyclic sequence [4, 5]

$$R_n = P_1 P_2 \cdots P_{n-1} P_n = 1. \tag{6}$$

When the pulse sequence performs the scaling of the interaction Hamiltonian H_Z by a factor k and reversals of the sign of the Hamiltonian (k < 0), the spin system evolves „backwards" during this pulse sequence and at $t_e = |k| \cdot Nt_c$ after the end of the pulse sequence the echo signal observes. This echo signal obtains the name of magic echo because it may be observed at the time $t_e >> (M_2)^{-1/2}$ (M_2 is the second moment of the NMR spectrum).

3. MODIFIED WHH-4 PULSE SEQUENCE

As a example consider the formation of the magic echo signal for the modified pulse sequence WHH-4 [4] (Fig. 1).

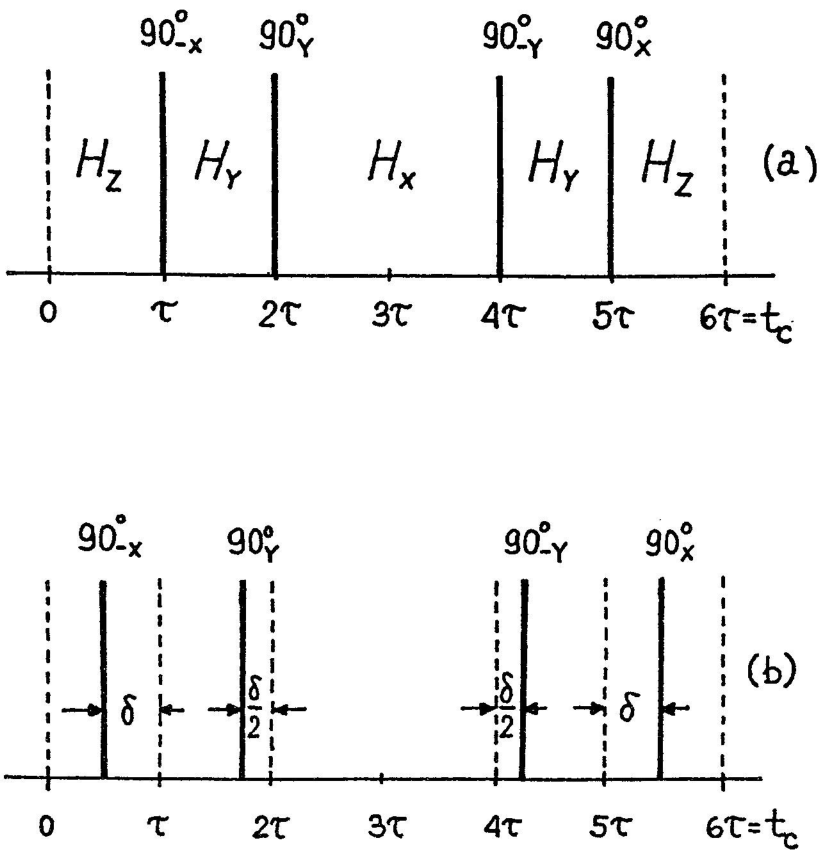

Fig. 1. Pulse sequence WHH-4 (a) and modified pulse sequence WHH-4 (b)

This pulse sequence fulfils the cyclic condition (6) and the Hamiltonians H_i have the forms

$$\begin{aligned} H_0 &= H_4 = H_Z\,, \\ H_1 &= P_1 H_Z P_1^{-1} = H_Y\,, \\ H_2 &= P_1 P_2 H_Z P_2^{-1} P_1^{-1} = H_X, \\ H_3 &= P_1 P_2 P_3 H_Z P_3^{-1} P_2^{-1} P_1^{-1} = H_Y. \end{aligned} \tag{7}$$

