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ADVANCED AND LAGGED NUCLEAR QUADRUPOLE ECHOES

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ABSTRACT

A sample exposed to a series of r.f. pulse pairs with pulse separation τ and repetition period T was considered. The echo signal amplitudes were calculated for the initially nonequilibrium, effectively two-level spin system. Echo signals were observed in a polycrystalline $KReO_4$ sample and the dependence of their amplitudes on τ was experimentally obtained. A good agreement of the theoretical results and experimental data was found.

INTRODUCTION

In the abovementioned situation it is possible to observe physically detectable spin echo signals within the time interval $\tau \leqslant t \leqslant T$. If T is large compared with the magnetic relaxation times of the sample, the basic echo-signal at the moment 2τ is observed. Decrease in results in the appearance of the secondary lagged-type and advanced-type signals at the moments (3τ, 4τ, etc) and ($T-2\tau$ and $T-\tau$) respectively. With the growth of τ the amplitudes of the advanced signals increase and the signals shift to the left on the time axis, the lagged signals shift to the right and their amplitudes decrease. Some reports on the lagged echoes were published (ref. I). We observed advanced echoes as well.

If the sample is subjected to a single-frequency excitation so that only one transition between the energy levels of a single spin may be excited, it is possible (ref. 2) to assign to the spins the effective value I/2 and to introduce a fictitious magnetic field inhomogeneons within the sample. The effective spins in the same magnetic field form an isochromatic group (ref. 3), magnetization components of the group varying according to Bloch equations (ref. 4). Since we are interested in the solutions to Bloch equations only within the time interval $\tau \leqslant t \leqslant T$, the periodic boundary conditions are to be used: in the laboratory frame of reference the initial values of the isogroup magnetization components coincide with their values at the moment T . The solutions to Bloch equation found in the above-mentioned interval are to be averaged according to the field distribution which was supposed to be normal.

Attempts have been made to realize such a program (ref. I). In (ref. I) the periodic boundary conditions have been formulated in the frame of reference rotating with the basic r.f. pulse frequency however, errors occurred both in the computation and in the physical interpretation of the results obtained.

In the paper presented the abovementioned program was accomplished. A non-traditional point of this realization lies in the obtaining of the initial values of the isogroup magnetization components from the periodic boundary conditions. It was at this very stage of computation that errors have been made in (ref. I). Here are the initial conditions obtained:

$$\begin{pmatrix} m_1 \\ m_2 \end{pmatrix}(0) = m \sin\xi_1 \exp\left\{-\frac{T}{T_2}\right\}\left\{\cos^2\frac{\xi_2}{2}\begin{pmatrix}\sin\\ \cos\end{pmatrix}(\omega+\Delta\omega)T - \sin^2\frac{\xi_2}{2}\begin{pmatrix}\sin\\ \cos\end{pmatrix}\left[\omega T + \Delta\omega\left(T-2\tau\right)\right]\right\}$$

$$+ m\sin\xi_2 \exp\left\{-\frac{T-\tau}{T_2}\right\}\left(1-2\sin^2\frac{\xi_1}{2}\exp\left\{-\frac{\tau}{T}\right\}\right)\begin{pmatrix}\sin\\ \cos\end{pmatrix}\left[\omega T + \Delta\omega\left(T-\tau\right)\right], \qquad \begin{pmatrix} I \\ 2 \end{pmatrix}$$

$$m_3(0) = -m\sin\xi_1 \sin\xi_2 \exp\left\{-\frac{T-\tau}{T_1} - \frac{\tau}{T_2}\right\}\cos\Delta\omega\tau +$$

$$+ m\left[1 - 2\exp\left\{-\frac{T}{T_1}\right\}\left(\sin^2\frac{\xi_1}{2}\cos\xi_2 + \sin^2\frac{\xi_2}{2}\exp\left\{\frac{\tau}{T_1}\right\}\right)\right]. \qquad (3)$$

The expressions (I)-(3) are put down in the frame of reference rotating with the frequency ω and to the first approximation with respect to the quantities $\exp\{-T/T_a\}$ $(a=1,2)$. Here T_1 and T_2 are the longitudinal and transverse relaxation times respectively, m gives, after averaging, the equilibrium value of lonqitudinal magnetization, ξ_1 and ξ_2 are dimensionless r.f.pulse durations, $\Delta\omega$ is the field strength in the frequency units acting in the rotating frame of reference on the effective spins entering the isogroup in question. In (ref. I) the terms (I)-(3) containing $\sin\xi_1$ were omitted. For $T \gg T_a$ the initial values (I)-(3) become equilibrium ones.

RESULTS

For the rotating frame of reference we obtained the following expressions of the amplitudes of the echo signals of interest:

$$M(2\tau)=M\sin\xi_1\sin^2\frac{\xi_2}{2}\Big[1-2\sin^2\frac{\xi_2}{2}\exp\Big\{-\frac{T-\tau}{T_1}\Big\}+$$

$$+2\Big(\cos\xi_1\cos^2\frac{\xi_2}{2}-\sin^2\frac{\xi_1}{2}\cos\xi_2\Big)\exp\Big\{-\frac{T}{T_1}\Big\}\Big]\exp\Big\{-\frac{2\tau}{T_2}\Big\}; \qquad (4)$$

$$M(3\tau)=\frac{1}{2}M\sin^2\xi_1\sin\xi_2\sin^2\frac{\xi_2}{2}\exp\Big\{-\frac{4\tau}{T_2}-\frac{T-\tau}{T_1}\Big\}; \qquad (5)$$

$$M(T-2\tau)=\frac{1}{4}M\sin\xi_1\sin^2\frac{\xi_1}{2}\sin^2\xi_2\cos\omega T\exp\Big\{-\frac{2(T-\tau)}{T_2}\Big\}; \qquad (6)$$

$$M(T-\tau)=M\sin^2\frac{\xi_1}{2}\sin\xi_2\cos\omega T\Big[\cos^2\frac{\xi_2}{2}-(1-\cos\xi_1\cos\xi_2)\exp\Big\{-\frac{\tau}{T}\Big\}\Big]\exp\Big\{-\frac{2}{T_2}(T-\tau)\Big\}, \qquad (7)$$

where M denotes the averaged magnetization values and the arguments on the left hand side are the observed moments of the corresponoding echo-signals. For $T \gg T_a$ the secondary signal amplitudes become infinitesimal.