Here [4, 5]

$$H_Z = \sum_{ij} b_{ij}\left[2I_Z^i I_Z^j - I_X^i I_X^j - I_Y^i I_Y^j\right], \tag{8a}$$

$$H_X = \sum_{ij} b_{ij}\left[2I_X^i I_X^j - I_Y^i I_Y^j - I_Z^i I_Z^j\right], \tag{8b}$$

$$H_Y = \sum_{ij} b_{ij}\left[2I_Y^i I_Y^j - I_X^i I_X^j - I_Z^i I_Z^j\right]\,, \tag{8c}$$

$$H_X + H_Y + H_Z = 0. \tag{8d}$$

Using eq.(7) and eq.(8d) it is easily obtain the expression for the average Hamiltonian $H_{av}^{(1)}$

$$H_{av}^{(1)} = \frac{1}{6\tau}\left[2H_Z(\tau-\delta) + 2H_Y\left(\tau+\frac{\delta}{2}\right) + H_X(2\tau+\delta)\right] = -\frac{\delta}{2\tau}H_Z. \tag{9a}$$

Note that the same average Hamiltonian we obtain introducing the „switch" function g(t) [6] (Fig. 2).

Indeed, from Fig. 2 we see that

$$H_{av}^{(1)} = \frac{1}{t_c}\int_0^{t_c} g(t')H_Z dt' = -\frac{\delta}{2\tau}H_Z. \tag{9b}$$

Assuming that at t = 0 the density operator $\sigma(0)$ has the form

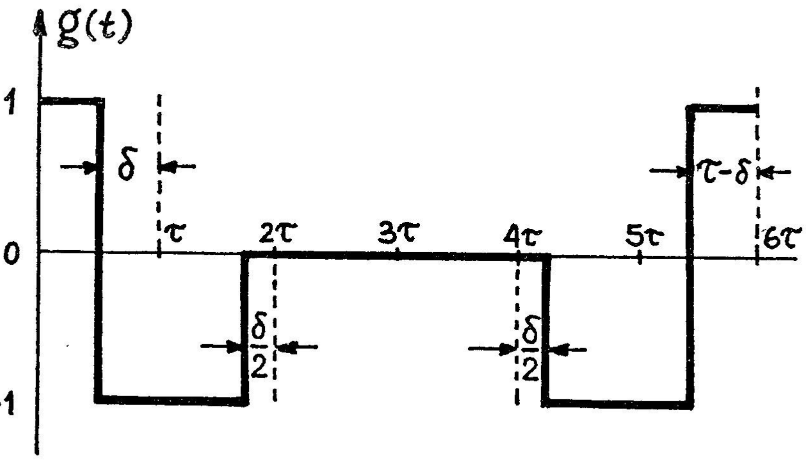

Fig. 2. „Switch" function g(t) for the modified pulse sequence WHH-4

$$\sigma(0) = I_X, \tag{10}$$

we obtain the following expression for NMR signal

$$V(t) = Tr\left\{I_X \exp\left[-iH_Z\left(t - 6N\tau\frac{\delta}{2\tau}\right)\right]I_X \exp\left[iH_Z\left(t - 6N\tau\frac{\delta}{2\tau}\right)\right]\right\}/Tr(I_X^2). \tag{11}$$

From eq. (11) follows that at $t = 3N\delta$ after the pulse sequence signal NMR reaches its maximum value, that is we are at the top of magic echo.

It $\delta = \tau/2$ the magic echo signals are observed at $t = 3N\tau/2$. The interesting case we have when $\delta = \tau$. For this case only the first and the finishing pulses 90_{-X}^0 and 90_X^0 in the cyclic pulse sequence are remained. As was shown by Rhim et al [7] the $90_{\pm Y}^0$ pulses can be replaced by $180_{\pm Y}^0$ pulses.

4. MAGIC ECHOES AND THERMAL MOTIONS

At this time assume that there are thermal motions of a nuclei in a solid. For this case the interaction Hamiltonian H_Z is a stochastic function of a time and average Hamiltonian may be written in the form [4, 5, 6]

$$H_{av}^{(1)} = \frac{1}{t_c}\int_0^{t_c} g(t')H_Z(t')dt'. \qquad (12)$$

The amplitude of the magic echo signal at $t_e = (3N\delta + 6N\tau)$ for this „dynamical" case is defined by the following expression

$$V(t_e) = Tr\left\{< \exp\left[-i\int_{6N\tau}^{t_e} H_Z(t')dt' - i\int_0^{6N\tau} g(t')\,H_Z(t')dt'\right] I_X \right.$$
$$\left. \exp\left[i\int_{6N\tau}^{t_e} H_Z(t')dt' + i\int_0^{6N\tau} g(t')\,H_Z(t')dt'\right] > I_X\right\} / Tr(I_X^2). \qquad (13)$$

In eq.(13) $< \cdots >$ denotes the average on the stochastic motions of a nuclei.

Now assume that, as in the case of „rigid" lattice, fot the amplitude of magic echo in eq.(13)

$$\int_{6N\tau}^{t_e} H_z(t')dt' + \int_0^{6N\tau} g(t')H_z(t')dt' \approx 0. \qquad (14)$$

Then expanding $\exp(\cdots)$ in eq.(14) we obtain

$$V(t_e) \approx 1 - \frac{1}{2Tr(I_X^2)}Tr\left(\begin{array}{l} < [\{\int_{6N\tau}^{t_e} H_Z(t')dt' + \int_0^{6N\tau} g(t')H_Z(t')dt'\}, \ [\{\int_{6N\tau}^{t_e} H_Z(t'')dt'' \\ + \int_0^{6N\tau} g(t'')H_Z(t'')dt''\}, \ I_X]] > I_X \end{array} \right) = \exp\left(-\frac{t_e}{T_{2ef}}\right).$$

(15)

Where

$$T_{2ef}^{-1} = \frac{1}{2t_e}\left[\int_0^{6N\tau} dt'\,g(t')\int_0^{6N\tau} d''h(t''-t'')g(t'') + \right.$$
$$\left. + 2\int_0^{6N\tau} dt'\,g(t')\int_{6N\tau}^{t_e} dt''h(t'-t'') + \int_{6N\tau}^{t_e} dt'\int_{6N\tau}^{t_e} dt''h(t'-t'')\right],$$

and

$$h(t'-t'') = \frac{Tr(< [H_Z(t'),[H_Z(t''),I_X]] > I_X)}{Tr(I_X^2)} \qquad (17)$$

is the correlation function for stochastic Hamiltonian $H_Z(t)$.

Assume that the correlation function has the form [1]

$$h(t'-t'') = \langle M_2 \rangle + \Delta M_2 \exp\left(-\frac{|t'-t''|}{\tau_c}\right), \tag{18}$$

where τ_c is the correlation time of the thermal motions and $\langle M_2 \rangle$ is the measured second moment of the motionally narrowed NMR line ($\tau_c^{-1} \gg M_2^{1/2}$), $\Delta M_2 = M_2 - \langle M_2 \rangle$; M_2 is the second moment of NMR line in the case of rigid lattice.

For calculating T_{2ef}^{-1} we represent the periodic function g(t) by Fourier series

$$g(t) = \frac{a_0}{2} + \sum_{k=1}^{\infty} (a_k \cos k\omega t + b_k \sin k\omega t), \tag{19}$$

where $\omega = 2\pi/t_c = \pi/3\tau$.

It is easily obtain that

$$a_0 = -\frac{\delta}{\tau};\ a_k = -\frac{2}{k\pi}\cos(k\pi)\left\{2\sin[k\omega(2\tau+\delta)] - \sin\left[k\omega\left(\tau+\frac{\delta}{2}\right)\right]\right\};\ b_k = 0. \tag{20}$$

Using eqs.(18), (19) and (20) we obtain

$$T_{2ef}^{-1} = \frac{1}{t_e}\left\{\Delta M_2 \tau_c 3N\tau\left(\sum_{k=1}^{\infty}\frac{a_k^2}{1+(k\omega\tau_c)^2} + \frac{a_0^2}{2} - a_0\right) + \Delta M_2 \tau_c^2\left[\left(1-e^{-\frac{6N\tau}{\tau_c}}\right)\left(1-e^{-\frac{3N\delta}{\tau_c}}\right)\right.\right.$$
$$\left.\left.\left(\sum_{k=1}^{\infty}\frac{a_k}{1+(k\omega\tau)^2} + \frac{a_0}{2}\right) - \left(1-e^{-\frac{6N\tau}{\tau_c}}\right)\left(\sum_{k=1}^{\infty}\frac{a_k}{1+(k\omega\tau_c)^2} + \frac{a_0}{2}\right)^2 - \left(1-e^{-\frac{3N\delta}{\tau_c}}\right)\right]\right\}. \tag{21}$$