The comparison of the results obtained with those given in (ref. I) shows that of two nonequilibrium corrections to the basic echo-signal amplitude only the first one is detailed correctly in ref. 1. At the same time, the expression suggested in (ref. I) for the amplitude in question contains a term describing a "ghost echo" (ref. 5) corresponding to the physically meaningless time $2\tau - T$. The solutions (5) and (6) were omitted in (ref. I), the first one being replaced with the physically meaningless solution corresponding to the "ghost echo" associated with the moment $3\tau - T$. Finally, in the opinion of the authors of (ref. I) the solution (7) "describes a free precession in the time interval $\tau < t < T$ " (ref. I).

A typical oscillogram of the echo signals observed in $KReO_4$ is shown in Fig. I. The dependence of the signal amplitudes on τ is given in Fig. 2; it conforms well to the expressions (4)-(7). The measurements have been made at liquid nitrogen temperature with the filling frequency $\omega = 2\pi \cdot 55,65$ MHz (transition 3/2 - 5/2 for ^{187}Re nuclei) and the repetition period $T = 10^{-2} \div 10^{-4}$ sec.

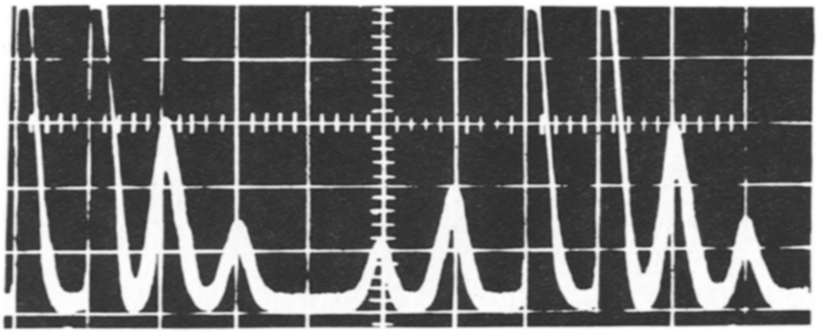

Fig. I. The oscillogram of $KReO_4$ spin echo signals. A $KReO_4$ sample was exposed to a series of pulse pairs with pulse separation τ = I00 msec. and repetition period T = 700 msec. From left to right the basic echo-signal and the secondary lagged and secondary advanced echo-signals are seen.

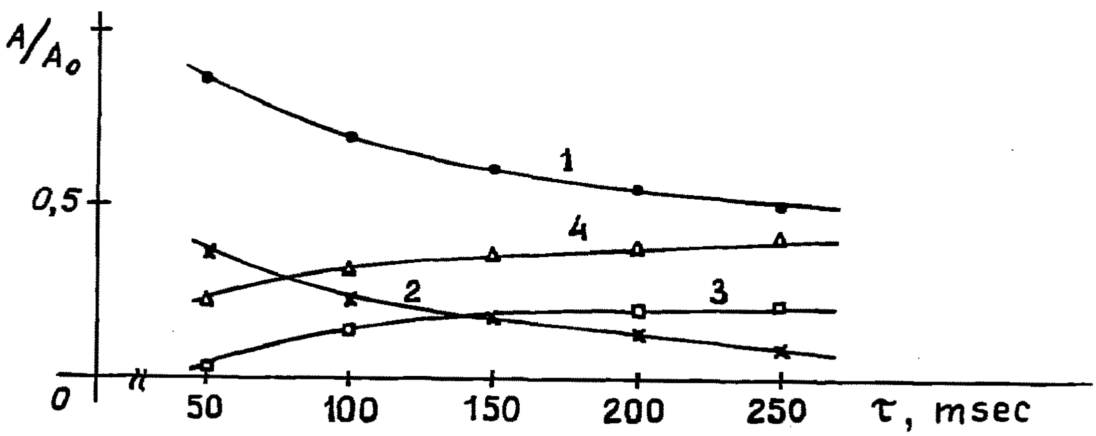

Fig. 2. The amplitude of the basic (I), secondary lagged (2), and secondary advanced (3) and (4) echo-signals as functions of the r.f. pulse separation τ . Repetition period T = 700 msec.

REFERENCES

I. B,F.Alekseev, V.D.Gadaev, Zh.Eksp.Teor.Fiz.Pism.Red., 22(I975)357; Izv.Vyssh.Uchebn.Zaved.Radiofiz., I9(I976)322.
2. A.Abragam, The principles of nuclear magnetism, Oxford,I968.
3. T.P.Das, A.K.Saha, Phys.Rev., 93(I954)749.
4. F.Bloch, Phys.Rev., 70(I946)460.
5. A.V.Alekseev, U.H.Kopvillem, Nuclear quadrup.reson., 2(I977)II5, Kaliningrad.