5. DISCUSSION OF OBTAINED RESULTS

The obtained formula (21) allows to analyse the relaxation of magic echoes, that produce the modified sequence WHH-4, for different values of τ, δ, τ_c and N. However we consider at first for simplicity the case for which $N\tau/\tau_c \gg 1$. For this case, using the conditions: $0 \le \delta \le \tau$, $\Delta M_2 \tau \approx 1$, $6N\tau \le t_e \le 9N\tau$, we obtain

$$T_{2ef}^{-1} = \frac{1}{t_e}\Delta M_2 \tau_c 3N\tau\left[\sum_{k=1}^{\infty}\frac{a_k^2}{1+(k\omega\tau_c)^2} + \frac{a_0^2}{2} - a_0\right]. \tag{22}$$

Remember that in this equation $t_e = 3N(\delta+2\tau)$ is the time position of the magic echo from the end of the first pulse of the cyclic pulse sequence.

If $\delta = 0$ then we have the pulse sequence WHH-4. For this sequence from eq.(20) we obtain

$$a_0 = 0,$$

$$a_k = -\frac{2}{k\pi}\cos(k\pi)\left[2\sin\left(\frac{2}{3}k\pi\right) - \sin\left(\frac{1}{3}k\pi\right)\right], \tag{23}$$

or for odd k and $k \neq 3n$ (n = 1,2,...)

$$a_k^2 = \frac{3}{k^2\pi^2}, \tag{24}$$

and for even k and $k \neq 3n$ (n = 1,2,...)

$$a_k^2 = \frac{27}{k^2\pi^2}. \tag{25}$$

Inserting eq.(24) and eq.(25) into eq.(22) we obtain

$$T_{2ef}^{-1} = \frac{9}{2\pi^2}\Delta M_2\tau_c\left(\sum_{l>0}\frac{3}{l^2}\frac{1}{1+(l\omega\tau_c)^2} + \sum_{k>0}\frac{1}{3k^2}\frac{1}{1+(k\omega\tau_c)^2}\right). \tag{26}$$

Here l has even values, k has odd values and k, $l \neq 3n$ (n = 1,2,...).

Formula (26) is in agreement with the result obtained by Haeberlen and Waugh [5].

Consider now the case when $\delta = \tau$. For this case from eq.(20) we have

$$a_0 = -1, a_k = \frac{2}{k\pi}\cos(k\pi)\sin\left(k\frac{\pi}{2}\right) \tag{27}$$

and

$$a_0^2 = 1, a_{2k+1}^2 = \frac{4}{\pi^2(2k+1)^2} \tag{28}$$

Inserting eq.(28) into eq.(22) we obtain

$$T_{2ef}^{-1} = \frac{1}{6}\Delta M_2 \tau_c \left(\frac{8}{\pi^2} \sum_{k=0}^{\infty} \frac{1}{(2k+1)^2 \left[1 + (2k+1)^2 \left(\frac{\pi}{2\beta} \right)^2 \right]} + 3 \right), \tag{29}$$

where

$$\beta = \frac{3\tau}{2\tau_c}. \tag{30}$$

Using the representation of a hyperbolic functions by the series [6]

$$1 - \frac{th\beta}{\beta} = \frac{8}{\pi^2} \sum_{k=0}^{\infty} \frac{1}{(2k+1)^2 \left[1 + (2k+1)^2 \left(\frac{\pi}{2\beta} \right)^2 \right]} \tag{31}$$

we may write eq.(29) in the following form

$$T_{2ef}^{-1} = \frac{1}{6}\Delta M_2 \tau_c \left(4 - \frac{th\beta}{\beta} \right). \tag{32}$$

The dependences of $T_{2ef}\Delta M_2\tau$ on τ_c/τ are shown for some values of N and $d = \delta/\tau$ in Fig. 3.

From Fig. 3 it can be seen that for given τ the effective relaxation time T_{2ef} decreases when the parameter d increases from 0 to 1. The minimum of $T_{2ef}\Delta M_2\tau$ for given N shifts to the large values of τ_c/τ with increasing d and so by determining the T_{2ef} minima in the temperature dependent measurements of the magic echo signals it is possible to investigate the largest correlation times of the slow molecular motions in solids than can be investigate by WHH-4 experiment.

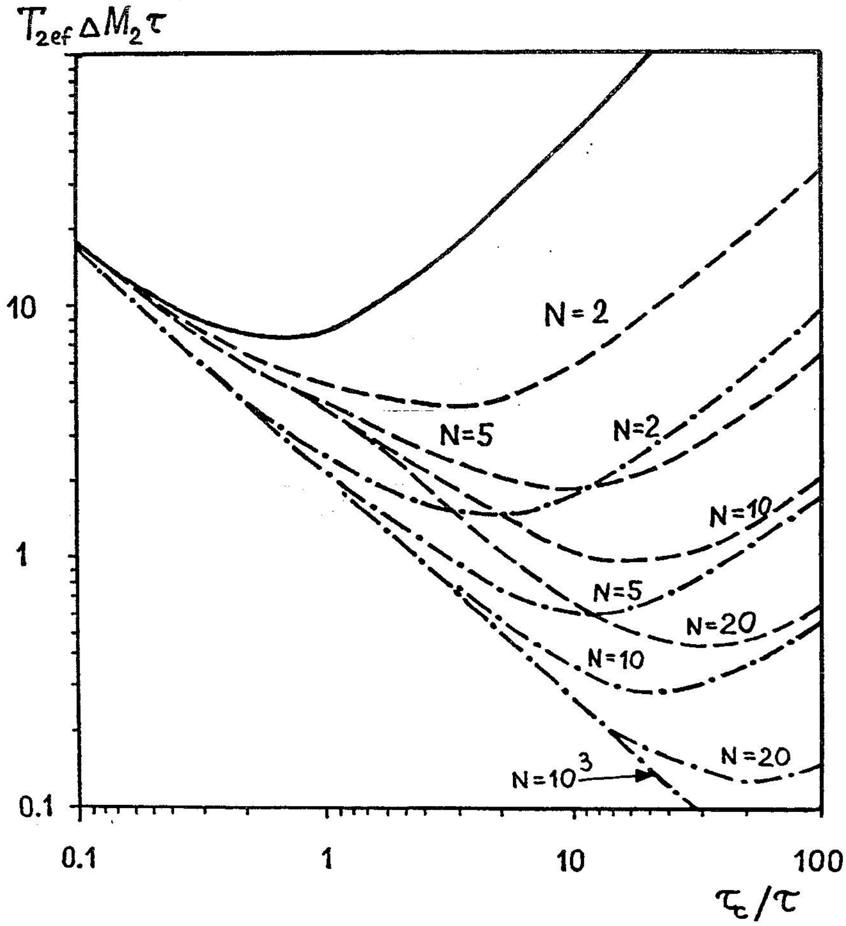

Fig. 3. Dependences of $T_{2ef}\Delta M_2\tau$ on τ_c/τ for WHH-4 pulse sequence (—) and for modified pulse sequence WHH-4 at $\delta = \tau/2$ (- - - -) and $\delta = \tau$ (- · - · - · -)

6. CONCLUSIONS

The main objective of this report was to consider the influence of the thermal motions of a nuclei in solids on the NMR magic echo signals. At the present time there are only few paper consecrating to this problem. However in NMR of solid, the correct description of the influence of a nuclei mobility on NMR singnals is remained still a difficult and unresolved problem. It would prove valuable to study as theoretically, so experimentally, of the thermal motions in solids by a different NMR methods including the magic echo methods.

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MAGICZNE ECHA W NMR CIAŁ STAŁYCH ZAWIERAJĄCYCH TERMICZNE RUCHY JĄDER

Streszczenie

Przedstawiono wyniki badań modyfikowanej sekwencji impulsowej WHH-4, która wywołuje magiczne echa w ciałach stałych z oddziaływaniami dipolowymi. W przypadku powolnych ruchów molekularnych obliczono zależności natężenia echa magicznego od parametrów sekwencji impulsowej i czasu korelacji τ_c.